Vejledning

**VANDBEHANDLING OG KORROSIONS-FOREBYGGELSE**

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DANSK FJERNVARME

*Original cover*

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The English translation is arranged by Silhorko-Eurowater A/S in agreement with the Danish District Heating Association. Silhorko-Eurowater A/S therefore takes responsibility for spelling mistakes or any other discrepancies compared to the original version.

The guide also refers to several external appenidices. These have not been translated.

The goal is to share useful recommendations to people working with water treatment in district heating plants outside of Denmark.

Danish district heating has a long and proven track record and encompasses valuable know-how worth sharing.

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## Recommendations

# WATER TREATMENT AND CORROSION PREVENTION

EUROWATER

## Introduction

This guide to water treatment and corrosion prevention in district heating systems is intended as a guide to operations managers and other operating crew as well as a guide to consultants and contractors working with Danish district heating systems. The guide applies to all water-born district heating systems irrespective of operating temperature.

### Purpose of guide

The purpose of this guide is both to express recommendations on water treatment in Danish district heating plants and to maintain and secure knowledge of water treatment in Danish district heating plants.

### Application of guide

Use the guide as a handbook for water treatment and corrosion prevention in conventional district heating systems. In special cases and in case of abnormal operating situations, the guide shall be substantiated by special knowledge.

The guide does not apply to water/steam circuits in combined heating and power plants, nor to water treatment for steam installations. In these cases, we refer you to specifications and recommendations for the relevant technologies.

Thus, the guide does not apply to special cooling circuits separated from district heating water such as motor circuits, heat pump circuits, and solar heating circuits.

### Purpose of water treatment

The purpose of water treatment is to secure the function and to preserve the large investments tied up in district heating systems within the best possible technical and financial framework. The water treatment shall secure the preventive maintenance in consideration of the individual plant whether new or old.

Plant and operating economy in water treatment shall therefore be weighed against the influence of the water quality on the operating and maintenance costs as well as the useful life of the plant. For these reasons, a somewhat higher production cost of make-up water will often be recovered on a longer view.

### Success criterion of water treatment

A success criterion of good water treatment in district heating systems is optimum technical and economical operation both in the short and in the long run. Likewise, low chemical consumption is a success criterion, since the environment will be the least stressed by discharge of district heating water and at the same time, the risk of corrosion will be reduced.

This means:

- Minimization of corrosion and formation of deposits
- Optimum plant and operating economy
- Minimum maintenance costs
- Minimum internal and external environmental impact.

**Guide composition**

With this guide, the previous edition from 1999 has been brought up to date. We have maintained the structure of the guide from 1999, i.e. the basis of the daily operation is contained in the specifications in *section 1: Water quality* and in the two sections on the ongoing follow-up, *section 8: Monitoring and control of water quality* and *section 9: Monitoring and control of corrosion*.

The principles of water treatment are described in *section 4: Methods for treatment and conditioning of make-up water* as well as in *section 5: Methods for treatment of circuit water*.

When assessing existing water treatment or considering new plants, *section 7: Choice of water treatment concept* provides a line of action. The remaining sections provide background information on materials, corrosion, chemicals, and environmental conditions.

**Changes in relation to previous guide editions**

The guide has been extended primarily in relation to new technology for water treatment and increased environmental considerations. As regards previous limit values, only a few changes in values for conductivity and hardness in the circulating water have been made. The guide still covers a broad spectrum of plants – from small to very large. The recommendation to use degassing/deoxidation on all plants to avoid addition of chemicals for binding oxygen has been strengthened. The use of oxygen absorbents has several undesirable side effects and is environmentally bad. In general, experience with the plants has been included, more figures have been used, and the language has been adapted to make the guide more readable.

Summary of changes in relation to previous recommendations:

- Limit values for conductivity and hardness in circulating water have been adapted so that they are in line with the other requirements and practical experience.
- Addition of chemicals other than sodium hydroxide is being dissuaded.
- The newest technology within water treatment and degassing/deoxidation has been illustrated.
- Greater focus on the meaning of oxygen removal, make-up water, and circuit water.
- Economic comparison for adding water in demineralization plant in relation to softened water and chemical addition.
- Elaboration on the problems of bacterial growth in district heating systems.
- Sludge removal to hinder corrosion.
- Update of legislation in the field.

Valuable contributions from the consultants of COWI, other specialists within water treatment as well as members of the Danish District Heating Association have all been included in the revision.

# Contents

# 1 WATER QUALITY

## 1.1 Water quality in the district heating network

The water quality in the district heating system shall secure against formation of deposits and corrosion in the entire district heating system in order to optimize the plant and operating economy in general. Obviously, there is a connection between size, age, condition of the plant, and the requested quality. In some cases, the best technical solution can be difficult to implement in old plants with a short useful life. Nevertheless, improvements will often be attainable and as to choice of water treatment concept, please see section 7 *Choice of water treatment concept*.

The water quality of circuit water can be divided into four classes reflecting the use of different qualities throughout the ages. The development has proceeded from untreated water to demineralized water, whereby the technological development and the need for plant optimization have increased the necessity to choose the technologically best solution. This has resulted in four qualities in Danish district heating systems:

- Demineralized water
- Partly demineralized water
- Softened water
- Untreated water.

In order to achieve these qualities, water is added:

- Demineralized water
- Softened water
- Untreated water.

The system with partly demineralized water is a mixture of demineralized and softened water, which is achieved because there is not enough capacity to use demineralized water alone or there is a mixture of new and old systems.

Besides choice of water quality, removal of oxygen from the water is necessary to reduce corrosion and adjust the pH-value to passivate steel faces. Unconditioned water is only found in very small systems.

## 1.2 Specification of circuit water

The leading requirements for water quality in district heating systems appear from table 1.2. The values are continuously affected by the environment and therefore it is impossible to sustain these values in all situations, however, it is important to find causes of deviations and to correct such deviations, alternatively to adapt the system to the given circumstances. Thus, it might be necessary to increase the frequency of analysis to find the cause of contamination. The water quality affects corrosion and the risk of forming deposits.

**Table 1.2 Water quality in systems**

| Quality of make-up water | | Untreated | Softened | Partly demineralized | Demineralized |
|---|---|---|---|---|---|
| Appearance | | clear | clear | clear | clear |
| Odour | | odourless | odourless | odourless | odourless |
| Solid particles | mg/l | <10 | <10 | <5 | <1 |
| Oil and grease content | mg/l | <1 | <1 | <1 | <1 |
| pH-value at 25 °C | | | 9.8 ±0.2 | 9.8 ±0.2 | 9.8 ±0.2 |
| Residual hardness | °dH | | <0.5* | <0.6* | <0.6* |
| Conductivity at 25 °C | µS/cm | | <1500 | <500 | <50** |
| Oxygen content | mg/l | | <0.02 | <0.02 | <0.02 |
| Chlorides, $Cl^-$ | mg/l | <300** | <300*** | <50*** | <3 |
| Sulphates, $SO_4^{--}$ | mg/l | | | | <2 |
| Ammonia content, $NH_3$ | mg/l | | <10 | <5 | <5 |
| Total iron, $Fe_{total}$ | mg/l | | <0.1 | <0.2 | <0.05 |
| Total copper content, $Cu_{total}$ | mg/l | | <0.02 | <0.02 | <0.01 |

*) As to partly demineralized and demineralized water, the limit values have been changed compared to the guide from 1999. The current values reflect acceptable values of hardness in water in contact with precipitated calcium in the net. This is the typical situation in older systems, in which contamination has previously occurred. As to clean or new systems, it is appropriate to stiffen the quality requirement to 0.1°dH, since calcium precipitations typically will not occur here. An increase in hardness will then be a sure sign of contamination and measures should be taken before calcium precipitation occurs.

**) Compared to the guide from 1999, the limit value is raised from 25 µS/cm. The 50 µS/cm is a value that both contains a contribution from sodium hydroxide and from impurities in the form of salts. Sodium hydroxide added to pH 9.8 results in a conductivity of 15 µS/cm. If pH is 10, which is within the acceptable range, the conductivity from sodium hydroxide alone will be 25 µS/cm. With a contribution of salts within the acceptable limits, a value close to 50 µS/cm is reached. The essential thing is to follow the tendency and assess, whether it is a rising tendency indicating contamination or whether the conductivity is high because of sodium hydroxide.

***) This together with temperature level advances special requirements for stainless steel. *See section 2.4: Stainless steel.*

The table is incomplete as to water quality because among other things the bacteriological part is not listed. Sulphides over the limit of detection of 0.02 mg/l should not be present in circuit water in district heating systems. We refer to the relevant sections in the guide concerning supplementary requirements and to the *section 7.4: Bacteriological activity.*

## 1.3 Specification of make-up water

In order to maintain the chemistry in the district heating system it is of major importance to use make-up water of a good water quality. The water quality requirements for make-up water used in district heating systems can be specified as shown in table 1.3.

**Table 1.3 Make-up water**

| **Quality class** | | **Drinking water** | **Softened** | **Demineralized** |
|---|---|---|---|---|
| Appearance | | clear and colourless | clear and colourless | clear and colourless |
| Odour | | odourless | odourless | odourless |
| Solid particles | mg/l | <10 | <5 | <1 |
| Oil and grease content | mg/l | free of oil and grease | free of oil and grease | free of oil and grease |
| Residual hardness | °dH | | <0.1 | <0.01 |
| Conductivity at 25 °C | µS/cm | | | <10 |
| Chlorides, $Cl^-$ | mg/l | <300 | <300 | <0.5 |
| Sulphates, $SO_4^{--}$ | mg/l | | | <0.2 |
| Total iron, $Fe_{total}$ | mg/l | <0.2 | <0.05 | <0.005 |
| Total copper content, $Cu_{total}$ | mg/l | <0.1 | <0.05 | <0.01 |

## 1.4 Specification of make-up water conditioning

Before conducting make-up water to the system, conditioning is needed. Typically, this is a pH-adjustment with either removal of oxygen before addition or carrying out chemical oxygen binding. It is important to perform the conditioning so that the piping for make-up water is protected against corrosion. The requirements for conditioning appear from table 1.4. Please note that untreated water should only be present in very small plants where admission of oxygen does not occur through frequent admission of make-up water.

**Table 1.4 Conditioning of make-up water**

| | **Circuit water** | | | |
|---|---|---|---|---|
| **Methods for make-up water conditioning** | Untreated | Softened | Partly demineralized | Demineralized |
| Unconditioned | x | o | | |
| pH-adjusted to pH = 9.8 ± 0.2 | | x | x | x |
| Chemically oxygen bound *) | | (x) | (x) | |
| Degassed **) | (x) | x | x | x |

*) Chemical oxygen binding is only necessary if the make-up water cannot be degassed.

**) Oxygen content < 0.1 mg/l and carbon dioxide content < 10 mg/l.

x Recommended conditioning.

o Cannot be recommended.

(x) Can be used as a supplement to the recommended.

## 1.5 Typical problems

A number of typical operational problems in district heating systems stem from (lack of) water quality and can be addressed by changing the water quality. For example:

- Oxygen corrosion in expansion vessels, holding tanks, pipe systems, and in radiators.
- Calcium precipitations on heating surfaces, in boilers and heat exchangers.
- Corrosion due to salts under coats, in armatures, radiators, holding tanks, joints, and general surface corrosion.
- Sludge and deposits on meters, adjustment devices, radiators, holding tanks, and in general in places with low flow.
- Stress corrosion of stainless steel.
- Sulphide attack on plant parts of copper and copper alloys.
- Circulation disorder due to air discharge in boilers and heat exchangers.
- Microbial corrosion and formation of deposits.

# 2 CORROSION, MATERIALS, DEPOSITS, AND PRECIPITATIONS

## 2.1 Corrosion chemistry

In this section, the typical corrosion forms in the most common metals are described.

## 2.2 Untreated steel

Black untreated steel and non-alloy steel are the most common materials in district heating systems. Water treatment and corrosion prevention primarily aim at protecting these materials against corrosion taking into account that other materials could be present. The main elements of corrosion prevention pertaining to unalloyed black steel are:

- Oxygen-free environment with an oxygen content < 0.02 mg/l
- Alkaline environment with pH = 9.8 ± 0.2
- Minimization of salts, formation of deposits, and precipitations.

On clean and untreated steel faces, a thin magnetite deposit will form at pH-values over approx. 9.5, which acts passivating on the steel face. The magnetite deposit is soluble at lower pH-values and can be liberated by mechanical influence or resulting from thermal and dynamic movement in the pipe system. In case of new plants, it is important to clean the surfaces before commissioning, i.e. iron scales, paint residue, and oil stains are removed by sand blasting and degreasing.

## 2.3 Surface treated steel

In general, surface treated steel is not recommended for use in district heating systems, since inspection and maintenance of the surface treatment will often not be possible, and poor maintenance can result in corrosion. Surface treatment can be coating, pickling, galvanization, etc. Where surface treatment is applied, make sure that the surface is without cracks and pores during the useful life of the plant. Should cracks or pores occur in the surface treatment, these openings could constitute the basis for pitting corrosion and crevice corrosion under the surface treatment. Galvanized surfaces are not recommended since they are unstable to corrosion in softened and demineralized water.

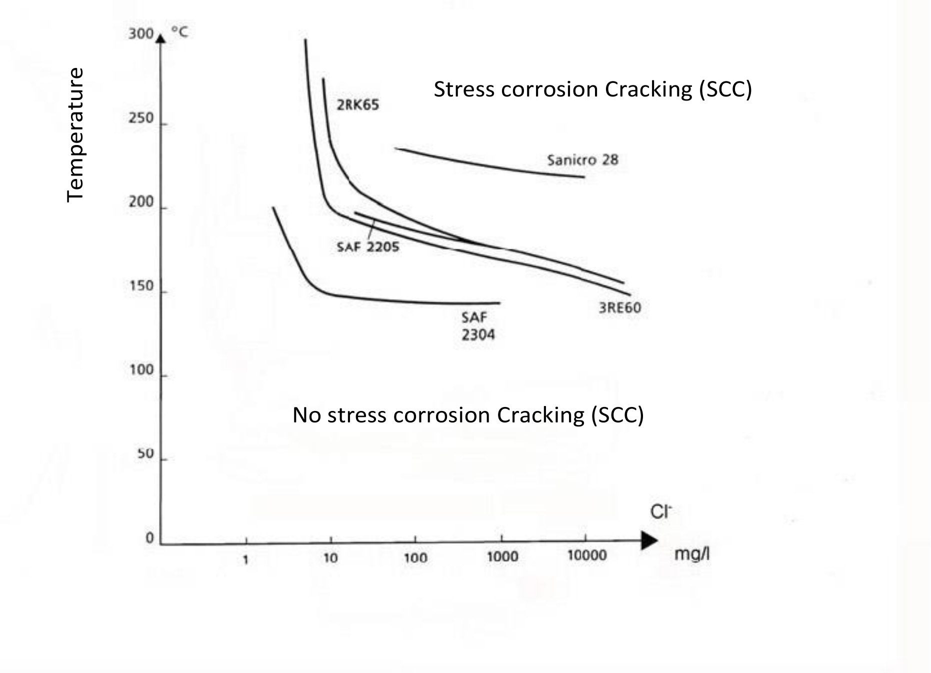
## 2.4 Stainless steel

To a great extent stainless steel is used in district heating systems because of its many good thermal and mechanical properties. However, stainless steel is not corrosion stable under all conditions. If the temperature on the one side of a stainless heat exchanger can increase over 80°C, and if the chloride concentration on one of the sides can exceed 5 mg/l, it is necessary to choose the correct stainless steel grade. There is risk of concentration of chlorides brought about by even minimal leakages in which small concentrations are multiplied in the cracks causing corrosion on both the primary and the secondary side of the heat exchanger. The special problems with corrosion in stainless steel are treated in appendix 4, which describes the reactions of the various stainless steel types to among other things temperature levels and chloride content in the district heating water.

Figure 2.4 shows application limits for some types of stainless steel with greater resistance to stress corrosion in relation to temperature and chloride concentration.

Figure 3 in appendix 4 shows application limits for AISI 304 and AISI 316 in relation to temperature and chloride concentration, but the unit is ppm, (mg/l). A possible fluoride content in the circuit water can also cause corrosion damage on stainless steel, just as stainless steel can be attacked by bacteriological corrosion. Fluoride originates typically from reuse of flue gas condensate.

**Fig. 2.4 Stainless steel grades and stress corrosion**



## 2.5 Copper and copper alloys

Copper and copper alloys in fittings and armatures form part of district heating systems, primarily in user installations, but also to some extent in the pipe system and installations of the heating plants. Copper and copper alloys have good corrosion resistance, but occasionally various corrosion types are seen in district heating water. The important elements for prevention of corrosion in this material group are:

- Oxygen-free environment with an oxygen content < 0.02 mg/l
- Weakly alkaline environment, pH < 10
- Lowest possible presence of ammonia and sulphide.

Possible corrosion types in various copper and brass alloys are shown in table 2.5.

**Table 2.5 Corrosion types in various materials**

| Corrosion type | Materials | Comments |
|---|---|---|
| Dezincification | Brass | High pH, high chloride content, and oxygen |
| Sulphide corrosion | Copper, tin bronze, copper phosphor solder | Sulphide content and oxygen |
| Erosion corrosion | Copper and brass | High water flow rates and oxygen |
| Stress corrosion | Brass | High mechanical tensile stresses, ammonia, and oxygen |

In district heating water pH-adjusted with sodium hydroxide, the corrosion rate increases strongly at pH-values over 10, therefore higher pH-values should be avoided in plants containing copper and copper alloys.

In district heating water pH-adjusted with ammonia, the corrosion rate increases strongly even at pH-values over 9 due to risk of concentrations, *therefore pH-adjustment with ammonia should not be used in district heating systems containing copper and copper alloy.*

**Stress corrosion** can occur in brass components with mechanical tensile stresses, such as in brass union nuts, if these are exposed to ammonia water and oxygen. Contents of ammonia and oxygen can be concentrated in cracks with leakages to open air whereby pH is increased and corrosion arises.

**Dezincification** occurs primarily in brass, which is a copper-zinc alloy. Dezincification does not occur in red brass or in the specifically developed dezincification resistant brass types that are alloyed with arsenic and have a somewhat lower zinc content.

**Erosion corrosion** occurs primarily in copper pipes and fittings, but can also occur in brass and red brass armatures, when large water flow rates occur locally. Typically, damage is seen as blank cavities on valve seats and valve cones as well as in piping immediately after elbows and T-pieces. Erosion corrosion arises at large water flow rates and is aggravated by high temperature and high alkalinity in the district heating water if oxygen is present at the same time. The water flow rate in copper pipes with district heating water should therefore be limited in general and especially in copper piping with many operating hours at full flow.

**Sulphide corrosion**, which specifically attacks phosphoric hard solders, can also result in rusting through of copper pipes. The sulphide corrosion appears as a black layer of copper sulphide ($Cu_2S$ – chalcocit) on the inside of the pipes and is caused by the presence of hydrogen sulphide and/or sulphide as well as oxygen. The hydrogen sulphide and the sulphide result from bacterial growth, in which sulphur-reducing bacteria convert sulphite and sulphate into sulphide.

**General corrosion/uniform corrosion** of copper practically never occurs in oxygen-deficient district heating water. Therefore, the circuit water does not contain dissolved copper ions that can aggravate corrosion of steel. Thus, steel and copper can be mixed in district heating systems at random. A special problem in connection with copper piping is copper chips that are conducted with the water current because of carelessness during execution and then settle in a steel pipe quickly giving rise to rusting through in the form of pitting corrosion.

## 2.6 Aluminium

Aluminium and aluminium alloys should not be used in district heating systems in which the metal gets into contact with the district heating water since aluminium components corrode vigorously at the pH-values used in district heating systems.

Special attention should be paid to user installations in which aluminium components occur in air heating systems, underfloor heating systems, and in certain radiator types as well as armatures. Furthermore, aluminium piping is used as root zone heating in horticulture. User installations containing aluminium components should be connected indirectly over the heat exchanger if the components cannot be exchanged for other components of corrosion resistant material types.

## 2.7 Plastic materials

Normally, plastic materials do not corrode, but together with the chemistry in the district heating water they can create a number of effects and reactions that have to be evaluated.

- Plastic piping for district heating systems must have oxygen barrier in accordance with DIN 4726 and DIN 4729 or better. The requirement of the DIN standard is max. 1 mg $O_2/m^2$ at 80°C. This is three or four times lower than the requirement in the standard DS/EN 15+32-2, therefore it is recommended to use the DIN standard to reduce the admission of oxygen as much as possible.
- Joining methods for plastic piping must be chosen in consideration of the oxygen barrier.
- Plastic piping without oxygen barrier allows oxygen diffusion into the district heating system and should not be applied.
- When plastic piping without oxygen barrier is used in user installations, the installation should be separated from the district heating system by a heat exchanger. In practice, an increased oxygen content in the return water from the property can often be measured when plastic piping without oxygen barrier has been used or when the barrier has been damaged during installation work.
- Certain types of plastic can release ammonium and organic substances to the district heating water.
- At $pH > 9.3$ ammonium is converted into ammonia and the organic substances can further bacteriological activity.
- In connection with carelessness during work execution, plastic piping can afterwards release plastic chips that clog valves, armatures, filters, etc.

No clear rules regulate how to make joints so that they can be called oxygen-tight.

## 2.8 Deposits and precipitations

Deposits (firm) inside piping, heat exchangers, and boiler walls arise from precipitation and crystallization of one or more salts or other minerals in the district heating water if the maximum solubility of the salts is exceeded. Another type is organic deposits resulting from microbial organisms. It is important to minimize formation of deposits and precipitations.

In holding tanks, there is likewise major risk of precipitations (loose not firm) consisting of rust or substances formed by addition of chemicals for binding residual hardness or oxygen. Therefore, the use of additives cannot be recommended when there is a holding tank. Furthermore, it is important to secure against penetration of oxygen resulting in corrosion and corrosion products precipitating on to the tank bottom.

## Salts

Precipitation of salts typically stem from residual hardness in the form of calcium and magnesium ions that precipitate as carbonates, sulphates, and silicates. The solubility decreases with rising temperatures and the salts precipitate. Residual hardness, also called scale forming substances, partly comes from the make-up water, but primarily from penetration of drinking water via leaky hot-water tanks and through filling of drinking water in case of new plants and repairs. The concentration of salts must be kept as low as possible. Thus, it is important to prevent penetration of drinking water from leakages and to minimize filling of drinking water during repairs. In case of major repairs, demineralized/softened water should be filled; perhaps water treatment equipment can be rented.

## Precipitations

District heating water often contains a certain volume of suspended matter in the form of particles that are deposited in areas or places with low water velocity. Normally, these particles are rust flakes, iron scales, welding slags, sand, earth, and corrosion products of various kind as well as regular foreign bodies and organic substances. The problems of deposits are among other things:

- Deposits and precipitations have low thermal conductivity and reduce the capability of thermal transmittance and thus the plant capacity. Also, pressure loss increases resulting in increased pump work and thus poor operating economy.
- As regards corrosion, precipitations and deposits are unwanted, since they add to the risk of pitting corrosion.
- Ferrous and thus magnetic corrosion products can cause deposits in meters and on sensors, which can result in reduced or failing functioning of these devices.
- In particular magnetite particles ($Fe_3O_4$) with a particle size of 1-10 µm are unwanted in circuit water since they have a strongly abrasive effect on among other things shaft seals, furthermore, they can deposit and cause disturbances in meters, etc. Magnetic inductive measurements can be disturbed by magnetite.

The volume of precipitations and particles in the circuit water can be reduced by means of partial stream filtration as mentioned in *section 5.1: Removal of impurities and sludge.*

## Oil and grease

Oil or grease in the water can originate from sources such as:

- Oil penetration from leaky fuel-oil heat exchangers.
- Oil films from pressure tanks and expansion vessels.
- Lubricating grease from lubricated taps.

These substances can cause clogging of filters, reduced functioning of meters, instruments, and sensors as well as formation of deposits and precipitations leading to bacteriological corrosion.

## 2.9 Organic deposit/biofilm

Bacteria in district heating systems form organic deposits/biofilm provided that there are enough nutritive substances in the water to feed the bacteria. They are able to penetrate all technical systems since they are so small, approx. 1 µm. Bacteria in district heating water enter the system via:

- Make-up water
- Contamination in case of pipe fractures
- Lack of cleaning in case of new plants and modernization.
- Mixing with central heating water from newly connected plants.
- Leaky heat exchangers and hot-water tanks.

When the growth conditions are present, the bacteriological activity can be increased. Usually, organic substances and sulphate provide the preconditions of biofilm growth. They change the character of the surface, and chemical changes take place on the surface, for example concentration of chloride. In this way, bacteriological (microbial) corrosion arises.

Bacteria can live freely in water, but close on 90 % are present in colonies on the inside surfaces as biofilm. Part of such stationary biofilm, for instance in the return piping, is not exposed to changing or high temperatures.

Biofilm in district heating systems can bring about much technical and environmental damage:

- Microbial corrosion.
- Reduced heat transfer.
- Increased pump costs.
- Increased chemical consumption.

By microbial corrosion is meant that bacteria in the biofilm change the chemistry on the steel face in such a way that a corrosive environment arises. Biofilm has a thermal conductivity that is five or six times poorer than that of mineral coats end even thin coats can therefore reduce the heat transfer dramatically. A coat of 0.1 mm can reduce the heat transfer by approx. 60 % if present on the heat exchangers. Increased pump costs resulting from biofilm can occur since the biofilm can lead to increased roughness of piping. Increased chemical consumption can occur since bacteria can decompose the agent added as chemical oxygen binding and as pH-adjustment. Both tannin and ascorbic acid can be decomposed.

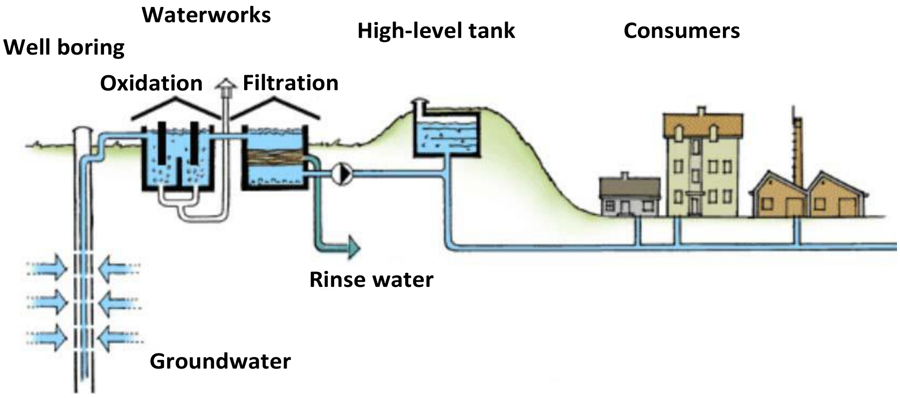
# 3 WATER SUPPLIES AND QUALITIES

## 3.1 Water supply sources

### 3.1.1 Waterworks water – drinking water

Traditionally, drinking water is used for production of make-up water for district heating systems. Drinking water has a well-defined quality with known limit values for contents of a number of substances. Ground water is pumped up, oxidized and filtered to produce the water. Usually, substances like iron and manganese are removed, but also methane, aggressive carbon dioxide, nitrite, ammonium, and phosphor as well as certain tracers.

**Figure 3.1.1.1 Diagram of the processes in a waterworks**



The most relevant quality requirements for drinking water cf. executive order No. 1310 of November 11, 2015, of the Danish Ministry of Environment. Where nothing else is stated in the table, the highest allowable values are used.

**Table 3.1**

| Parameter | Unit | Quality requirement | Comment |
|---|---|---|---|
| pH-value | | 7-8.5 | |
| Oxygen content | mg $O_2$/l | 5 | Minimum requirement |
| Conductivity | mS/m | | As a minimum, the conductivity in the water shall be 30 mS/m at 25°C |
| NVOC | mg C/l | 4 | |
| Evaporation residue | mg/l | 1500 | |
| Hardness | °dH | | The water hardness shall be between 5 and 30 |
| Ammonium | mg $NH_4$/l | 0.05 | |
| Nitrate | mg $NO_3$/l | 50 | |
| Chlorides | mg Cl/l | 250 | |
| Sulphate | mg SO4/l | 250 | |
| Copper | mg Cu/l | 0.1 | |
| Iron | mg Fe/l | 0.2 | |
| Manganese | mg Mn/l | 0.05 | |
| Cadmium | µg Cd/l | 2 | 5 at taps |

With increasing rates and growing resource awareness as to groundwater reserves, it is relevant to consider the use of other affordable and non-resource limited water sources of lower and more diverse quality (see section on wastewater). The use of other water supplies than drinking water requires greater attention to contents of foreign substances and their effect on the water treatment or consequence for formation of coats and bacterial growth as well as for corrosion conditions in the district heating systems.

### 3.1.2 Technical water

In this guide, technical water is defined as water conducted in piping and not fulfilling the requirements in the said executive order. This could be water from contaminated groundwater borings that has been purified to drinking water quality. In Denmark, this water is not allowed as drinking water since it has been purified. When the technical water comes from other sources, quality and deviations from drinking water quality must be assessed in each individual case.

### 3.1.3 Rainwater

Rainwater is free of calcium and thus soft, therefore a softening plant can be omitted when using rainwater as water supply. Rainwater is also free of salts generally speaking, but can contain a number of substances and foreign elements dependent on where and how it is collected, which make special requirements for the wastewater treatment. The most substantial deviations from drinking water quality are:

- High contents of organic substances and bacteria.
- Low pH-value of 4.0-6.0 dependent on the collecting surface.
- High contents of suspended matter.
- In case of water collection from metal roofs, the rainwater can contain strongly increased values of the metal in question.
- Water collected from roads and open spaces containing oil and bitumen residue as well as salt during winter will as a consequence be unsuitable as water supply without previous purification.

### 3.1.4 Surface water

The use of surface water from lakes and water courses can in certain situations be relevant and dependent on soil conditions and source conditions it will have a hardness corresponding to something between groundwater and rainwater. The most substantial deviations from drinking water quality are:

- High contents of organic substances and bacteria including humus content from acid soil conditions.
- Seasonal variations in quality.
- Very varying pH-value dependent on soil and source conditions.
- High contents of suspended matter.
- Contents of nutrient salts including nitrates from agricultural areas.

### 3.1.5 Blowing down condensate from steam installations

Where drain water or surplus condensate from steam turbines with e.g. frequent start/stop is available, this condensate can be used with advantage as make-up water. The condensate must be analysed to ensure that it complies with the quality requirements for make-up water.

### 3.1.6 Flue gas condensate from biomass and natural-gas firing

Some chip-wood and natural-gas fired as well as a few straw-fired heating plants have flue gas condensation, whereby large water volumes are produced that can be used for production of demineralized water. The quality of the water depends on the treatment of the water. In case of chip-wood plants, the water can be treated in a chip filtration plant or by admixture of chemicals and subsequent mechanical purification. In case of flue gas condensation in natural-gas fired plants, treatment of water is not included and oil residue can occur as well as unburnt carbon hydrides (UHC) and possible metal rests in the form of ions or particles from the flue gas cooler. Flue gas condensate from natural gas has a low pH-value and is aggressive in untreated condition, which requires pH-adjustment before reuse or discharge.

In order to use the water it is necessary to make analyses with a view to which purification method to include. There is a limited number of analyses of flue gas condensate. Analysis examples are stated in table 3.1.6.

**Table 3.1.6 Examples of analysis values from flue gas condensate**

| **Wastewater analyses** | | **Chip-wood fired** | **Natural-gas fired** |
|---|---|---|---|
| pH-value | | 7-8.8 | 3-7 |
| Conductivity | mS/m | | 33-150 |
| Chloride | mg/l | | <1-4.3 |
| Sulphate | mg/l | 230-580 | 3.5-12 |
| Nitrite | mg/l | 4.5-10 | 60 |
| Nitrate | mg/l | 0.2-1.3 | 3.7 |
| COD | mg/l | <10 * | |
| Sediment | mg/l | <0.2 | |
| SS | mg/l | 6-24 | |
| TOC | mg/l | | 81 |
| Lead | µg/l | 0.6-6.5 | |
| Cadmium | µg/l | 2-31 | |
| Chromium | µg/l | 2.1-12 | |
| Copper | µg/l | 1-20 | |
| Zinc | µg/l | 80-890 | |
| Mercury | µg/l | 0.05-0.33 | |
| Nickel | µg/l | 0.6-4.3 | |
| | | | |
| PAH | µg/l | <0.01 | 4.7-8.6 |

*the purification method is decisive for concentrations.

Other types of process water can also be used, but the quality must be examined and evaluated before deciding whether to be used.

## 3.2 Water analyses

The purpose of water analyses is to check that the specifications for water quality, section 1 *Water quality*, are not exceeded, to determine the method for treatment of make-up water, and to dimension the plants.

### 3.2.1 General analyses

The most important substances on which dimensioning is based are shown below. Beyond these, supplementary analyses may be needed dependent on the condition of the water.

| **Cations**: | **Anions:** |
|---|---|
| Calcium, Ca | Hydrogen carbonate, $HCO_3$ |
| Magnesium, Mg | Chloride, Cl |
| Sodium, Na | Sulphate, $SO_4$ |
| Potassium, K | Nitrate, $NO_3$ |

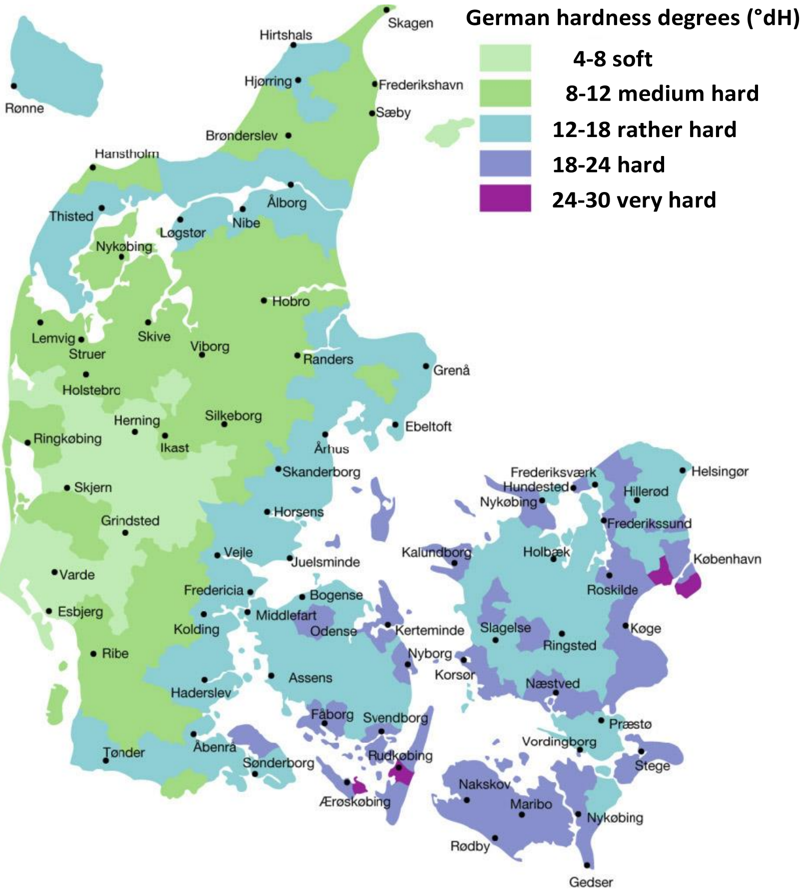
Beyond these substances, silicate is important with a view to treatment of demineralized water, and barium is often referred to as problematic in reverse osmosis systems. Problems with barium are seldom seen in Denmark. Similarly, it is useful to know the contents of organic substances stated as TOC (Total Organic Carbon) or NVOC (Non Volatile Organic Content), because contents from a few mg/l can give problems in the further treatment.

Normally, drinking water analyses are available from the individual Danish local authorities and can often be used to determine the best suitable water treatment. Dependent on purification method, supplementary analyses can be needed. If for example a reverse osmosis system is to be used, the analyses should be supplemented with the Silt Density Index (SDI) since water with an index over four requires further treatment (particle removal) before it can be used in a reverse osmosis system without damaging the membranes. If drinking water is used as source, the expected contents of a number of substances can be found in the existing databases such as the groundwater chemistry database of GEUS (Denmark's and Greenland's Geological Surveys), therefore water analyses can be omitted in many cases. Furthermore, the local water supply will normally have access to current drinking water analyses for the individual supply areas.

### 3.2.2 Hardness degrees

The expected hardness degrees appear from the map on the next side over the average drinking water hardness in Denmark. Current data can always be obtained from the local authorities in Denmark.

**Fig. 3.2.2 Water hardness in Denmark**

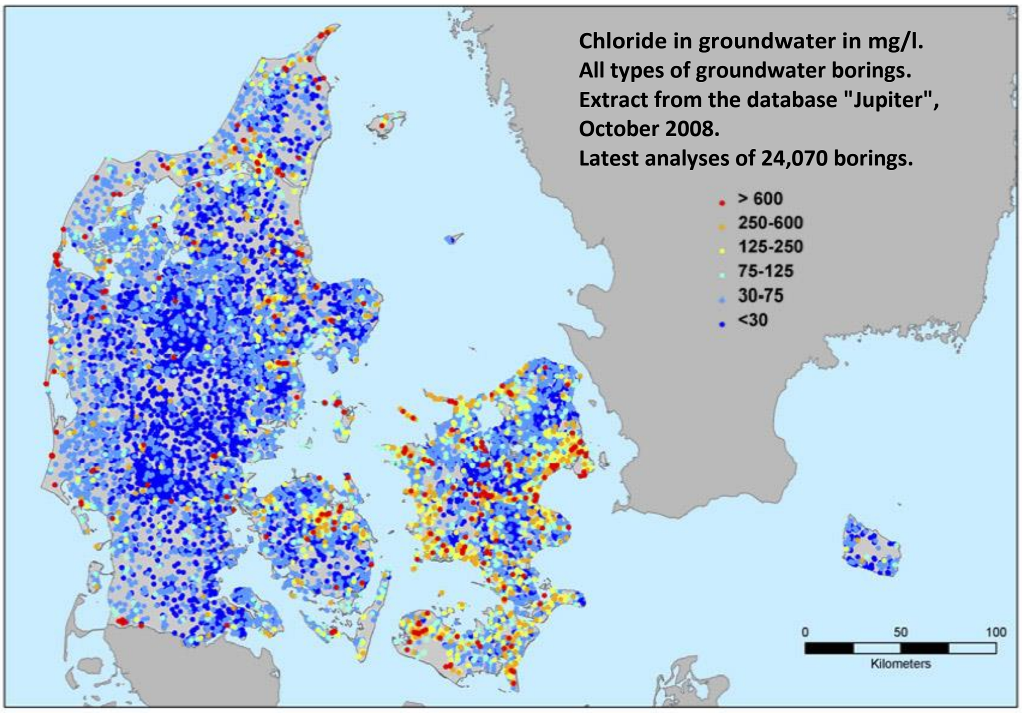


In areas with water hardness under 5°dH or where aggressive $CO_2$ is present in the borings, a water hardening process is carried out in the waterworks by addition of lime powder or by slowly running the water over broken marble stones so that the water obtains a higher hardness content.

### 3.2.3 Chloride content

The chloride content in drinking water varies in Denmark. Especially in coastal areas, there is risk of high contents and extended catchment increases the risk. In areas with high chloride content, the increased corrosion risk and thus the extra requirement for water demineralization should be considered.

**Figure 3.2.3** Geographic distribution of chloride analyses from all types of groundwater borings, totalling approximately 24,000 borings divided into six concentration intervals. Highest chloride values are illustrated uppermost. Based on data from the GEUS database "Jupiter" from October 7, 2008.



## 3.3 Water penetration into the district heating system

To some extent, most district heating plants will see unintentional water penetration. In some cases, a partial stream purification plant is necessary to maintain a good water quality. In any case, sudden changes in contamination levels (chloride, sulphate, hardness) indicate failures that should be remedied as soon as possible.

In all plants with direct user connection, central heating water from user installations and waterworks water from pressure tests most likely is not completely flushed, but often conducted to the district heating system. Usually, the employed water treatment is sufficiently robust, so that these small impurities do not result in an appreciable fall of pH or calcium precipitation.

The preparation system for hot service water is connected directly on the primary side in most user installations. Usually, the waterworks pressure is higher than the district heating pressure and penetration of unclean water/waterworks water is at risk – both in directly connected user installations and in user installations with heating installations connected via heat exchanger.

Penetration of waterworks water occurs via leaky hot-water tanks and heat exchangers. This type of water penetration can to some extent be prevented by having a district heating pressure that is higher than the waterworks pressure. However, this can be difficult to maintain throughout the net and in periods with low load, it can seldom be sustained. Thus, leakages can be difficult to detect since penetration of water occurs dependent on the load and are not detected until later through measurements. It is important to keep an eye on water consumption. If it is necessary to tap water from the system, this indicates water penetration.

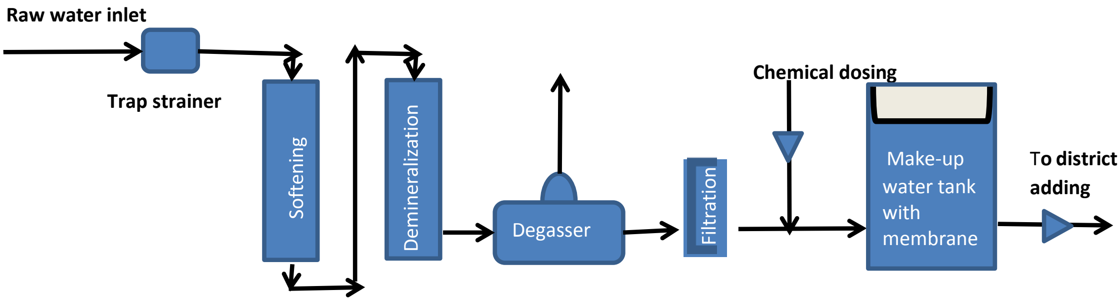
The plant's own operational and maintenance routines also involve risk of unintended water penetration. Examples of common routines: Filling of street piping using fire hose after repair or service works as well as emergency operation with drinking water after major pipe breaks. Both situations can be limited or totally avoided, provided that the plant has a reservoir of appropriate size with treated and conditioned make-up water, which can be filled into the plant immediately. Another possibility is to rent demineralization equipment for adding water in certain cases.

When dimensioning the plants, it is important to delimit the system so that water waste can be confined in case of repairs, i.e. that sufficient blocking possibility of the system is allowed for.

# 4 METHODS FOR TREATMENT AND CONDITIONING OF MAKE-UP WATER

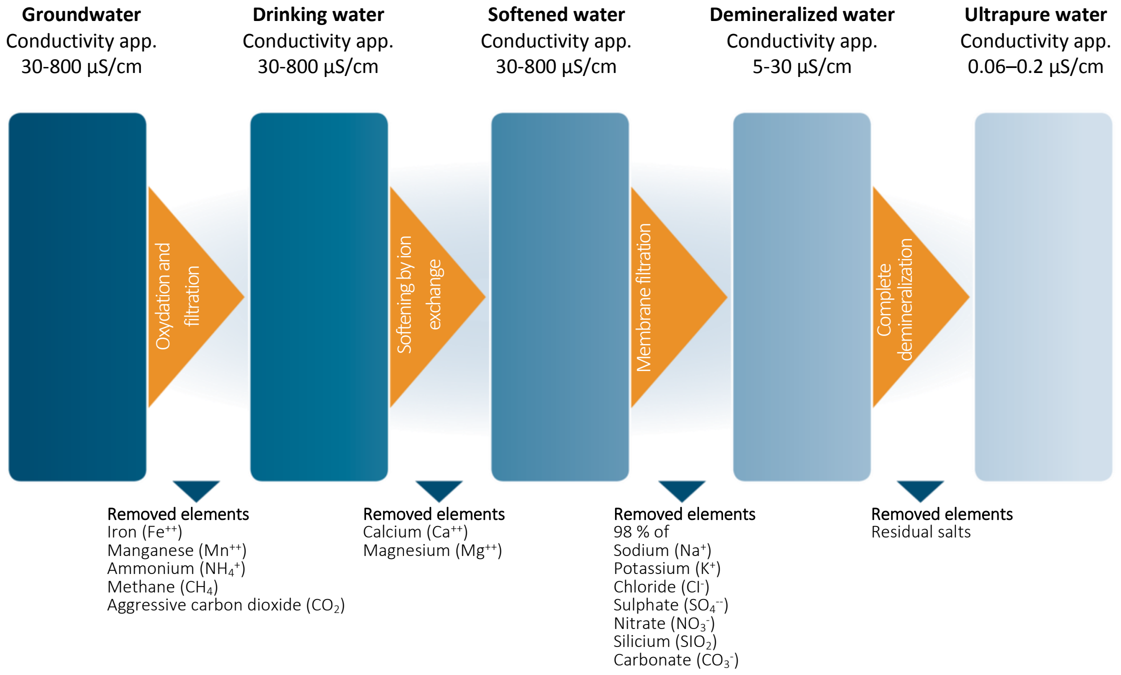
All make-up water for district heating systems must be pre-treated and conditioned before being filled into the district heating system. The extent depends on the chosen make-up water class and of the water quality. The below figure 4.0.1 shows a typical concept with all elements forming part of a demineralized and deoxidized water quality. In case of other qualities, some components are omitted that are not relevant.

**Fig. 4.0.1 Diagram of common concept for demineralized and deoxidized water**



The typical contents of substances in drinking water, softened water, and demineralized water are shown as well as removal of these through the processes in Fig. 4.0.2.

**Fig. 4.0.2 Removal of elements in the water shown in the various treatment steps.**



## 4.1 Filtration

In order to achieve unproblematic operation of the water treatment plant, the drinking water should always be filtered before being conducted to the water treatment plant or filled directly into the district heating system. Drinking water contains many unwanted impurities such as sand, clay particles, and silt (smaller than clay particles) as well as rust and manganese shells, etc. To this end, normally a self-purifying filter or a trap strainer with metal screen and bottom drainage is used. In case of other water sources than drinking water, further filtration through a bag filter, sand filter with backwash or ultrafiltration will normally be needed dependent on the degree and type of contamination. Surface water can contain organic material, large particles, algae, humus, and ochre thus requiring individual and often comprehensive treatment.

Fig. 4.1.1 shows fields of application for the various filtration techniques. Figure 4.1.2 shows how the row of membrane techniques can be combined. In practice, more than two or three membrane techniques are seldom combined.

**Fig. 4.1.1 Application areas of various filtration techniques (µm)**

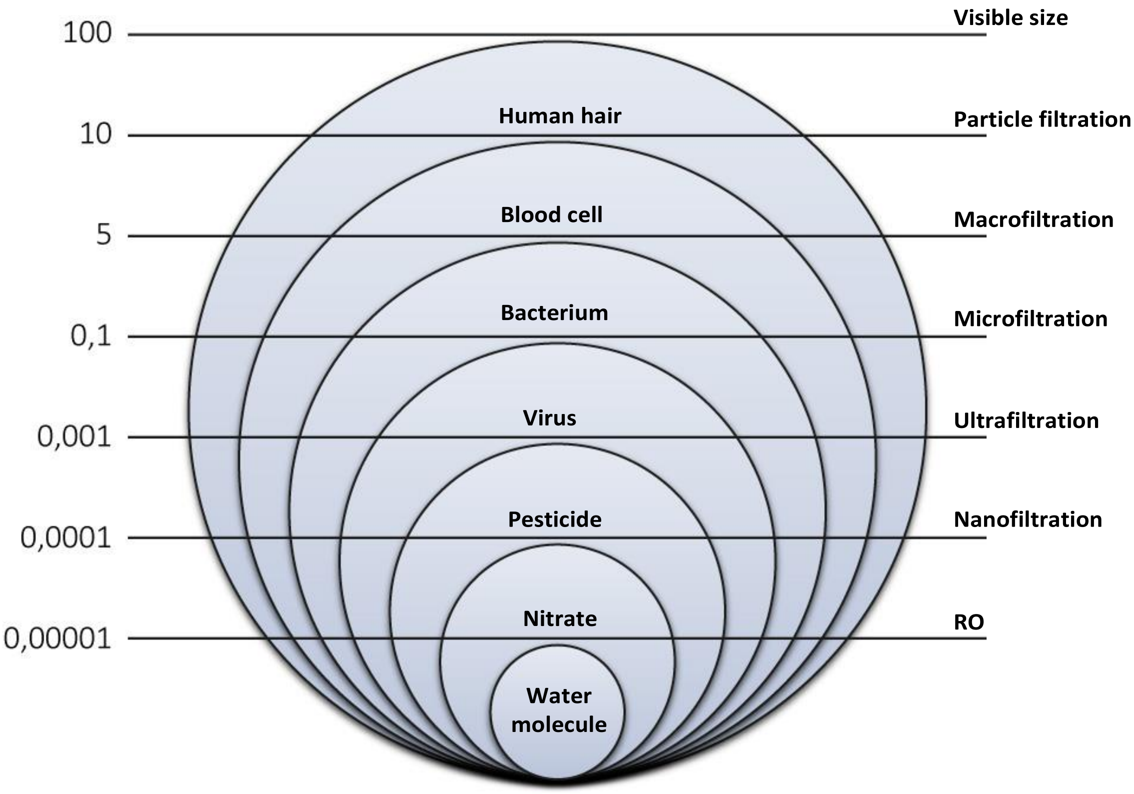
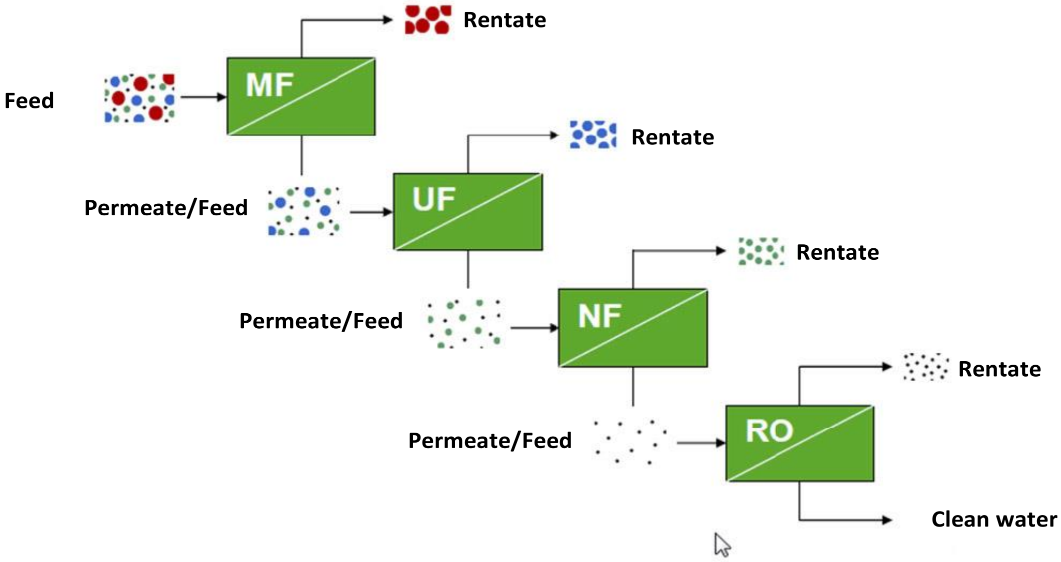


Fig. 4.1.2 Filtration types and particle sizes



## 4.1.1. Cartridge filter

If a reverse osmosis plant is used, it is necessary to install a cartridge filter or a mass collector in the form of a bag filter with a filter density of approx. 1 µm before the membrane section in order to protect this and to extend the useful life. In some cases, ultrafiltration can be an advantage to reduce the load on the reverse osmosis system.

After the softening plant and the ion exchange plant, a cartridge filter or a mass collector should also be installed, the latter in the form of a bag filter with a filter density of 5-10 µm to collect the fines liberated in these plants.

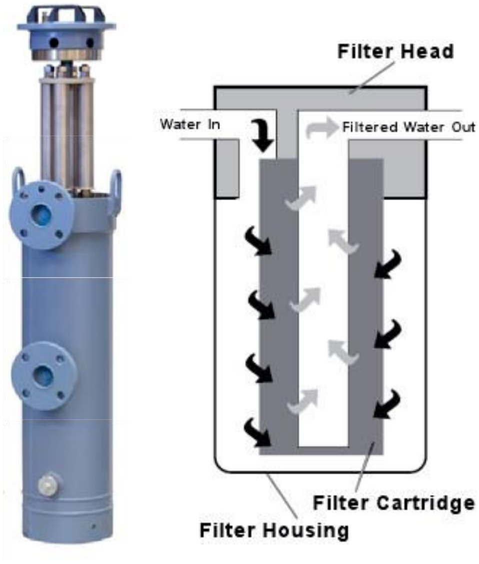


Fig. 4.2.1 Cartridge filter and filtration principle

## 4.1.2 Ultrafiltration

When other types of water than drinking water are used, ultrafiltration can be necessary. Ultrafiltration is a membrane technique like reverse osmosis, but far less pressure is required to push the water through the membranes. Ultrafiltration often proceeds as so-called "dead-end" filtration in which all feed-water is pressed through the membranes in the course of minutes, then the membranes are backwashed shortly with permeate at high flow to remove the deposited substances. This cycle is repeated. The permeate consumption for backwash amounts to approx. 10 % of the produced volume.

Ultrafiltration retains particles/molecules of 0.01-0.1 µm. Thus, organic substances of large molecule size are removed, which might result in contamination of the membranes in the subsequent step with reverse osmosis filtration. Ultrafiltration also retains viruses and bacteria so permeate will be sterile after this treatment. In this way, reverse osmosis membranes are well protected against bacterial growth on surfaces, which could reduce the function substantially.

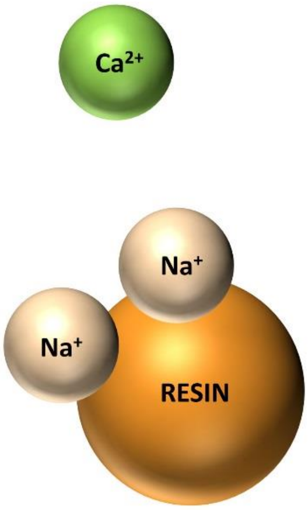
## 4.2 Softening

Hardness in water is removed in softening filters that are the most frequently used method to produce softened make-up water and for pre-treatment of water for demineralization through reverse osmosis. The function is based on a cation exchanger in sodium state so that it is willing to take up calcium and magnesium ions. After a certain period of operation, it is returned to sodium state through regeneration with a salt solution.

The term hardness in water means contents of calcium and magnesium ions ($Ca^{++}$ and $Mg^{++}$) in balance with bicarbonate ($HCO_3^-$). When heated, a reaction takes place in which bicarbonate decomposes and forms calcium and magnesium carbonates ($CaCO_3$, $MgCO_3$) together with carbon dioxide and water. The sparingly soluble calcium and magnesium carbonates precipitate on the heated faces, where they cause deposits that usually are white (boiler scale).

By softening, calcium and magnesium ions are exchanged for sodium ions from the sodium chloride (boiled salt) that is used for regeneration of the softening plant. In this way, the hardness producers in the water turn into sodium carbonate, which is water-soluble and does not cause deposits. The softening filter also functions as a mechanical filter in practice that collects dirt. Figure 4.2.1 shows the principle in softening, in which two sodium ions on the ion exchanger are exchanged for calcium and magnesium.

**Fig. 4.2.1 Principle of ion exchange, softening**

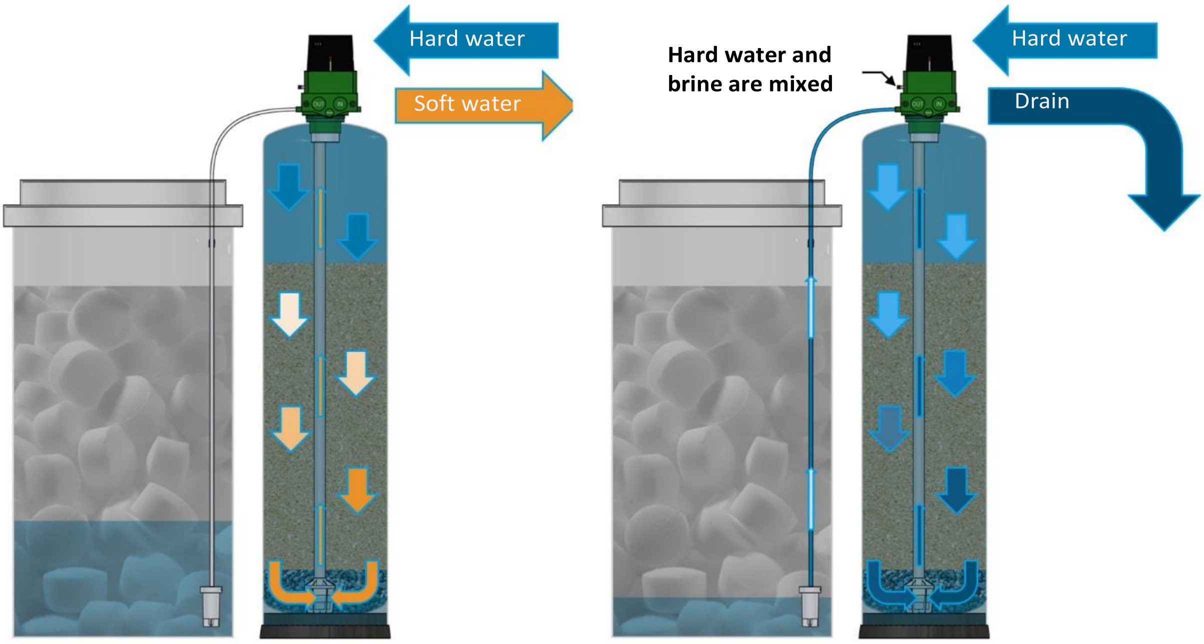


After treatment of a certain volume of water, the ion exchanger becomes saturated losing its ability to take up calcium and magnesium so that regeneration of the ion exchanger is necessary. The water volume that can be treated before regeneration depends on the water hardness in relation to plant size and is calculated for each plant. Usually, the ion exchanger preserves its capacity, but it is important to keep an eye on the function and to take samples for analyses of hardness after the plant. At the same time as regeneration, the ion exchangers are backwashed so that dirt and broken ion exchanger grains are removed. If the ion exchanger is overloaded with impurities, the risk of grain cracking increases. Also, make sure that the bed layer of ion exchange resin does not decrease. If so, refill with new resin or change ion exchange resin.

By regeneration with sodium chloride, the calcium and magnesium ions are flushed out as calcium chloride and magnesium chloride and run as wastewater to drain together with the collected impurities.

After the softening plant, the make-up water has liberated itself from deposit-forming salts, but contents of remaining salts have not been substantially changed and the conductivity remains high in softened water. Bicarbonate in water reacts as a weak acid and the chemical dosing with sodium hydroxide for pH-adjustment of softened water requires a considerably larger consumption of demineralized water. The oxygen content of the water is not changed by softening. Usually, the oxygen content is 6-8 mg/l. If the water is not conditioned, it is strongly corrosive. The principle of a softening plant is shown in figure 4.2.2.

**Fig. 4.2.2 Operating principle of softening plant**. To the left the operating situation is shown and to the right regeneration.



## 4.3 Demineralization

In demineralization, the purpose is to remove all salts from the water including chlorides, sulphates, and carbonates, resulting in low conductivity. With smaller plants, it may be advantageous to buy water from a larger plant. Many plants connected with large plants buy and add water from the transmission net. For own production of demineralized water, a reverse osmosis system or an ion exchange plant is used. Small plants can be rented under a contract including continuous monitoring and service from the supplier.

### 4.3.1 Reverse osmosis system (RO system)

### Principle

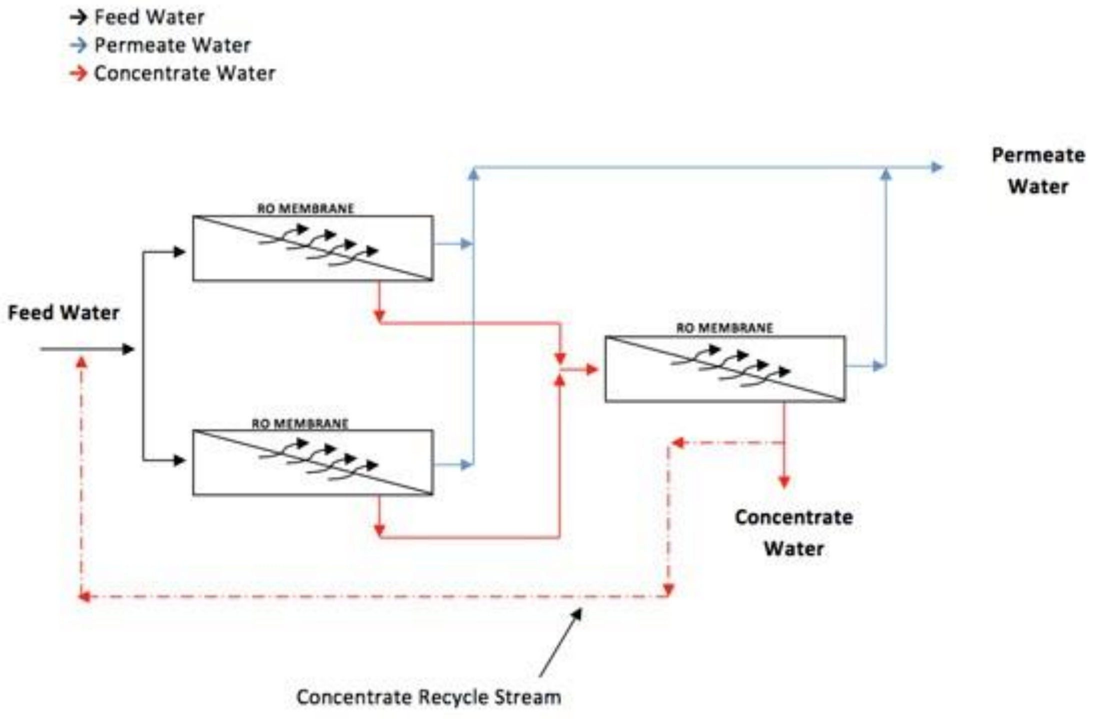
The principle of reverse osmosis is that saline water is pressed onto a membrane. Through the microscopic pores (0.001-0.0001 µm) in the membrane surface, mainly water molecules are able to pass because the water molecule is one of the smallest molecules that is liquid. The microscopic pores of the osmosis membrane are adapted to the water molecule and therefore do not let other substances in the water through, such as salts, heavy metals, chemicals, viruses, and bacteria, because all these substances are larger than a water molecule. Most dissolved substances are rejected, but gasses like oxygen ($O_2$,) nitrogen ($N_2$), and carbon dioxide ($CO_2$) as well as molecules smaller than the water molecule will pass through the osmosis membrane.

By increasing the pH-value, it is possible to bind $CO_2$ as bicarbonate, which is unable to pass through the membrane. Increased pH ensures that silicate is kept dissolved and can be removed in the reverse osmosis system without causing deposits. The filtered liquid is called permeate, while the retained concentrated liquid is called concentrate. Not all ions can be retained 100 %. Some part (1-2 %) will pass through the membrane depending on both molecule size and membrane. In order to reach a low residual concentration of ions, it can be necessary to use more RO systems in series or in combination with ion exchange or supplemented with electronic deionization (see chapter on EDI section 4.3.3).

## Construction of the RO system

The construction of the reverse osmosis system depends on water quality and origin as well as the quality requirements for the demineralized water. The RO system is designed with sections connected in series and in parallel, in which some of the concentrate perhaps is recirculated to achieve maximum recovery of the water for permeate and to have minimum waste of concentrate.

**Fig. 4.3.1.1 Schematic diagram of a two-step reverse osmosis system**



The water is pressed through the membrane system at a pressure of between 10 and 50 bar dependent on plant type and membrane choice. Usually, 80-85 % of the water (permeate) is pressed through the membrane for use as make-up water in new plants. This figure is only 75 % in older plants while 15-20 % is conducted to drain as concentrate containing the unwanted salts from the water. Alternatively, the concentrate can be reused for backwash of filters before being conducted to drain or somehow reused somewhere in the production.

### Pre-treatment

In order to protect the membranes against precipitation of among other things calcium and magnesium salts, it is necessary to pre-treat the water before it is conducted to the reverse osmosis system. As pre-treatment either use softening or addition of anti-scaling chemicals preventing coats of germs from growing. In each case, it must be examined which is the best solution with a view to engineering and economy. To protect against clogging and mechanical blocking of the membranes, install a fine bag filter or a cartridge filter (1µm) before the RO system. In case of other impurities including organic substances, ultrafiltration can be applied. The high-pressure pump is dimensioned to overcome the pressure loss through the membranes connected in series as well as the osmotic pressure, which depends on the concentration of dissolved salts and the temperature.

### Environment and operating costs

Reverse osmosis uses few chemicals apart from sodium chloride (boiled salt) for softening and/or a possible anti-scaling agent and is therefore a good solution as regards environment. The energy consumption for the plant and the discharge of wastewater must correspond to the costs for chemicals in a demineralization plant based on ion exchange. For most district heating plants, reverse osmosis will be the most affordable and simplest way to produce a make-up water quality, which complies with the requirements for demineralized make-up water, as specified in table 1.3. High wastewater discharge duties can influence the result.

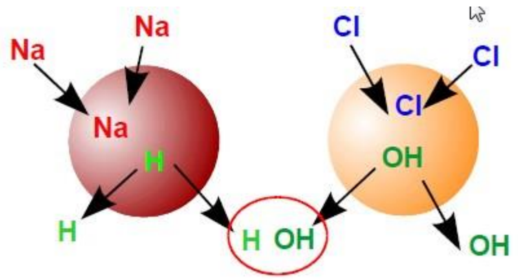
## 4.3.2 Ion exchange plant (both anion and cation exchangers)

Usually, an ion exchange plant comprises a cation filter, a degasser, and an anion filter. To achieve optimum operation, weak and strong cation and anion exchangers can be charged to reduce chemical consumption. This is optimized dependent on water quality.

With common water in Denmark, the plant usually comprises a weakly acidic cation exchanger, which removes calcium and magnesium corresponding to the bicarbonate content in the water – the temporary hardness. A strongly acidic cation exchanger then removes the remaining cations such as sodium, potassium as well as residual magnesium and calcium. The ions are exchanged for hydrogen ions. These react with bicarbonate to form carbonic acid, which can be removed as carbon dioxide in a carbon dioxide degasser, leaving a rest of up to 10 mg/l of bicarbonate.

Figure 4.3.2.1 shows the function of ion exchangers. The anion exchangers are grouped in a weakly basic anion exchanger for removing chlorides, sulphates, and nitrates and in a subsequent strongly basic anion exchanger for removing residual carbonate and silicate. Furthermore, residues of organic acids like humus are removed. Anions taken up by the strongly basic anion exchanger will release hydroxide ions through ion exchange and these react with the rest of the hydrogen ions from the cation exchangers, which have not been used for forming carbon dioxide. The product of the reaction between hydroxide and hydrogen ions is water. After the anion exchangers, the water is of neutral pH-value.

**Fig. 4.3.2.1 Ion exchange process for cation and anion**



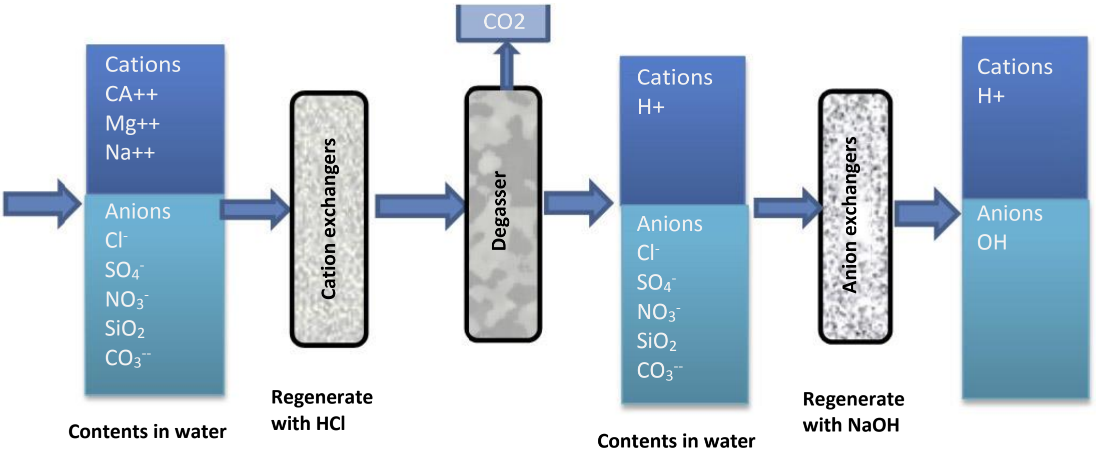
If completely demineralized water is required or wanted, install a mixed bed filter or an electronic deionization system (EDI system) after the filters. Popularly speaking EDI is an electrically regenerated mixed bed, see section 4.3.3. In both cases, a mixture of cation and anion exchangers (mixed bed) removes the remaining salts.

Hydrochloric acid and sodium hydroxide are used for regeneration of the filters. A regeneration plant with chemical tanks and neutralization tank with pumps is needed. The wastewater is conducted to the municipal sewage treatment plant. Usually, the water consumption for regeneration will be 6-8 % of the produced water volume. As an alternative, the plant is regenerated externally, but this can only be done in case of very small plants.

When requiring large volumes of make-up water, you may consider installing an ion exchange plant for production of make-up water. Such ion exchange plants were previously very common, but they have now been replaced by reverse osmosis systems to an increasing extent. Occasioned by the technical and economic development of RO systems, it is often unprofitable and environmentally unwise to build new ion exchange plants comprising both cation and anion exchangers as shown in Fig. 4.3.2.2.

Working environment considerations when handling acids and bases as well as discharge of wastewater often make reverse osmosis systems more attractive. However, the wastewater duties have been increased so much in Denmark that the advantage of RO systems is reduced.

**Fig. 4.3.2.2 Three-step ion exchange plant with $CO_2$-degasser**



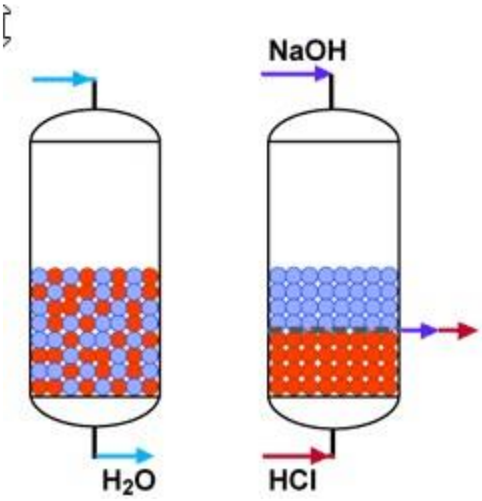
## 4.4 Polishing filters

If completely demineralized water is required, the RO system or ion exchange filters are often followed by a mixed bed filter or an EDI system (electrically regenerated mixed bed) comprising a mixture of cation and anion exchangers so that the remaining salts can be removed.

### 4.4.1 Mixed bed filters

In a mixed bed filter, the cation exchangers and the anion exchangers are mixed so that the water meets a cation exchanger and an anion exchanger by turns. Thus, it is possible to take up the last rest of salts. Before regeneration, the media are separated and the cation exchangers are regenerated with hydrochloric acid and the anion exchangers with sodium hydroxide. Then they are backwashed and mixed again, see Fig. 4.4.1.

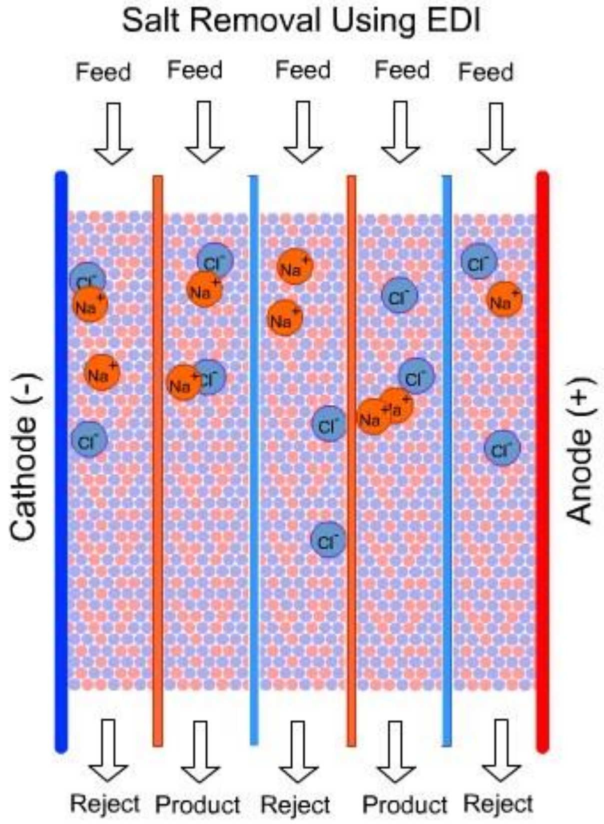
**Fig. 4.5.1 Mixed bed filter in operation to the left and during regeneration to the right**



### 4.4.2 EDI process

A typical EDI system comprises one or more cells as shown in Fig. 4.4.2. A cell consists of a number of rectangular chambers delimited by semipermeable membranes that only allow the passage of either cations or anions. Each cell is surrounded by a cathode and an anode. An external source of power creates a transverse direct-current field. Each chamber is filled with mixed-bed ion exchangers and dependent on the surrounding membranes, conditions for either concentration of ions or removal of ions are created. Each chamber is equipped with inlet for pre-treated water and outlet for either product water/permeate (completely demineralized water) or concentrate.

Fig. 4.4.2 Cell structure in EDI system with ion exchangers in the cells



The pre-treated water is conducted into the product chambers and the concentration chambers at the same time. Both cations and anions are ion exchanged in the product chambers. The negatively charged anions (for example Cl-) are attracted to the anode (+) and repelled by the cathode (-). At the electrodes, water is decomposed and forms oxygen and hydrogen ions (H+) at the anode as well as hydrogen and hydroxide ions (OH-) at the cathode. Hydrogen and hydroxide ions migrate towards the opposite pole, but on their way, they are taken up by the ion exchanger grains and in this way regenerate the mixed bed media continuously. The product stream makes up usually 90 % and the concentrate approx. 10 % of the pre-treated water. Follow link to an animation of the process: www.eurowater.com/edi

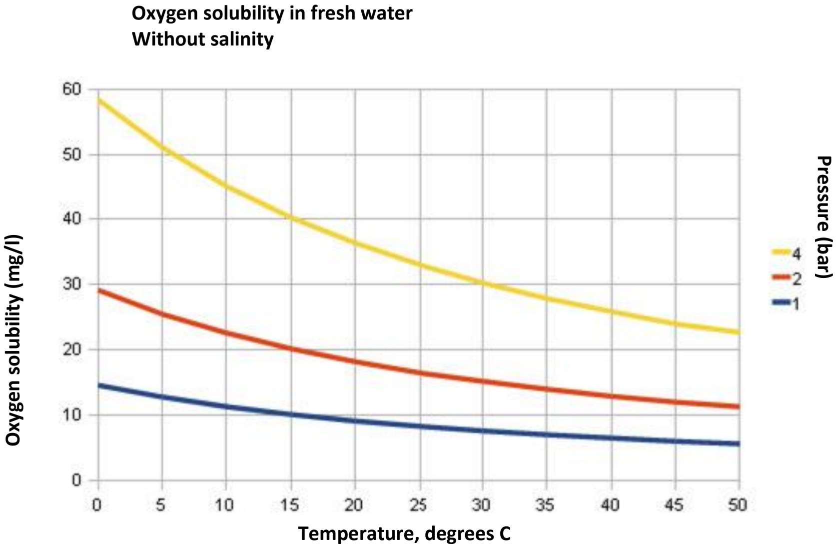
## 4.5 Degassing

Water contains dissolved atmospheric air that primarily is oxygen, nitrogen, and carbon dioxide in varying quantities. Waterworks water and water, which has stood in open contact with air, become aerated. If no degassing takes place, such water will therefore add unwanted oxygen volumes and other gasses to the district heating system. Oxygen can be bound by chemical binding as described in *section 4.6: Chemical oxygen binding*, but the other gasses will remain in the make-up water and could later cause problems in the plant if not removed. Dissolved $CO_2$ makes the treated water acid and aggressive, until it is neutralized with for example sodium hydroxide. The $CO_2$ content that is not degassed will increase the chemical consumption for neutralization marginally.

### 4.5.1 Solubility of gas in water (Henry's law)

The quantity of gas that can be dissolved in water depends primarily on pressure and temperature. With higher pressures, more gas can be dissolved, which again is released at falling pressure. With lower temperatures, more gas can be dissolved, which again is released at rising temperatures. Example: At 20°C, 20 litres of gas can be dissolved in 1 $m^3$ of water at 1 bar and 110 litres at 6 bar. At 80°C, only approx. 5 litres of gas can be dissolved in 1 $m^3$ of water at 1 bar and approx. 65 litres at 6 bar. The oxygen that constitutes approx. 21 % of atmospheric air follows the general solubility. Figure 4.5.1 shows the solubility of oxygen.

**Fig. 4.4.1** Solubility of oxygen in clean water at varying pressures and temperatures



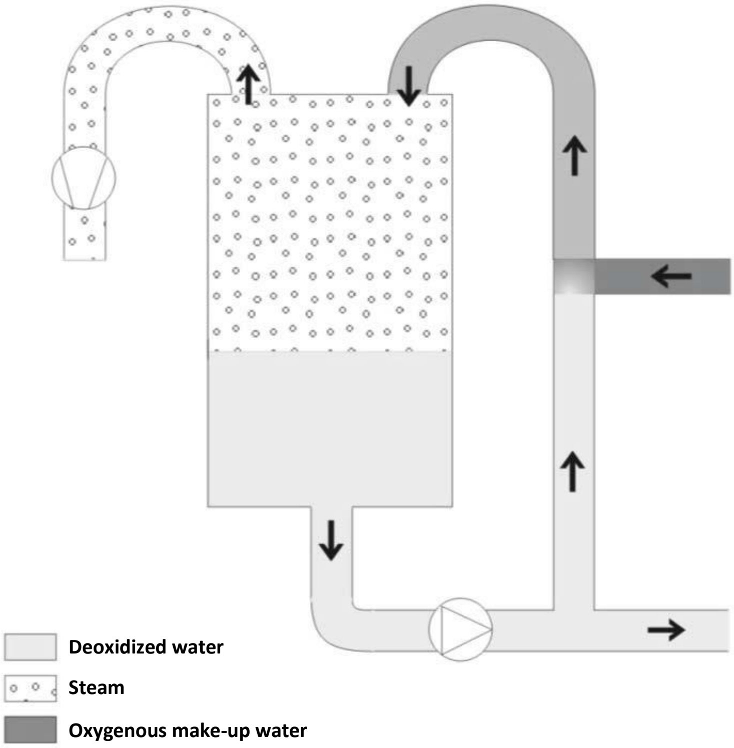
In practice, this means that if the make-up water contains atmospheric air, then the oxygen will be used when the plant corrodes (alternatively be bound by chemical oxygen binding agents, if these are able to react before the reaction with iron). The carbon dioxide will be used when neutralized with sodium hydroxide and nitrogen will be left in the water, where it can cause a great deal of trouble.

Operating trouble will often show as air in heating installations at certain users, where the thermostatic valves on the flow pipe to the radiators will give the pressure loss that causes the release of air. The pressure loss can also be released in the differential pressure regulators, where these are installed in the flow pipe. The symptoms of air in the system are – besides operating trouble at the users in question – an elastic system with pressure changes and varying water level in the pressure tank or in the equalizing tank. Degassing of make-up water can occur after several different methods that all use the above correlation known as Henry's law.

### 4.5.2 Thermal degassing under pressure or vacuum

The functioning of thermal degassing is that the make-up water is heated to the boiling point before being pumped into the district heating circuit, whereby the dissolved gasses are released. The heating can occur in the tank or in a heat exchanger before the water is conducted to the tank. The flow principle in such a thermal degassing system under pressure can be as shown in figure 4.5.2.1.

**Fig. 4.5.2.1 Thermal degassing system**

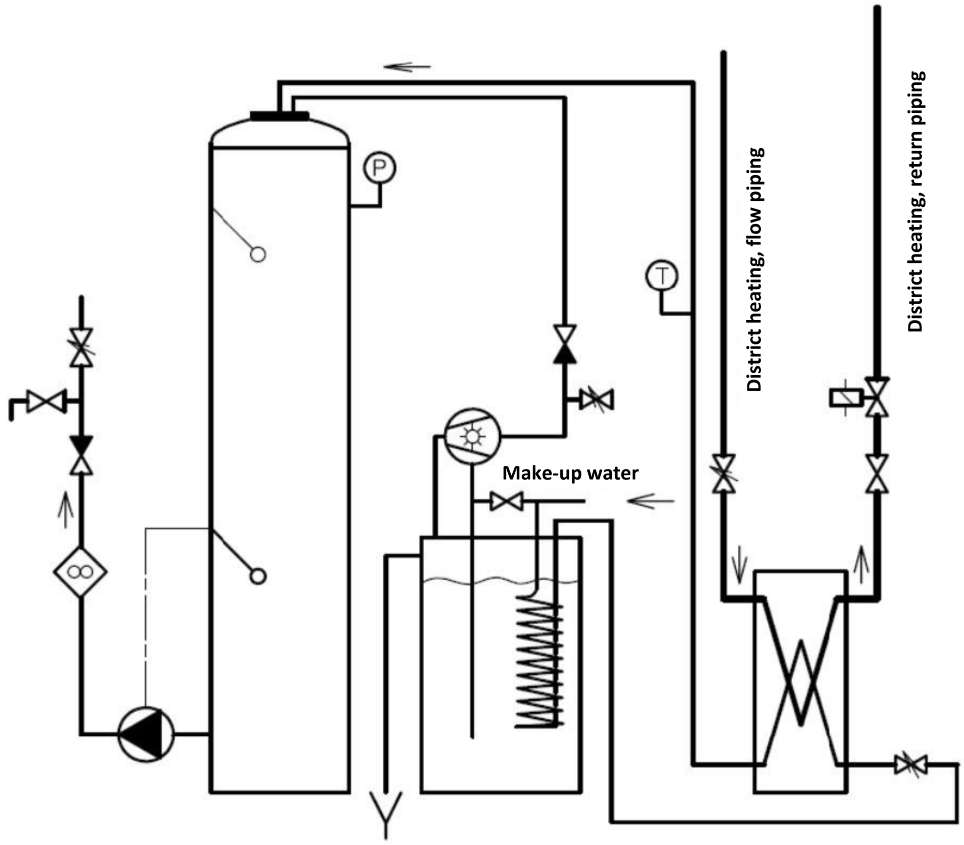


Thermal degassing under pressure presupposes heating of the make-up water to over 105°C for instance at 1.2 bar. Therefore the method is primarily used in places where steam is available or where the boiler water temperature is over 110-115°C. The oxygen content in the make-up water can be reduced to under 0.02 mg/l by thermal degassing under pressure.

Vacuum degassing functions according to the same principle as thermal degassing, but the boiling point is lowered effectively by means of vacuum in the degassing chamber. Vacuum degassers can function as continuous systems, which normally is the case for large systems, or in batch (batch degassers), which can be used in small systems.

Degassing systems are often built as a combination of the two principles so that the boiler point is lowered by means of vacuum to the level available for heating. The technical construction of such a continuous system can be as shown in figure 4.5.2.1.

**Fig. 4.5.2.2 Technical construction of thermal degassing**



Degassing by lowering of the boiling point with vacuum without using steam can usually reduce the oxygen content in the make-up water to approx. 0.1 mg/l.

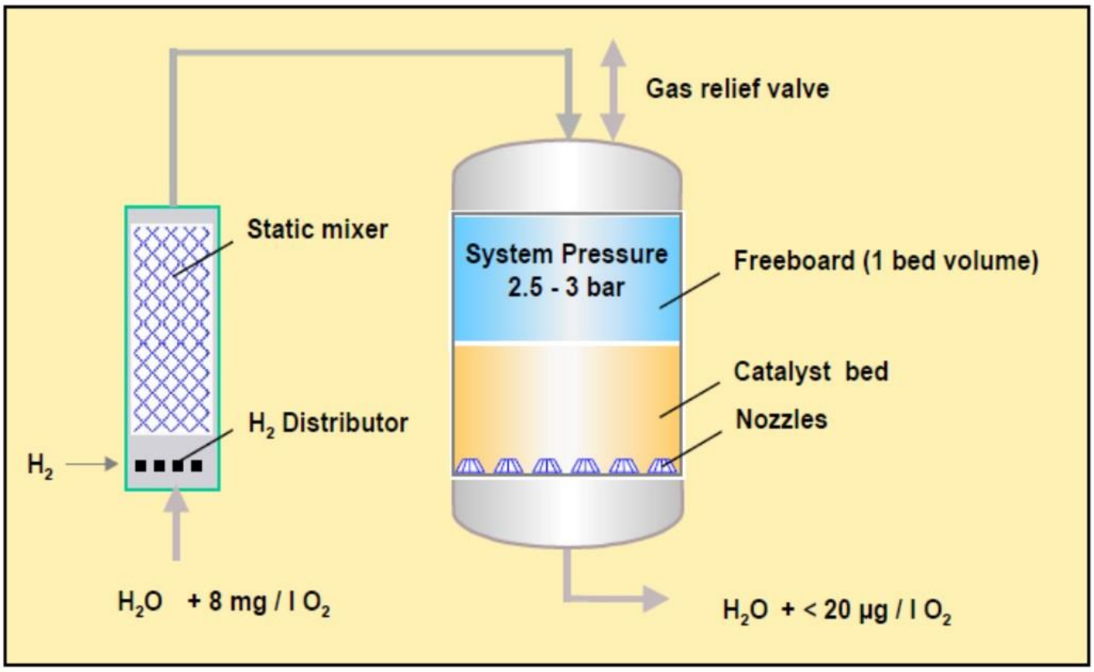
In case of small systems with limited requirement for make-up water, batch degassers can be advantageous to use. They expose a water volume batch-wise to a vacuum that releases the dissolved gas quantities. The effect depends on the applied vacuum and the time cycle used.

## 4.5.3 Catalytic deoxidation

In catalytic deoxidation, oxygen reacts with hydrogen to form water over a catalyst. The hydrogen will react with the oxygen content in the water to form water: $2\ H_2 + O_2 \rightarrow 2\ H_2O$.

The catalyst system uses a catalyst mass the inner surface of which is coated with palladium. On the palladium faces, large quantities of hydrogen in an active state can be stored. The hydrogen is admitted continuously from a pressure gas cylinder and bind on the surface of the catalyst.

Fig. 4.4.3 Construction of catalytic deoxidation system



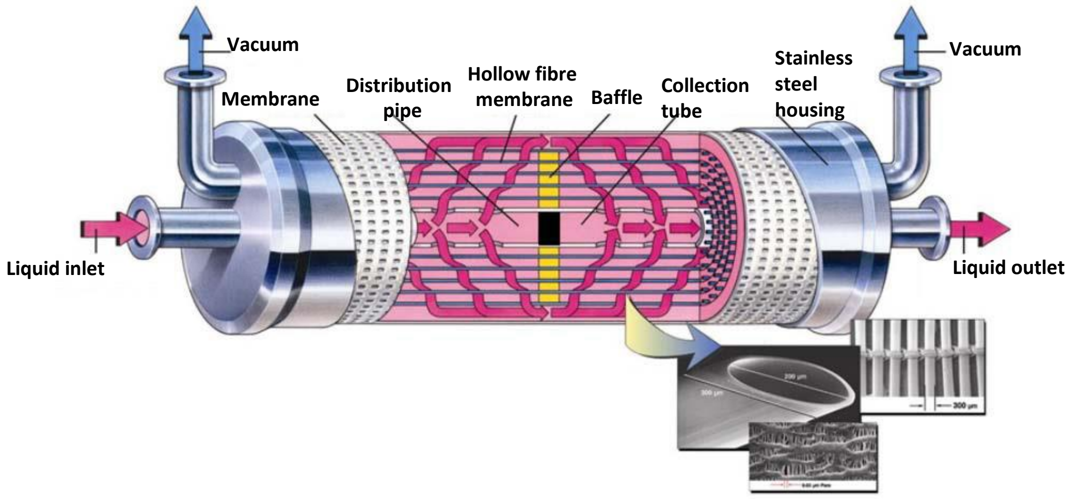
Catalytic deoxidation does not remove other dissolved gasses like nitrogen and carbon dioxide from the make-up water. Carbon dioxide will be bound by sodium hydroxide and form carbonate, whereas nitrogen can cause trouble by liberation of gas in connection with pressure fall in the system (see description in section 4.4.1).

The catalyst mass is the most expensive and most sensitive component in the system. It is important to protect this by prior installation of an efficient particle filter so that the surface is not blocked by filth. The smallest particles that nevertheless manage to slip through and are caught in the catalyst mass can be removed through regular backwash, perhaps with a solution of sodium hydroxide. This protection is very important, if the system is used wholly or in part for deoxidation of the circulating water (return water).

### 4.5.4 Membrane degassing

The membrane technology is relatively new. In this type of degassing, water is conducted through a system with a membrane, which can only be penetrated by gasses, whereby both nitrogen and oxygen are removed and conducted into a vacuum tank. Then the degassed water can be used as make-up water. It is necessary to remove hardness as a minimum in order to use the system. Figure 4.5.4 shows a schematic diagram of a plant.

Fig. 4.5.4 Schematic diagram of membrane degassing

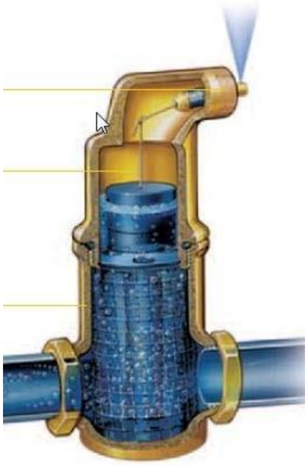


## 4.5.5 Microbubble air separator

In the systems, there is risk of gas penetration, which causes problems and reduced effect. Furthermore, nitrogen, which is not removed through catalytic deoxidation, can cause problems. These gasses can be removed by means of a microbubble separator that is installed in the warmest place in the system. At the high temperature, air bubbles are formed after throttling, and aided by a close-meshed net in the separator the microbubbles are collected to large bubbles, which then can be eliminated via a degassing valve (see description in section 5.4). At the same time, even small particles will be retained and can be tapped as sludge in the bottom of the filter, see fig. 4.5.5.

The microbubble separator is not sufficient to remove oxygen from the system. If the make-up water is pre-heated to close to the flow temperature, the oxygen can be removed down to approx. 1 mg/l, which is not enough in case of somewhat larger consumption of make-up water. With small systems requiring small quantities of make-up water, it can be an acceptable solution – it is better to remove oxygen down to 1 mg/l than not doing anything at all and it is an affordable solution.

Fig. 4.5.5 Schematic diagram of microbubble separator



Typical oxygen content in various forms of make-up water is stated below.

**Table 4.5 Oxygen content in make-up water**

| Conditioning of make-up water | Oxygen content | Oxygen admission |
|---|---|---|
| Unconditioned | 5-10 mg/l | 5-10 g oxygen per $m^3$ make-up water |
| Thermally degassed with steam | < 0.02 mg/l | < 20 mg oxygen per $m^3$ make-up water |
| Thermally degassed with vacuum | < 0.1 mg/l | < 100 mg oxygen per $m^3$ make-up water |
| Catalytical deoxidation | <0.02 mg/l | < 20 mg oxygen per $m^3$ make-up water |
| Membrane degassing | < 0.02 mg/l* | < 20 mg oxygen per $m^3$ make-up water |
| Microbubble separator | app. 1 mg/l ** | App. 1000 mg oxygen per $m^3$ make-up water |

* The oxygen level depends on the gas used on the gas side of the membrane.
** The supplier has no specifications, but measurements have shown a level of 1 mg/l.

If deoxidation of make-up water is omitted, the consequence is increased corrosion in the pipe system at and after the admixture point for make-up water. The large steel quantities in the system will consume oxygen for corrosion and thus it becomes difficult to measure oxygen out in the systems since it has already been used. Oxygen can result in heavy corrosion in holding tanks and in flue gas exchangers of untreated steel in combined heating and power plants as well as increased amount of sludge. In several cases, corrosion in these components could be traced back to lack of deoxidation of make-up water.

## 4.6 Chemical oxygen binding

As an alternative to degassing or better as a supplement to vacuum degassing, make-up water can be deoxidized by chemical oxygen binding with the chemicals used for treatment of the circulating district heating water, see *section 6: Chemical addition and its effect.* In chemical oxygen binding, an organic substance is often added that can cause increased bacteriological activity. Chemical oxygen binding can also result in formation of sulphate or organic acids that impair the water quality, therefore mechanical deoxidation of make-up water is preferred to chemical binding.

In chemical oxygen binding, partial stream filtration for sludge forming substances is necessary. If high concentrations of sulphate or organic acid residues are present in the district heating water, the corrosion risk is increased, therefore the contents of chemical oxygen absorbents must be followed closely, and efforts are made to reduce the consumption of chemical oxygen absorbents. An increasing consumption of oxygen absorbents indicates oxygen penetration into the system, which should result in an investigation to reduce the oxygen penetration.

## 4.7 pH-adjustment

In order to achieve the required pH and thus to ensure passivation of the steel face, it is necessary to dose sodium hydroxide or perhaps ammonia (also see *section 2.5: Copper and copper alloys*). In case of large make-up water volumes, it is necessary to adjust pH when adding water.

For pH-adjustment, the same product should be used that is used for the circuit water. The dosage can be regulated according to a pH-electrode (requires frequent calibration control), but dosing can also be regulated by a pulse transmitter on the water meter of the water treatment plant. In demineralized water, dosing to a certain conductivity can be used. This corresponds to the conductivity of the right concentration of sodium hydroxide added to the make-up water's own conductivity. It is important to ensure a good admixture of the make-up water and the dosed product, therefore a mixing pipe with plastic fillers is recommended.

If pH-adjustment of the make-up water is omitted, fluctuating pH-value in the piping immediately after the addition point of the make-up water results and in case of large make-up water volumes, this spreads to the whole system. The periodically falling pH-value releases magnetite, which can cause operating trouble and deposits elsewhere in the district heating system. Bag filters or cartridge filters can remove the corrosion products, but do not solve the problem.

## 4.8 Magnetic water treatment

There is no documented effect of magnetic water treatment of make-up water or circuit water in district heating systems. Magnetic water treatment does not remove water hardness. Magnetic water treatment can therefore not be recommended for district heating installations.

## 4.9 Irradiation with ultraviolet light (UV treatment)

Disinfection of make-up water or circuit water in district heating systems with UV light has a very limited effect and will especially for circuit water mean a substantial investment and large operating costs without corresponding security for a satisfactory effect. UV treatment of make-up water can kill living bacterial cells, but not bacterial spores. Given the right living conditions, these bacterial spores can be revived in the district heating system and quickly multiply up to the equilibrium point between cell number and the given living conditions. UV treatment alone can therefore not be recommended for district heating installations.

## 4.10 Make-up water tank

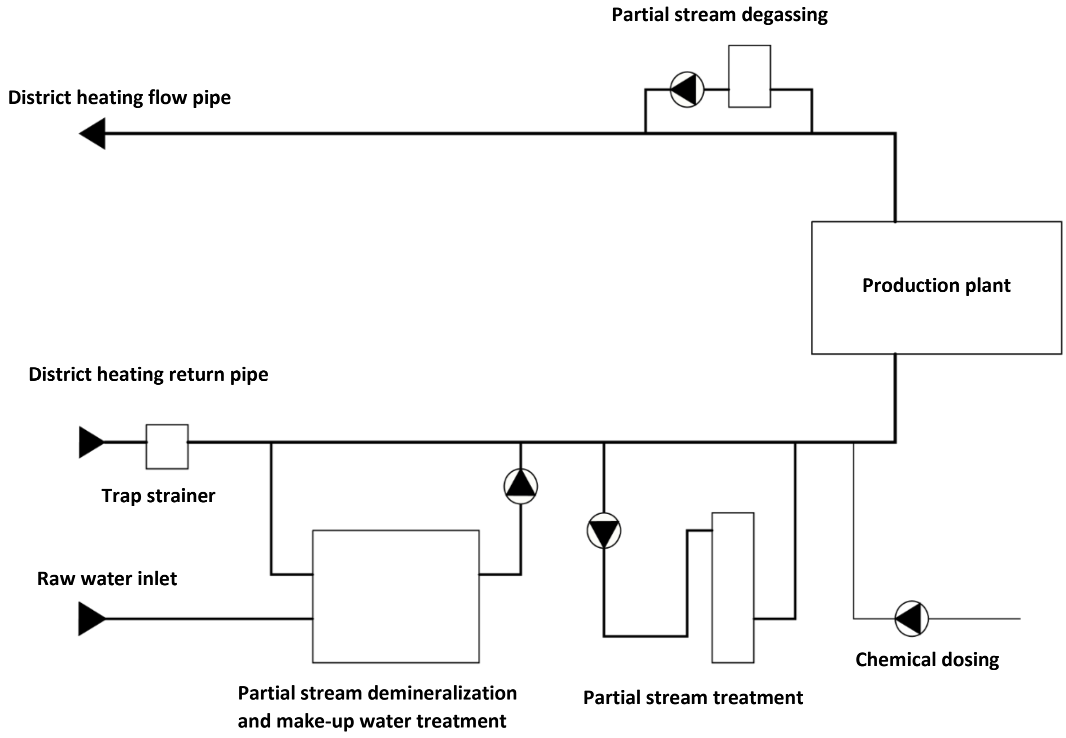
It is recommended to install a make-up water tank so that conditioned make-up water is available for small repairs and operational failure of the district heating installation. This reduces downtime and ensures that water of poor quality is not used. The make-up water tank must be airtight and filled with inactive gas over the water surface or the water surface must be covered by an airtight and diffusion-tight rubber membrane. The make-up water tank can be combined with the equalizing tank in the expansion system. Do not store softened or demineralized water in untreated concrete tanks, since that would increase water hardness.

Make-up water from open make-up water tanks must be degassed before filled into the district heating installation. In practice, unpressurized holding tanks are often used as make-up water tanks, therefore the steam generator or the nitrogen plant in these cases should have sufficient capacity to refill inactive gas when using make-up water.

# 5 METHODS FOR TREATMENT OF CIRCUIT WATER

In order to maintain the water quality, it is necessary to treat the circulating district heating water. The water must continuously be treated and chemicals added to comply with the quality requirements, perhaps also degassed and demineralized to maintain the chosen water quality in the circuit water. Figure 5.0 shows a diagram of how a system can be constructed with partial stream treatment, chemical addition, and partial stream degassing.

**Fig. 5.0 Diagram of plant for treatment of circuit water**



## 5.1 Removal of impurities and sludge

Cleaning of circuit water can either be done with trap strainers in the main stream or through partial stream filtration.

### 5.1.1 Trap strainers

In order to secure against coarse impurities that could be left after repair works etc., coarse filters with a density of approx. 3 mm should be installed in the return pipe. In addition to coarse filters, trap strainers are usually installed as total stream filters before sensitive plant components like meters, heat exchangers, and certain regulating valves. The mesh size of these coarse filters is approx. 0.5-1.0 mm.

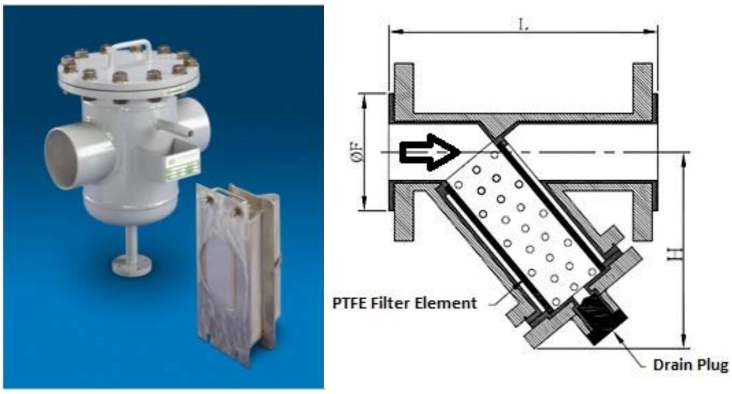
### 5.1.2 Mainstream filters

Mainstream filters are designed to catch coarse impurities. It is important to choose a type that is easy to service. Therefore, the filters should be installed so that they are easy to exchange and to clean the inserts without interrupting the supply. Select mainstream filters of a type and size so that the pressure fall through the filter is limited and so that the need for service and cleaning is limited.

Examples of mainstream filter types:

- Integral screen filters in for example small meters and port filters in heat exchangers.
- T-filters also called basket filters are affordable and simple trap strainers for large pipe dimensions.
- In-line filters with filter inserts. This filter type come in many designs with or without flushing via bottom cock and with various filter inserts with or without magnetic properties.
- Combined in-line trap separator with flushing via bottom cock and microbubble separator.
- Top-hat filters also called insertion filters that are installed between two flanges. This filter type is not service-friendly and should only be used in connection with commissioning of plants and afterwards removed.
- Traditional Y-filters also called trap collectors that only should be used in secondary installations, in user installations, and in small pipes.

**Fig. 5.1.2 Examples of filter types with in-line filters with or without drain possibility**



## 5.1.3 Partial stream filters

Partial stream filtration usually takes place in the part of the return flow, in which 5-10 % of the return water is pumped through a partial stream filter and back to the return pipe. In this way, the circulating district heating water is cleaned continuously of small and medium-sized particles as well as sludge. Since the filter is installed outside the main stream, it can be taken out to be cleaned without interrupting the circulation in the district heating system.

Branching for the partial stream filter must always be taken from the bottom of the return pipe and preferably in a place with calm and laminar flow.

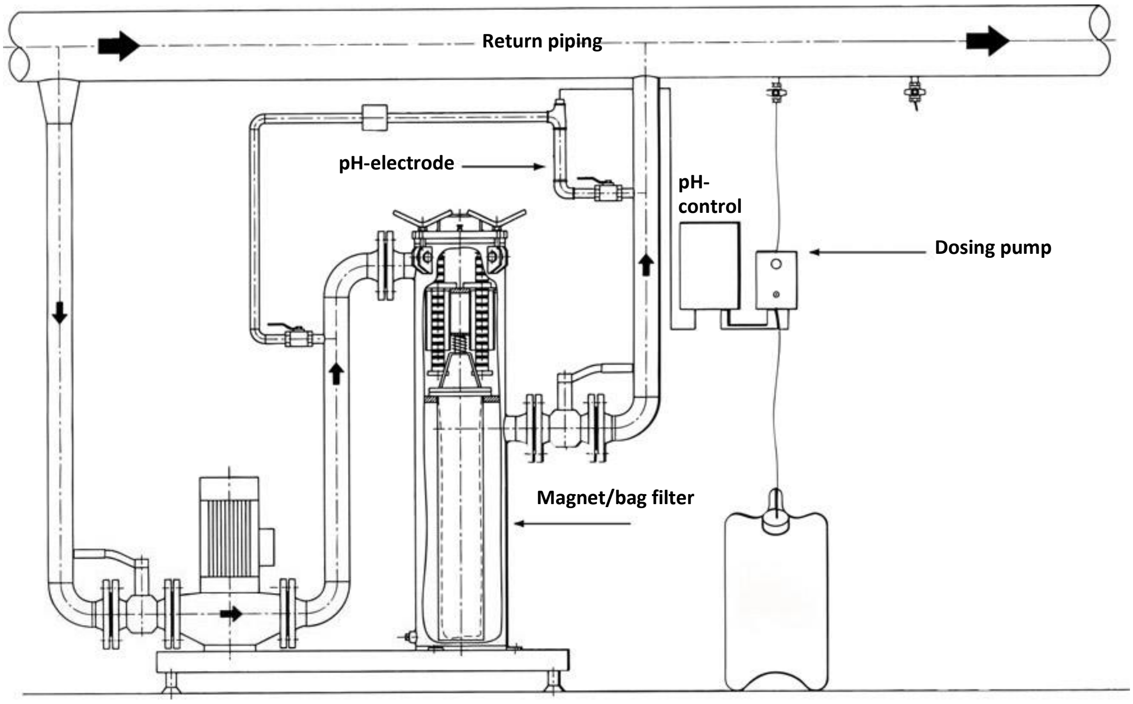
The partial stream filter must have a filter density of minimum 5-10 µm for plants in normal operation, but it is recommended to begin with 50 µm for new plants or after major contamination of the system. The partial stream filter can with advantage be combined with a magnet filter, which retains iron chips and other magnetic particles as well as corrosion products.

There are various types of partial stream filters:

- Cartridge filters give good filtration. The disadvantage is that they usually cannot be cleaned on site and therefore the cartridge must be exchanged at appropriate intervals, which means a continuous operating cost. Large plants have a filter that can be backwashed under air intake.
- Bag filters are a very service-friendly solution, because the bags can be cleaned and washed several timers, before they must be exchanged. Repeated washing will wear away the bags resulting in reduced efficiency.
- Magnet filters can be integrated in bag filters or installed as pre-filters to cartridge and bag filters.
- Sand filters, which are very efficient but voluminous, have a large water consumption for backwash.

Figure 5.1.3 shows a typical installation of a partial stream filter of the bag filter type with magnetic insert. Moreover, the installation contains equipment for pH-measurement and dosing apparatus for pH-adjustment of the circuit water.

**Fig. 5.1.3**Typical installation with partial stream treatment and pH-adjustment in bypass on return piping



## 5.2 pH-adjustment

In the district heating system, a pH-value of 9.8 ± 0.2 is aimed at. It is important to keep this as constant as possible. If the pH-value falls, magnetite is released from the passivated steel faces, and the magnetite turns into sludge in the water. Magnetite sludge has a harmful, abrasive effect on movable parts and gaskets, and it deposits on sensors and in meters, etc. resulting in reduced functioning. At the same time, the corrosion risk is increased in areas of slow flow, for example holding tanks, in which magnetite can also deposit.

The pH-measurement depends on temperature and should be done at 25°C, which is the temperature at which the measurement instrument is normally calibrated. If the probe sits at a higher but constant temperature, it is possible to calibrate at this higher temperature of for example 35 or 40°C, which is normal in the return pipe. Newer instruments measure the temperature and compensate for difference in calibration temperature. However, the instruments cannot compensate for the change in pH resulting from changes in the chemical balances in the water. It is necessary to compare the plant meters with measurements done at 25 °C, so that this difference is known. Dependent on the composition of the district heating water, the measurement at the return temperature will be 0.2-0.5 lower than pH measured at 25 °C. As to the temperature dependence of pH-measurements and changes in pH-values resulting from temperature changes, please see appendix 9[1]. As an example, a pH-value at 50 °C shows 10.5 and only 9.5 at 25°C. For adjustment of pH, sodium hydroxide (NaOH) is normally recommended.

In systems receiving make-up water from transmission systems or from power plants, ammonia ($NH_3$) can have been used as pH-adjusting chemical. With the recommended content of $NH_3$ of maximum 5 mg/l in district heating systems, the required pH-value is not reached, therefore the recommended pH-value of 9.8 ± 0.2 is ensured through dosing of sodium hydroxide.

With a good and correct conditioning of make-up water, pH-adjustment of the circulating water is only necessary to compensate for penetration of unwanted and uncontrollable make-up water. The pH-adjustment can be done manually by continuous monitoring with sampling to determine pH and by daily regulation of the dosing pump for the pH-adjusting chemical. Often, dosing is controlled automatically by a pH-electrode that is placed as cold as possible in the water system to be regulated and at the same time at a position that is representative of the system. This means that the electrode is to sit in the circulating water in the return pipe. Set the setpoint so that pH at 25°C is 9.8, i.e. the setpoint shall normally be lower. Since the electrode has to be taken out regularly for calibration, it is most practical to place the pH-electrode in a bypass on the partial stream at the partial stream filter on the return pipe. This position is shown in figure 5.1.2. In systems with very pure, demineralized water, the dosing of sodium hydroxide can best be controlled by means of conductivity. The conductivity meter is more robust and does not need to be calibrated as often as the pH-meter. Please note whether the other parameters are stable.

## 5.3 Chemical oxygen binding

Where chemical oxygen binding is used in a system for make-up water and circuit water, the circuit water must be in possession of an oxygen binding potential for neutralization of the smaller oxygen penetration that takes place via leakages, diffusion, and contamination as well as regular operating failures.

Requirement for chemical oxygen binding depends on the risk for oxygen penetration that can be caused by:

- Inadequate degassing of the make-up water.
- Raw water penetration.
- Plastic piping without oxygen barrier in the system typically coming from floor heating systems in private houses.

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[1] Appendix 7 – pH-measurement in district heating systems

Usually, the oxygen binding potential for circuit water is ensured via continuous dosing of an oxygen absorbent into the circuit water. If an oxygen binding potential is not constantly present everywhere in the system, penetrating oxygen will immediately be transformed into corrosion on the unprotected steel faces in the system. Lack of oxygen binding potential cannot always be measured via an increased oxygen content in the water, but has to be determined in some other way.

Often the oxygen absorbent is dosed together with the pH-adjusting chemical, but there is no certainty of any correlation between the two needs, especially in district heating systems with a small make-up water consumption.

Oxygen absorbents should be dosed according to requirement and the application limited, cf. *section 4.5: Degassing*.

It is recommended to dose the oxygen absorbent independent of the requirement for pH-adjustment.

## 5.4 Partial stream degassing

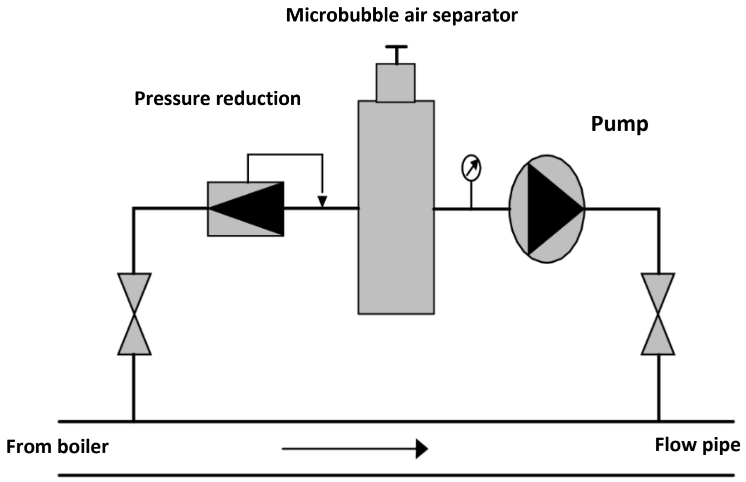
Irrespective of whether the make-up water is degassed, air from holding tanks, pressure storage tanks, and via diffusion through gaskets and leaky piping as well as from unintentional raw water penetration will be absorbed in the circulating water.

In district heating systems in which boilers are connected directly to the distribution system, the degassing often takes place automatically via boilers, where the air discharge will occur resulting from the temperature increase. The boilers are then equipped with automatic air dischargers. If the boilers are positioned too low in relation to the supply area or if the boilers are separated from the distribution net by heat exchangers, there is a need for more efficient and continuous or periodical degassing of the circuit water.

Degassing of the circulating water can be performed on a partial stream that is conducted back to the make-up water degassing as described in *section 4.5: Degassing*. It is recommended to establish mechanical filtration before the partial stream degasser to avoid fouling of this by particles/dirt in the return water. Both plants for catalytic deoxidation and membrane degassing are sensitive towards this kind of dirt. Among plants for catalytic deoxidation, some have an ion exchanger before the deoxidation, which removes the solid particles so that the catalyzer is not contaminated. Older systems can also be equipped with such a cleaning and perhaps supplemented by robust mechanical filters.

Another method that has proved very efficient is installation of a microbubble air separator in a partial stream. The partial stream is taken from the top of a conduit at the warmest place in the flow pipe in the plant and via a pressure reducing valve the pressure is reduced to close to atmospheric pressure whereby the dissolved air is released. Then the partial stream is conducted via the microbubble air separator to a pump, which pumps the degassed water back into the flow pipe.

**Fig. 5.4 Microbubble air separator installed in a bypass on the flow pipe**



The microbubble air separator is especially suited for tight plants, in which the separation of air can be effected with few operating hours a year.

## 5.5 Partial stream demineralization

In plants with partially demineralized water and in plants with demineralized water, a partial stream demineralization plant can be installed with advantage to maintain the chosen water quality.

Usually, partial stream demineralization is carried out on a partial stream from the return pipe in the district heating plant.

The partial stream demineralization plant can be constructed as a reverse osmosis plant or an ion exchange plant according to the same principles as described for plants for make-up water treatment in *section 4.4: Demineralization*. Partial stream demineralization can therefore be done in that a partial stream from the return pipe is conducted back to the raw water inlet and the make-up water treatment to the extent that excess capacity is available. However, a number of conditions must be considered in order to obtain an operational solution including:

- Mixture of drinking water and district heating water can result in unintentional formation and precipitation of calcium.
- The most frequently used membranes in reverse osmosis plants have limitations as to pH and operating temperature.
- The anion exchangers' rate of decomposition is temperature-dependent, therefore an increase of the return temperature can accelerate the wear.

The governing parameters for the requirement for partial stream demineralization will normally be chloride content and conductivity.

When changing plant concept from soft water supplemented with softened water to partially demineralized water supplemented with demineralized water, a partial stream demineralization plant can be the first step towards lowering the conductivity and the salt content in the circuit water, especially in plants with a small make-up water consumption.

## 5.6 Prevention of biofilm

Prevention of biofilm is mainly done by removal of the living conditions for bacterial growth in the district heating systems, since it is unrealistic to keep these free from bacteria.

Disinfection of the system is difficult to do efficiently, but can be done by means of biocides as described in *section 6.8: Biocides*.

Disinfection of make-up water would be of poor value, because the system is contaminated through pipe works and by user connections, where the central heating water is not flushed as per instructions, but is conducted to the district heating system.

Circuit water disinfection is usually unnecessary, but can be a possibility, if the biological activity as described in *section 8.4: Bacteriological activity* becomes too great and is a real nuisance or a risk for the system. It can be difficult to remove all bacteria, which incurs risk of regrowth, and that bacteria become resistant as to the biocide, if this is not changed.

Growth of harmful bacteria in the district heating systems must be limited to the greatest extent possible. Aerobe (oxygen-demanding) bacteria are of no importance, since they do not thrive in an oxygen-free or oxygen-poor environment. On the contrary, anaerobe (non-oxygen demanding) bacteria thrive in oxygen-free waters and at all temperatures and pH-values present in district heating systems, if the right conditions are available. The most important preconditions is that nutrition is available for them.

A common bacterial type is sulphate-reducing bacteria (SRB) that do not require oxygen, but use organic carbon compounds as energy source and reduce sulphate to sulphide. This happens under formation of among other things hydrogen sulphide ($H_2S$). Hydrogen sulphide emits a very characteristic foul odour of rotten eggs. The sulphate is removed by the use of demineralized water.

# 6 ADDITION OF CHEMICALS AND THEIR EFFECT

All water treatment concepts include addition of chemicals to the circuit water and to the make-up water as a central part of the water treatment. Irrespective of the products' trade names and the suppliers' system names, the water treatment concepts contain the same basic elements in the form of chemicals. Besides the primary purpose of the individual chemicals, it is important to be aware of the secondary effects of the chemicals and the correlation between chemicals. All pH-adjusting chemicals lead to precipitation of residual hardness at increasing pH-values and high temperatures, so that it is ncessary to have a partial stream treatment plant in order to remove solid substances.

## 6.1 Sodium hydroxide

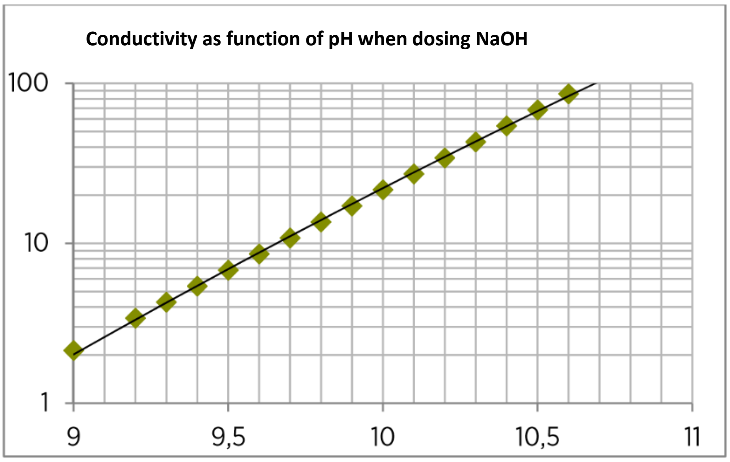
Sodium hydroxide (NaOH) is the most common chemical for pH-adjustment of both circuit water and make-up water. The product is strongly caustic and requires special precautions during transport, storage, and handling in pure state. The product can be bought in various dilution ratios and is the main component in a number of mixed products.

The necessary quantity of sodium hydroxide to increase the pH-value to 9.8 depends on the source of water and of the water treatment concept, typically the dosing is for –

- demineralized water: approx. 2 g of pure NaOH per $m^3$ of make-up water
- softened make-up water: approx. 50 g of pure NaOH per $m^3$ make-up water.

The requirement in softened water depends on the carbonate content ($HCO_3^{-}$, $CO_3^{--}$), which comes from the water's hardness and from the carbonate resulting from the free carbon dioxide in the groundwater or from the rainwater if this is used as water source. The carbonate content passes unimpeded through a softening filter. The disadvantage of pH-adjustment with sodium hydroxide is that the substance contributes towards raising the total salt content and thus the conductivity in the circuit water, but it still is the best possibility, since it is not possible to operate neutrally because oxygen penetration will always occur out in the system. Fig. 5.1 shows the correlation between conductivity in µS/cm and pH in demineralized water, in which only sodium hydroxide has been added. In high concentrations, sodium hydroxide can cause stress corrosion in steel. The risk occurs at temperatures over 60°C, but the phenomenon has not been seen in district heating systems.

**Fig. 6.1 Conductivity (µS/cm)** as function of pH when dosing sodium hydroxide into demineralized water



## 6.2 Ammonia

Ammonia ($NH_3$) is used in a number of transmission systems as pH-adjusting agent in connection with demineralized water with a low conductivity and in connection with steam installations. Operationally, plants with demineralized water and addition of ammonia give a very small buffer effect in case of unintentional drinking water penetration and other contamination of the circuit water, therefore the system is unsuitable for distribution systems with user connections.

Ammonia dosing for district heating systems containing copper piping as well as armatures and fittings of brass and other copper alloys cannot be recommended because of risk of corrosion and crack formation as mentioned in *section 2.5: Copper and copper alloys.*

A further disadvantage of using ammonia is that it makes heavy demands on precautionary measures in connection with transport and storage of the liquid ammonia or the ammonia solution, and there are very severe working environment requirements in connection with handling and work with the ammonia dosing. In general, ammonia cannot be recommended as conditioning agent for district heating systems. All district heating water can contain a larger or smaller quantity of ammonia from various sources, but concentrations under what is specified in table 1.2 are acceptable under normal conditions.

Sources of ammonia in district heating water is not fully elucidated, but can be:

- Added $NH_3$ as pH-adjustment of demineralized water.
- Conveyed with the make-up water as nitrate and nitrite or ammonium.
- Formed by bacteria, which convert free nitrogen in the water into ammonium.
- Formed by nitrate-reducing bacteria, which convert nitrate into ammonium.
- Certain plastic pipe types discharge small quantities of ammonium.
- Certain biocides and water treatment chemicals contain ammonium.

## 6.3 Phosphates

Tribasic sodium phosphate ($Na_3PO_4$) is the most common agent for preventing formation of deposits from residual hardness and hardness from penetration and emergency addition of drinking water. Tribasic sodium phosphate increases the pH-value in the same way as sodium hydroxide, but because of the higher mole mass, larger volumes have to be used to achieve the same effect.

The needed quantity of tribasic sodium phosphate depends on the residual hardness in the make-up water and of the need for a buffer in case of drinking water penetration into the system. A tribasic sodium phosphate surplus in the circuit water of 20-50 mg/l is advisable in plants with risk of drinking water penetration from user installations. By surplus, we mean the dissolved phosphate that can be measured. In case of emergency addition, the tribasic sodium phosphate surplus must be raised substantially. In plants with little probability of drinking water penetration, the tribasic sodium phosphate surplus can be reduced to 5-10 mg/l.

The disadvantage of using tribasic sodium phosphate is that the substance contributes to raising the total salt content and thus the conductivity in the circuit water. Hardness control using tribasic sodium phosphate also contributes to increased sludge formation in the system, which can cause deposits and subsequent problems.

## 6.4 Sulphite

Traditionally, sodium sulphite ($Na_2SO_3$) has been used extensively as oxygen absorbent in central heating installations and in district heating systems. By the oxygen binding, sulphate ($SO_4^{--}$) is formed.

Sulphur-reducing bacteria can reduce sulphate to sulphide as mentioned in *section 5.8: Prevention of biofilm*, if at the same time organic material is present in the circuit water, but sulphur-reducing bacteria also exist that can decompose sulphite directly into sulphide without the presence of organic substance. For these reasons, sulphite should not be used as oxygen absorbent in large plants and in plants with copper piping or with heat exchangers of stainless steel, since that would increase corrosion.

Like other salt additives, sulphite contributes to raising the total salt content and thus the conductivity in the circuit water.

## 6.5 Tannin

Tannin, also known as tannic acid, is complex organic compounds with molecular weights of 600-2,000. Chemically, the structure covers compounds of sugar and phenol molecules.

Tannins occur as:

- Hydrolysable tannins, which in basic environment absorb oxygen, thus they are termed chemical oxygen absorbents.
- Condensing tannins (non-hydrolysable tannins) do not absorb oxygen, but on the other hand they bind carbonates and bicarbonates in the complex organic structure. Therefore, they are a means to prevent formation of deposits from residual hardness.

Furthermore, tannin has a capability to build up a protective layer of iron tannate (gamma ferric oxides) on untreated steel faces.

The needed tannin concentration is difficult to measure. Measuring methods have difficulty to distinguish between the two types of tannin. Measurement of oxygen content and residual hardness in circuit water is needed when using tannin-based water treatment, but the result can show a larger oxygen content and greater residual hardness than in reality, because the oxygen and the bicarbonates can be “neutralized” by the tannin. The result depends on the measurement method and of whether the bound oxygen is included.

The rate of decomposition of tannin increases with rising temperatures, and one of the decomposition products is carbon dioxide ($CO_2$). In normal district heating installations, the carbon dioxide uses sodium hydroxide and thus contributes to raising the total salt content and the conductivity.

The extent and possible effects of other decomposition products such as organic acids from proteins that often accompany raw materials with tannic acid content have not been clarified. Especially in low-temperature plants, there is risk that the remains from the decomposition are not completely decomposed, but end as organic acids. The tannin consumption is 5-40 g of tannin for binding 1 g of oxygen dependent on type of tannin.

## 6.6 Amines

Amines are a large group of substances. Some are much used as organic oxygen absorbents. Amines are also pH-adjusting like ammonia.

Chemically, amines are ammonium compounds, in which one or more of the hydrogen atoms in $NH_4^+$ are replaced by another chemical compound. Amines are sold under many names such as Helamin, Morfolin, Cyclohexylamin, and DEHA (diethyl hydroxylamine).

Amines for water treatment can be divided into three groups. Some amines are oxygen absorbent, and some are neutralizing, while others are film forming so-called “fatty” amines. These “fatty” amines form film on steel faces in boilers and on heat exchangers, etc., which contribute to corrosion protection in the same way as tannins.

The oxygen binding occurs by decomposition of amines to lower organic compounds under liberation of carbon dioxide ($CO_2$), therefore amines are sodium hydroxide consuming and contribute to raising the total salt content and the conductivity in the district heating water.

When using amines as oxygen absorbent, make sure that the reaction velocity at temperatures under 50-60°C is sufficient to ensure the oxygen binding in the return pipe.

## 6.7 Other oxygen absorbents

A number of other oxygen absorbents have been or are used to a greater or smaller extent. Some of these are mentioned in the following text.

### Vitamin C

A rarely used absorbent is vitamin C. This is a sodium salt of ascorbic acid called sodium ascorbate. The recommended concentration of vitamin C used as oxygen absorbent is 0.5-2.0 mg/l.

The advantages of vitamin C used as oxygen absorbent is that it is non-toxic and environmentally neutral and at the same time reacts quickly, also at low temperatures.

The oxygen binding occurs through decomposition of the vitamin C to lower organic compounds under liberation of carbon dioxide ($CO_2$). Therefore, vitamin C also consumes sodium hydroxide and contributes to the raising of the total salt content and the conductivity in the district heating water.

### Hydrazine

A very efficient method to bind oxygen and to increase the pH-value is to add hydrazine ($N_2H_4$), but because of toxicity and suspicions of carcinogenic properties, it has not been allowed in distribution systems in Denmark since 1982.

## 6.8 Biocides

Biocides (agents for bacterial fight) can be used for fighting microorganisms in district heating water. The bacteria living in biofilm are protected by the substances binding them together and are therefore substantially more difficult to fight than the few bacteria living freely in water. For this reason, biofilm must be in focus when using biocides. It is not enough to document with a water sample that the bacteria are gone. The frequency and concentration of treatment are determined based on an assessment of the extent of biofilm in the system. Biocides should only be used when a specific bacterial problem has been detected.

Closer determination of bacterial species and choice of methods for fighting require test of bacterial types, which can be done by culture of samples in laboratories or with special test kits supplied by the suppliers of biocides. Newer methods with DNA test have made it possible to do quick tests.

When choosing biocides, it is important to know and assess the toxicity of the substance at the wanted concentration in the circuit water as well as to know and assess the lapse of time in which the toxicity is present.

The leakage conditions in the system should be examined and calculated before biocides are applied, so that the leakage to the users' hot-water systems, to earth or sewer and drain systems has been assessed.

Bacteria should not be fought by continuous biocide addition, since that would give rise to resistance, but instead by shock dosing using varying biocide types.

After the biocide treatment, the system is not bacteria-free, but the nuisance will be reduced to an acceptable level for some time.

## 6.9 Dyes

Usually, dyes are only used in case of special need for leakage detection in district heating systems. For short-term use, fluorescent green dyes like uranine and pyranine are recommended, which are active even in very small dilutions. Therefore, they can be used in concrete ducting systems to determine whether moisture is leaking district heating water or penetrating groundwater.

Dyes can also be used for leakage detection in the users' hot-water systems and to prevent use of district heating water for extraneous purposes.

Leakage detection should be coordinated with the local water supply, so that the waterworks can lower the water pressure while at the same time the district heating plant increases the district heating pressure and adds dye.

## 6.10 Composite products

Usually, composite products contain phosphate, sodium hydroxide, and oxygen absorbents. They should only be applied if the chemical content is known and fully specified. When dosing composite chemicals, frequent analyses should be carried out to make sure that the concentrations are correct. In plants with stable operating conditions and a continuous, substantial make-up water consumption, the use of composite products can be an efficient and affordable solution, since the requirement for chemicals is relatively constant, and the needs for chemicals for pH-adjustment, oxygen binding, and prevention of deposits follow each other.

In tight plants or in unstable or abnormal operating situations, the requirements for chemicals for pH-adjustment, oxygen binding, and prevention of deposits do not follow each other. The use of composite products therefore causes too much or too little dosing dependent on control parameter and they should not be used.

## 6.11 Requirement specification for environmental declarations

All chemicals used in district heating systems should be accompanied by complete environmental declarations specifying all constituents by their internationally approved chemical names.

Furthermore, the declaration should state whether the product is on the list of hazardous substances and the measures of precaution for transport, handling, and storage as well as application to be taken, both as to internal and external environment.

As appendix to the declaration, paradigm appendices can be included for the environmental approval, green accounting, and work site evaluation of the district heating plant, cf. *section 11: Environmental conditions*.

## 6.12 Marking and use of chemicals

All chemicals used for water treatment and corrosion prevention are covered by these regulations.

General rules

The Environmental Protection Agency's list of laws, consolidate acts, etc. concerning chemicals.

The most relevant links are:

Regulation (EC) No. 1272/2008 of 16 December 2008 of the European Parliament and of the Council concerning classification, labelling, and packaging of substances and mixtures, etc. (CLP).

Legal information: Legal notice No. 144 of 14.04.1982. Notice on prohibition against use of toxicants in certain heating systems.

Legal information: Legal notice No. 849 of 24/06/2014. Notice of law on chemicals.

Legal information: Legal notice No. 1075 of 24/11/2011. Notice on classification, labelling, sale and storage of chemicals and mixtures. Classification notice.

Regulation (EC) No. 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the registration, evaluation, authorization and restriction of chemicals (REACH).

The supplier is responsible that the products are correctly classified, packaged, and labelled.
As to up-dated information on the current regulations on chemicals, please see the list on the Danish Environmental Protection Agency's homepage.

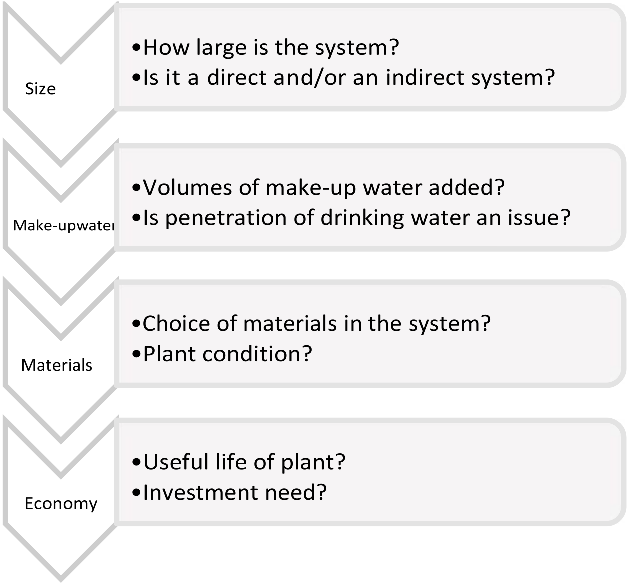
# 7 CHOICE OF WATER TREATMENT CONCEPT

Water chemistry in the district heating system is affected by many conditions:

- The chosen water quality.
- Penetration of contaminated water/drinking water.
- Quality of make-up water.
- Leakages in the system and thus the requirement for make-up water.
- Addition of chemicals.

Many district heating systems are perhaps started as small plants and later they have been extended to become large systems, but the water chemistry has not been changed.

A number of substantial conditions have an influence on our considerations concerning change of water treatment concept and new systems:



Size
- How large is the system?
- Is it a direct and/or an indirect system?

Make-upwater
- Volumes of make-up water added?
- Is penetration of drinking water an issue?

Materials
- Choice of materials in the system?
- Plant condition?

Economy
- Useful life of plant?
- Investment need?

Environmental conditions also influence our choice. A possible reduction of chemical consumption and a more secure work environment can also be valued.

In order to reduce corrosion and formation of deposits in district heating systems, the optimum solution is to use demineralized and deoxidized water in the system. However, other conditions can point to the use of softened water.

In large water systems, there is seldom doubt that the use of demineralized and deoxidized water with dosing of sodium hydroxide will be worth it.

With small systems that have been running on softened water without problems for many years, it is more difficult to decide on a change. On the other hand, it will often be profitable to establish degassing instead of using chemicals.

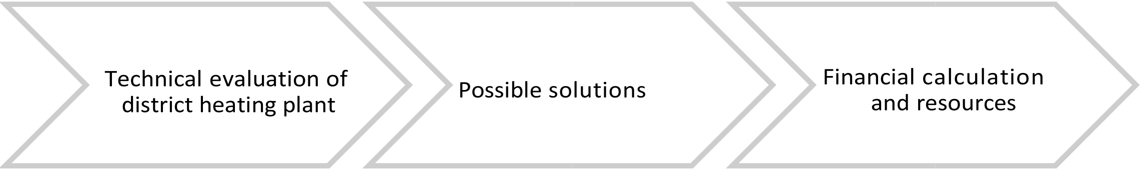
Several conditions influencing daily operation and maintenance can give occasion for considerations on changes in water treatment:

- Penetration of drinking water is a frequent problem in district heating systems. It often happens via the consumer's water heater, but also happen by leakage in the district heat exchanger. It depends on the pressure conditions, which vary with summer and winter load. Therefore, it can be difficult to find such a failure.
- Both in direct and indirect systems there is risk of siltation in heat exchanger and in radiators in the system, if silting chemicals like tannin and phosphate are added. The use of these chemicals also causes deposits in areas with low water velocity, which can result in corrosion attacks under the deposits.
- Calcium deposits on heating surfaces in boilers and heat exchangers reduce efficiency.
- Local corrosion attacks resulting from oxygen in the water causing leakages.

Planned investments in the district heating system like extension or renewal of production plants or renovation of old piping also give occasion for considering whether the water treatment concept is to be improved to protect the value of these plants in the best possible way.

On change to completely or partly demineralized water, older plants, which have used untreated or softened make-up water with a high total salt content, will see more leakages than before during the first one or three years, because old leakages clogged with salt and calcium deposits gradually become leaky as the deposits decompose.

Choice of water treatment concept comprises the following processes:



## 7.1 Description of district heating system

The first step when choosing water treatment concept is to make a description of the district heating system that is to be protected. This summary is the background material for an evaluation of the best water treatment concept. Example of summary elements:

- Plant size and type.
- Water volume in plant.
- Age of plant.
- Existing water treatment system and state of water chemistry.
- Water exchange rate – number of yearly water exchanges in the net.
- Direct or indirect user connections.
- Direct or indirect connection of production plants like boiler plants.
- Operating state of production plants – periods in operation and on stand-by.
- With or without holding tank in the system
- Direct or indirect connection of holding tank.
- Temperature levels in the system.
- Materials in plant in relation to water chemistry.
- Corrosion state of plant.
- Bacteriological state of plant.

### 7.1.1 Materials and constructions

The materials and constructions forming part of the plant are of importance in the description. Ordinary black steel with no surface treatment still makes up the major part of the parts in the district heating installation that are in contact with water, whether district heating piping, production plants, or user installations.

In itself, plastic piping in systems does not make demands on the water treatment, but can result in increased oxygen admission to the system through diffusion. The problem is in particular present, when plastic piping without oxygen barrier is used. If in doubt whether the right types of plastic are used in a user installation, carry out an indirect connection with heat exchanger to protect the district heating system. In new systems, plastic piping with oxygen barrier is chosen.

Copper piping and fittings as well as armatures and supporting bushes of brass and brass alloys in PEX-piping make particular demands on circuit water as to the upper limit of the pH-value and an upper limit of ammonia content. As to the specific requirements, please see *section 2.5: Copper and copper alloys.*

Pay special attention to soldering alloys and alloys that are dezincificated in district heating water with pH-values > 10.0. Together with the temperature level in the plant, stainless steel in systems makes heavy demands on compliance with the maximum chloride concentrations dependent on the stainless steel type used. As to allowable combinations of materials, chloride concentrations, and temperature, please see *section 2.4: Stainless steel.*

### 7.1.2 Plant condition as to physics and corrosion

In existing systems, an examination and description of the existing conditions concerning water quality and corrosion form part of the plant characterization.

Besides the chemical analysis in relation to water quality requirements as specified in *section 1: Water quality*, parameters like oxygen content and conductivity are important for the assessment of what kind of water treatment concept to choose in future.

Internal corrosion examinations of for example holding tanks and production plants can be very relevant to the assessment of water treatment concept.

The physical contamination rate of the plant with sludge and other particles in the water cycle must form part of the assessment.

### 7.1.3 Bacteriological condition of plant

An assessment of the plant's bacteriological condition can form part of the characterization. This can be done by analyses of biofilm taken from the plant and through examination of corrosion damage.

If the water quality complies with the chemical requirements, and deposits or clogging of pumps and filters are detected, it can be advantageous to let experts go into possible biological contamination.

If a water sample shows no bacteria in the water, this does not necessarily mean that the plant is free from bacteria. For one thing, the chosen cultivation method for the sample could be wrong in relation to the bacteria in the system, for another there can be biofilm in other areas of the plant without this being detected in a water sample.

## 7.2 Technical solutions

### 7.2.1 Demineralized and deoxidized water

This concept is the technically best solution, and it is normal practice in large plants to use demineralized and deoxidized water as make-up water. The make-up water can be produced by either ion exchange technique or reverse osmosis. To an increasing extent, reverse osmosis is preferred because of the reduced consumption of chemicals compared to ion exchange, but with increased costs for wastewater discharge, there can again be economy in using ion exchange. The oxygen can be removed from the make-up water in several ways: Vacuum degassing, membrane degassing or catalytic oxygen removal. The make-up water shall be conditioned with sodium hydroxide during the addition.

In this connection, it makes sense to consider a plant for partial stream treatment and degassing of the circulating water, in which a partial stream is treated to make-up water quality again. When changing from a poorer water quality, this will substantially accelerate the movement towards a (partly) demineralized water quality, especially in systems with a relatively small water exchange rate. When an improved water quality has been obtained, this kind of partial stream treatment is the most important tool for removal of salts from the penetrating drinking water and for maintaining a good water quality in the circulating water. The requirement for partial stream treatment will of course depend on the condition of the system, but often there will always be a certain contamination with drinking water. Partial stream treatment will also be in readiness in case of major contamination, which can be cleaned out subsequently without having to discharge large volumes of water from the system.

The disadvantage of the concept is the lower buffer capacity in demineralized water conditioned with sodium hydroxide. This means that pH falls more than in softened water in case of contamination. Therefore it is important to control and correct pH regularly in the circulating water. Contaminations are easier to detect in (partly) demineralized water than in softened water, because pH falls and parameters like hardness, conductivity, chloride, and sulphate increase.

### 7.2.2 Softened water

For decades, softened water has been used in Danish district heating systems and can be an acceptable solution for small systems with good tightness. Water is affordable to produce, since only a softening plant is needed. The risk of serious corrosion attacks is higher than with demineralized water, because the high salt content expedites local attacks as soon as oxygen is present. Formerly, it was common practice to dose chemicals for oxygen binding and protection of deposits, but this practice results in sludge formation and corrosion problems (attacks under sludge layer, microbial corrosion). Now the recommendation is to use degassed/deoxidized make-up water conditioned with sodium hydroxide to the right pH-value. The quality of the circulating water can be maintained by partial stream treatment and/or partial stream deoxidation. In very small and closed systems, chemical addition to remove oxygen can be a solution, usually with a view to economy.

Softened water has a higher buffer capacity than demineralized water, i.e. pH falls less by penetration of drinking water into the system. Oxygen in the penetrating water will be used for corrosion, often locally, and calcium and magnesium will precipitate as calcium precipitations to a higher degree than in demineralized water. It is harder to detect the contamination, since only a slightly falling pH-value and thus increased consumption of sodium hydroxide as well as increased hardness indicate this.

### 7.2.3 Untreated circuit water supplemented by drinking water

This concept is only used for central heating systems and small closed district heating nets for instance in neighbouring heating projects as well as for block heating units. If the system is tight and only very limited quantities of make-up water are added, the system will soon be free of oxygen and the pH-value will settle on 9.0-9.5, after which the system is stable.

Water analyses will show a very low residual hardness, since calcium carbonates and magnesium salts will crystallize as deposits or sludge. Should leakages arise, oxygen enters the system and corrosion increases dramatically.

It should be assessed whether there are technical or financial obstacles to the application of demineralized and degassed water with sodium hydroxide addition. As an example, the water can be supplied from a tank lorry or from a rented system. If the plant is old, and change to demineralized water is not the solution, a possible adjustment of the process could be considered, i.e. establishing degassing instead of using chemical addition.

Only in a few cases, the use of drinking water will be chosen. By and large, this is only possible with single plants that never receive additional water.

## 7.3 Economic assessments

When comparing water treatment concepts or methods for production of water, assessment of investments and operating costs are important. Among other things they can comprise:

**Investment**

- Initial cost of plant based on budgetary price of offer from supplier.
- Costs for mounting and connection of plant.
- Costs for possible adjustment of existing water treatment.
- Depreciations over several years often stated as per $m^3$ of make-up water.

**Operating costs**

- Raw water.
- Discharge of wastewater.
- Consumption of power and heat.
- Chemicals for process and conditioning.
- Maintenance such as exchange of membranes every 3-5 years.

Offers from suppliers can help in the decision-making, and costs for chemicals, power consumption, etc. can be calculated compared to investment price.

Likewise, it can be calculated whether it is advantageous to buy water via the transmission system or as small volumes delivered by tank lorry from larger plants alternatively to rent a plant.

### 7.3.1 Example of financial calculation

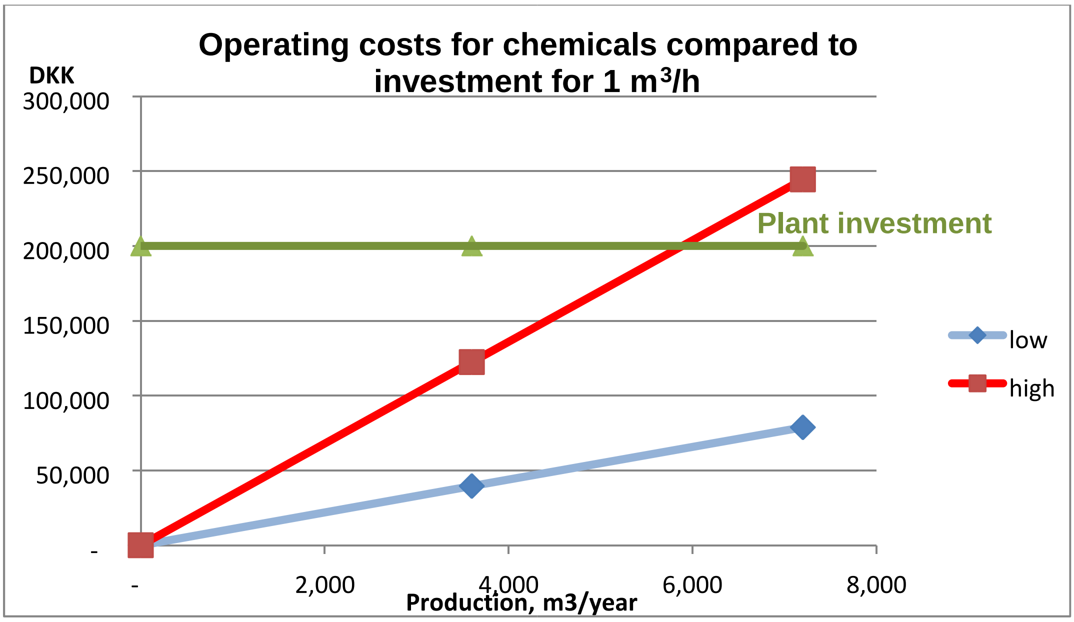
The following example of a $1m^3$ plant gives an idea of the price level for demineralized and degassed water with sodium hydroxide dosing compared with softened water with chemical addition including oxygen absorbent.

The initial cost of reverse osmosis system and degasser: The prices vary from DKK 185,000 to 240,000 so an average price is DKK 200,000. Softening is not included, since this is not bought in both cases. In the calculation, a loss of 20 % for concentrate and wastewater duties of DKK 30 per $m^3$ are included.

There is a large price difference for chemical dosing. Prices range from DKK 17 per $m^3$ to DKK 40 per $m^3$ of make-up water. In Fig. 7.3.1.1, this is termed low and high chemical price respectively.

With the high chemical price, the plant investment is already paid back at a production of approx. 5,800 $m^3$, with the low chemical price, approx. 12,000 $m^3$ must be produced and added.

**Fig. 7.3.1.1. Investment for production of demineralized water compared to the additional price of adding softened water with commercial chemicals in relation to water consumption**



Example is only for one plant of 1 $m^3/h$.

The following formula can be applied for calculation of the price increase as function of plant size:

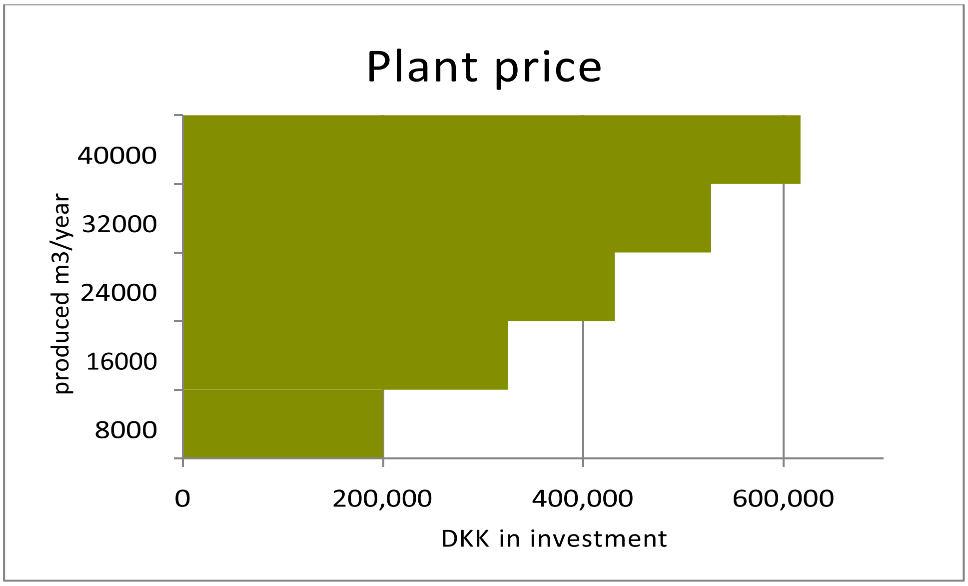
$$C1/C2 = (P1/P2)^a$$

C1. Investment costs of plant 1
C2. Investment costs of plant 2
P1. Price of plant 1
P2. Price of plant 2
a. Proportionality factor.

With technical plants, a proportionality factor of 0.7 is usually used as in the next figure.

The evaluation should be made in each individual case to reach a correct comparison, and the plant sizes are in jumps - not sliding. Fig. 7.3.1.2 shows an estimate of plant prices in relation to a maximum production in $m^3$/year.

**Fig. 7.3.1.2 Estimate of plant investment in relation to production capacity**



## 7.4 Evaluation

When a possible water treatment concept has been chosen, the concept must be evaluated as to:

- The quality-maintaining or quality-improving effects on the district heating system.
- The environmental impacts that it involves.
- The requirements made on staff and maintenance works.
- The plant economy and operating economy arising from the plant.

The right choice of water treatment concept is the concept giving the greatest positive influence on plant characterization and thus the greatest life-prolonging effect at the lowest possible cost, when both plant economy and operating economy are considered. Environmental impact can be included in this evaluation as both a plant cost and an operating cost.

Furthermore, at regular intervals the water treatment plant should be re-evaluated, for example every five years to make sure that the chosen plant still is optimum. In case of change of water treatment concept or change of chemicals, it is important to note that the existing chemicals in the circuit water do not disappear; they are slowly diluted as a result of water exchange. For example, this happens when changing from softened water to demineralized water, when the deposits out in the system gradually decompose. When new chemicals are added, the salt concentration can therefore be increased and a reaction between old and new chemicals can take place.

Plants with large drinking water penetration can only be treated with partial stream treatment until a solution to the penetration problem has been found.

The requirements for make-up water condition also depend on the water exchange rate. A large water exchange makes heavy requirements on degassing/deoxidation, whereas a small water exchange makes lesser requirements. The decisive thing is the ratio between total oxygen volume added per time unit and m$^2$ of steel face that can corrode.

# 8 MONITORING AND CONTROL OF WATER QUALITY

Monitoring and control of the water quality is an important part of the plant's plan for operation and maintenance. The monitoring is an important part of ensuring the functioning of the plant, but must also be adapted to the policy of the plant on this issue as well as to the personnel resources available. If necessary, plant monitoring is performed by an external firm.

Possible control levels are:

- Continuous measurements.
- Periodic measurements performed by the plant's staff.
- Periodic measurements performed by suppliers.
- Periodic measurements performed by external laboratories.

Measurements performed by suppliers must be regarded as a service and help to the plant's own measuring programme and cannot be replaced by measurements done by independent laboratories.

Laboratory measurements or some other kind of independent measurement should be performed every year or every six months to control the water treatment programme.

For control of water chemistry, trend curves of measurements are a great help. Since water chemistry is individual on the plants, it is important to follow the development to control whether changes have happened in the system. Changes are a sign that irregularities have occurred.

These could be:

- Failures or irregularities in water treatment.
- Penetration of impurities into the system partly as drinking water, partly as air.
- Faulty dosing either because of the dosing pump, the pH-meter or erroneous concentration of chemicals.

## 8.01 Water systems with demineralized water

In demineralized water, the conductivity is the most important expression of water quality. If conductivity is compared with pH-value, it can be determined whether the water quality is under control. If on the other hand there is no relation between conductivity and pH, this indicates that impurities penetrate the system. A hardness measurement can clarify whether water penetrates the system and supplementary measurements of chloride and sulphate will show the degree of contamination. If the pH-value is falling, this can imply that air penetrates into the system, since carbon dioxide reacts with sodium hydroxide and thus lowers the pH-value. Figures 8.0.1 and 8.0.2 show examples of appropriate trend curves to show the chemistry in a system with demineralized water.

**Fig. 8.0.1 Trend curves for conductivity and pH**

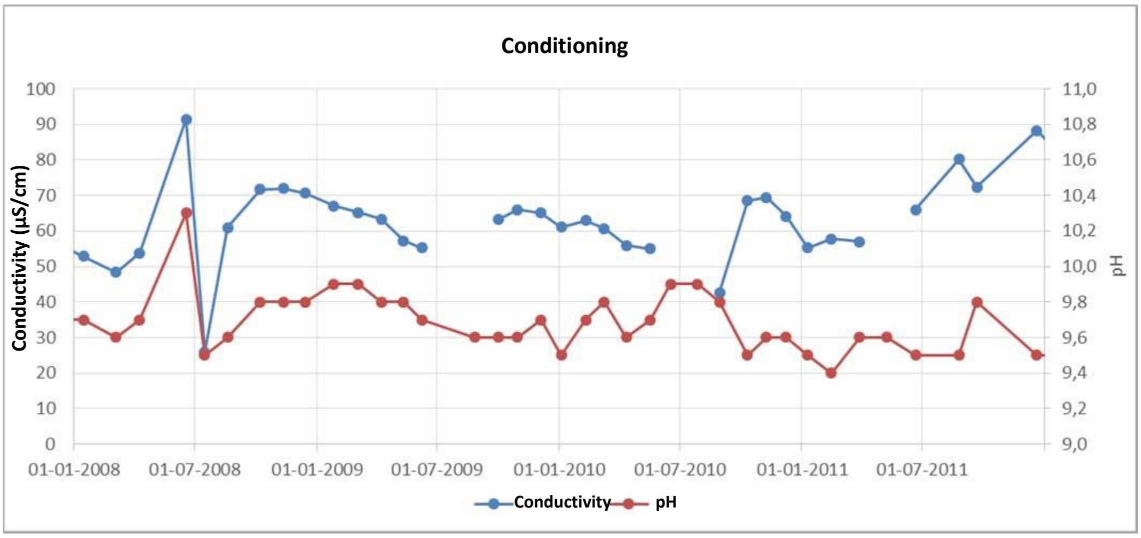
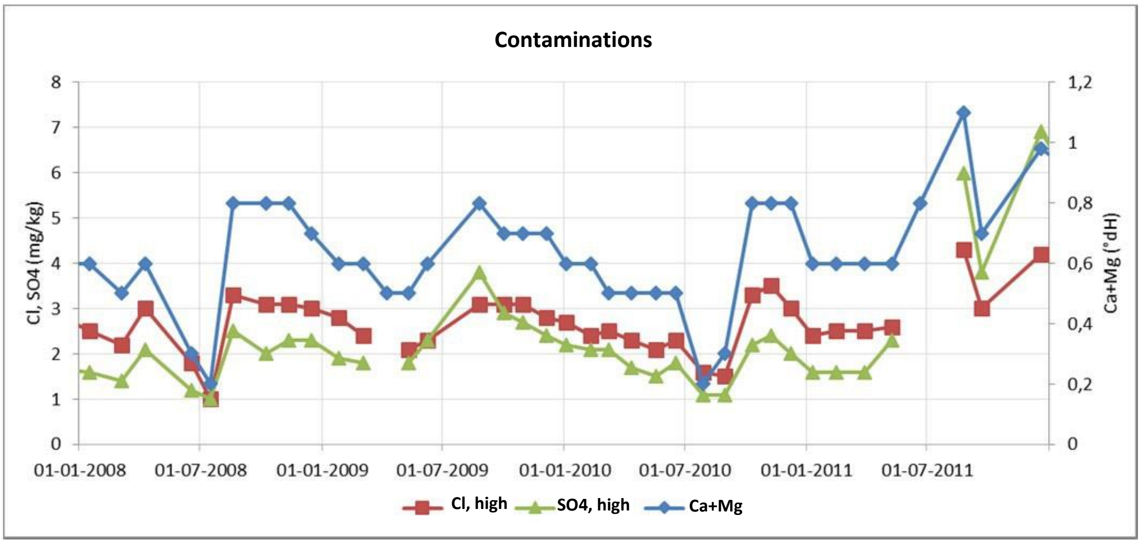


**Fig. 8.0.2 Trend curves for contamination in form of chloride, sulphate, and hardness (Ca+Mg)**



The trend curve with conductivity and pH gives a survey over pH-control and dosing of lye into the district heating water. If pH and conductivity follow each other, this expresses that the change in conductivity is caused by a change in the sodium hydroxide content and thus in pH-value. If the conductivity is changed without a corresponding change in pH, this will probably be due to contamination. This possibility can be checked by looking at the trend curve with chloride, sulphate and hardness, which sums up the development in the most common contaminations. For example, there is a jump in pH and conductivity in the spring of 2008, while contamination is falling because of continuous partial stream treatment. This is a question of overdosing sodium hydroxide into the system. During the summer of 2008, conductivity is heavily increased, while pH grows modestly. Since all three components of contamination jump at the same time, this must be a question of contamination during the summer. Similar incidents happen in the summer of 2010 and 2011 following periods in which the partial stream treatment has improved the water quality.

Microbial activity on the other hand is difficult to detect by measurements, but there are other indicators as mentioned in section 8.4.

Oxygen measurements in the system can best be done with continuous meters, but this requires regular control of the meters. Random sampling can be performed with a transportable oxygen meter or with an equipment that measures with colour control of a sample taken under special conditions.

## 8.02 Water systems with softened water

In systems using softened water, it is harder to detect penetration of impurities and water hardness is the most common indicator. Therefore, it is necessary to follow the hardness in the system. The make-up water should also be controlled as to hardness to make sure that the functioning of the softening plant is correct. Trend curves for pH, conductivity, and hardness are important tools to follow the development, cf. the comments on the figures 8.0.1 and 8.0.2. For a system with softened water, the trend curve for hardness can conveniently be shown together with pH and conductivity.

Indicators of poor water quality:

- Sludge in filters.
- Changes in residual hardness.
- Increasing or fluctuating oxygen content.
- Increasing consumption of chemicals.
- Changes in conductivity.
- Changes in clarity or odour.
- Sulphide content in the water.

During periods with failure, increase the analysis frequency until the cause has been found and the problem solved.

## 8.1 Continuous measurements

As a minimum, continuous measurements should be carried out of the circuit water's pH-value. On large plants, the oxygen content in the circuit water should also be measured continuously or controlled periodically in some other way to ensure a low content. If pH is measured at another temperature than 25°C – for example at the 40-45°C of the return water – attention should be paid to whether the measured pH-value falls with the temperature. In order obtain the specification of pH 9.8 at 25°C, the measured value at the return water's temperature must be lower. In demineralized water, a pH-value of 9.4-9.5 at 40°C will normally correspond to pH 9.8 at 25°C. With softened water, the difference is smaller, here pH 9.6 at 40°C will often correspond to pH 9.8 at 25°C.

On all plants, the consumption of make-up water should be registered with a water meter, which either is read daily and manually or logged hourly by a SCADA system. Conditioning of make-up water should on large plants be continuously monitored with measurements of pH and oxygen. The pH-value cannot be measured stably in demineralized or fully demineralized water. Instead, conductivity before or after dosing of sodium hydroxide into the make-up water can be measured. This is a robust method of controlling both quality and addition of chemicals.

In plants with demineralized water or partially demineralized water, continuous measurement of conductivity in both circuit water and make-up water should be done on large plants.

## 8.2 Periodical measurements and sampling

Periodical measurements are done daily, weekly, monthly as well as every six months or every year according to a plan that is adapted to the requirements and possibilities of each plant. The plan can be static, but it is recommended periodically to run a more intense measurement programme in order to get full insight in how the chemistry behaves in the plant. Having got the full insight, the measurement frequency can often be lowered for a number of parameters, while the attention to other parameters is intensified. Such a dynamic measurement programme presupposes that own personnel with the required qualifications is available for the control.

Water analyses are performed every six or twelve months dependent on water source and its stability. If the only water source is drinking water, the analysis frequency can be reduced or be completely omitted, since the waterworks can inform of the quality and the analysis results for the drinking water. On the other hand, the analysis frequency can be increased for critical parameters in relation to alternative water sources. Supplementary analyses of circuit water after partial stream filters and partial stream treatment filters are carried out concurrently with the circuit water analyses, but only relevant parameters for the component in question are analysed.

As required, examinations of bacteriological activity and of biofilm are performed, cf. *section 8.4: Bacteriological activity*.

### 8.2.1 Sampling

Sampling and equipment for sampling:
In order to evaluate the water quality it is important to take a representative sample, which can be difficult, since there is not always a test cock installed. Some of the most important precautions are:

- Samples for routine monitoring of the water quality should preferably be taken from a test cock for the purpose. The test cock is designed so that the tap is horizontal, has an inner diameter of 6-8 mm, and sticks 4-6 cm inside the inner surface of the district heating piping to get a sample of the flowing water. The material for the tap and the subsequent piping should be of stainless steel to avoid contamination with corrosion products from the test cock itself. Immediately after the test cock, a block valve is installed, for example a ball valve that is completely opened when using the test cock. Subsequently a cooler can be installed (when sampling from the flow pipe water) and one or more regulating valves (for example needle valves for manual sample and pH-meter/conductivity meter).
- It is necessary to rinse the test cock thoroughly so that all stagnant water is removed before the sample is taken. If plastic tubes are used, there is risk of oxygen diffusion into the sample. In some cases, it has been observed that a drain has been used for sampling, and in order to minimize water waste the sample is taken immediately. This practice results in a sample with a falsely high particle content from deposits in the bottom of the pipe and drain.
- Sample bottles should be filled completely and closed tightly immediately after the sampling. Carbon dioxide from the air is taken up by the water and changes pH and alkalinity, if the sample stands too long.
- When taking samples to determine contents of iron and copper, it can be difficult to avoid precipitation of particles into the sample that is taken. It is important **not** to take a sample with

overflow, i.e. letting the water run into the sample bottle and over the brim, since too many particles and concentrations of iron and copper will be too high.

- All equipment for sampling should be clean and preferably rinsed with the same water quality that the sample represents.

### 8.2.2 Example of analysis programme – softened water:

An example of a measuring programme for a small plant with softened circuit water and softened make-up water could be as mentioned on the next page. The measuring programme comprises both circuit water and make-up water to a relevant extent. Several measurements have been shown that might be unnecessary if you can see from trend curves that there is control of the system.

**Table 8.2.2. Analysis programme for softened water**

| **Measurement** | **Operating measurements** | | **Control measurements** |
|---|---|---|---|
| Control level | Continuous | Sampling | External laboratory |
| Appearance | | Weekly | Yearly |
| Odour | | Weekly | Yearly |
| pH | Recommended (operating temperature) | Weekly (25°C) | Yearly (25°C) |
| Hardness | | Weekly | Yearly |
| Oxygen, $O_2$ | | Weekly*) | Yearly |
| Conductivity at 25°C | | Weekly | Yearly |
| Particle content | | | Yearly |
| Oil content | | | Yearly |
| Chloride, $Cl^-$ | | Weekly**) | Yearly |
| Sulphate, $SO_4^{--}$ | | | |
| Ammonia, $NH_{3\ \mathrm{total}}$ | | | Yearly |
| Iron, $Fe_{\mathrm{total}}$ | | | Yearly |
| Copper $Cu_{\mathrm{total}}$ | | | |
| Phosphate surplus | | Weekly*) | Yearly*) |
| Alkalinity | | Weekly*) | Yearly*) |
| Oxygen binding potential | | Weekly*) | Yearly*) |
| Sulphide | | Monthly | Yearly |

*) Extent and measurement method depend on the chosen water treatment concept and the chemicals used.

**) Measure the chloride content in the make-up water weekly or before or after each backwash to detect possible changes in value. If the chloride content in the make-up water increases, this could be a result of insufficient backwashing of the softening filter or that the softening filter is defective, so that the sodium chloride from the regeneration is conducted with the make-up water.

**Example of analysis programme – (partly) demineralized water:**

An example of a measurement programme for medium plant with partly demineralized circuit water and demineralized make-up water could be as stated below. The measurement programme comprises both circuit water and make-up water to a relevant extent.

| Measurement | Operating measurements | | Control measurements |
|---|---|---|---|
| Control level | Continuous | Sampling | External laboratory |
| Appearance | | Weekly | Every six months |
| Odour | | Weekly | Every six months |
| pH | Recommended (operating temperature) | Monthly (25 °C) | Every six months (25°C) |
| Hardness | | Weekly | Every six months |
| Oxygen, $O_2$ | Recommended | Monthly | Every six months |
| Conductivity | Recommended | Monthly | Every six months |
| Particle content | | Monthly | Every six months |
| Oil content | | Monthly | Every six months |
| Chloride, $Cl^-$ | | Monthly | Every six months |
| Sulphate, $SO_4^{--}$ | | Monthly*) | Every six months |
| Ammonia, $NH_{3\ total}$ | | | Every six months |
| Iron, $Fe_{total}$ | | | Every six months |
| Copper $Cu_{total}$ | | | Every six months |
| Phosphate surplus | | Weekly*) | Every six months*) |
| Alkalinity | | Weekly*) | Every six months*) |
| Oxygen binding potential | | Weekly*) | Every six months*) |
| Sulphide | | Monthly*) | Every six months |

*) Extent and measurement method depend on the chosen water treatment concept and the chemicals used.

### Documentation

All measurements – both continuous and periodical – shall be documented by a logbook or through data storage for example in the plant's SCADA system.

If automatic data storage is used, it is important that the documentation of test results is stored on a daily, weekly, and monthly basis several years back. Such a documentation will be valuable internally in the assessment of the operating and maintenance plans and perhaps externally in relation to actions for damages.

Logbook over calibration of the applied measuring instruments shall be kept by entering values before and after calibration.

## 8.3 Bacteriological activity

Analyses of bacteriological activity is not a routine analysis and it is therefore important to detect any indication of such growth. A certain indication of sulphur-reducing bacteria is that free sulphide is detected in the water through water analyses.

Another indication of bacteriological activity is the formation of biofilm on the inner side of piping, heat exchangers, and other components. The biofilm is very susceptible to sedimentation, therefore sedimentation in other areas than the bottom of piping and vessels is an indication of biofilm that normally cannot be seen or felt. By heavy growth of biofilm, surfaces feel greasy and slippery. If heavy bacteriological activity is suspected, the procedure to detect whether this is the case is as follows:

- First indicator is the odour of rotten eggs (hydrogen sulphide – $H_2S$).
- Second indicator is slime in the filters.
- Third indicator is corrosion products, which feel soft and smell of burnt hair when burning.
- Fourth indicator is a sludge sample, which is suspended in circuit water, after which the pH-value is measured. If the pH-value is lower than in the circuit water before the suspension, this is an expression of bacteria presence in the sludge.

If there is indication of activity, further examination can be done. Identification of type of bacteria requires DNA analysis. Today, this can be performed relatively simple.

# 9 MONITORING AND CONTROL OF CORROSION

As district heating systems are traditionally constructed, there is no possibility of continuously following a possible corrosion in the plants. Feedback on detected corrosion from sanitary and heating technicians and from the district heating plant's own repair technicians in connection with repair and maintenance works on the pipe system and user installations is therefore an important part of monitoring and control. If corrosion is suspected or in case of corrosion testing, methods for monitoring and control are available.

## 9.1 Corrosion measurements

Corrosion measurement on selected plant parts can be done by a number of non-destructive inspection methods, also called NDE methods:

- Ultrasonic testing of material thickness.
- Radiography (X-raying) examinations for hidden cracking and solid inclusions.
- Magnetic particle flaw detections for cracking.
- Eddy current examinations for hidden cracking and laminations.

Non-destructive inspection methods are specialist work, which can be part of the systematic and planned operation and maintenance as well as in special examinations in case of leakage or suspicion of damage.

A diver with video inspection equipment can perform inside inspection of water-filled holding tanks. Based on the video film and the diver's comments, it can be assessed whether there is abnormal or substantial corrosion or other damage inside the holding tank.

Likewise, insufficient cleaning of tank walls and bottom before water filling can be detected and measurement of pitting corrosion and the extent of pitting corrosion can be done. Then, the extent of sedimentation can be seen and removed with a “vacuum cleaner”.

## 9.2 Corrosion coupons

One method to measure corrosion risk for specific types of metals or alloys is to use corrosion coupons that are inserted into the circuit water. The term corrosion coupons denotes small pieces of metal placed on a holder and inserted into the circuit water. The same material is used for the coupons as the material to be investigated for corrosion. However, the corrosion conditions are not the same throughout the district heating system, therefore the corrosion coupon system does not give any security as to detection of corrosion damage.

The coupons can be used as a supplementary measuring method on plants, where a problem has been found or where you want to examine new materials or joining methods, typically copper alloys and soldering alloys. Furthermore, the coupons can be used for biofilm analysis and for testing of biocide addition, but cannot be used as control of whether there is microbial activity or biofilm in the district heating system.

Corrosion coupons can be inserted into a tank in a bypass as well as directly in the main stream. In order to do this without having to interrupt the main stream when the coupons are examined, coupon holders are used that are inserted through a stuffing box and a ball valve.

# 10 SPECIAL CORROSION CONDITIONS

In addition to the general corrosion conditions mentioned in the previous sections there is a number of special conditions, which have been found and which should give occasion for special considerations as to certain plant components.

## 10.1 Boilers in direct system

Production plants such as boilers can either be connected directly to the district heating net and thus be part of the circulation system or be a separate circuit with heat exchanger to the district heating net.

Production plants on stand-by will often have a low water flow whereby there is risk of sedimentation and deposits of impurities and suspended sludge particles, etc. Therefore, it is necessary to ensure a certain circulation in the water circuit so that there is uniform water quality everywhere in the boilers. If not, the risk of corrosion especially in boiler piping and boiler bottom is imminent. With separate plants in which the production plant is separated from the district heating net by a heat exchanger, it is possible to maintain a better water quality in the production plant than in the rest of the plant.

Demineralized water can be a relevant choice in closed boiler circuits, irrespective of whether softened water or partially demineralized water is used in the distribution net.

New peak load and reserve load boilers, which are separated from the district heating system by a heat exchanger, and which are on stand-by at lower temperature, must be cleaned by boiling out or scaling with acid before commissioning. Given the right conditions as to presence of organic material and sulphate, the lower and constant temperature can further bacteriological corrosion. The water quality in closed boiler circuits should be controlled in order to register and correct deviations from the required quality.

## 10.2 Holding tanks

Holding tanks have become more common and are now found in almost all plants. As opposed to the pipe plant, holding tanks are characterized by a relatively large water volume compared with the steel face. Usually, the water temperature fluctuates between 40 and 95°C and these fluctuations occur with short and regular intervals. In principle, the water is stagnant and there is ample opportunity for sedimentation and deposits of impurities and suspended sludge particles, etc.

Holding tanks can either be connected directly to the production plant and the district heating net and thus be part of the circulation system or the holding tank can be a separate circuit with heat exchanger to the production plant and/or the district heating net. Serious corrosion damage has been seen in many holding tanks and the problems are most pronounced in unpressurized tanks with steam cushions, in which the tanks are installed in direct connection with the district heating system.

Corrosion damage often occurs in the transition zone between the steam cushion and the water and as “curtains” down the tank walls from the water surface. Condensing steam has a natural pH-value of 6.5 to 7.0, which causes heavy corrosions together with even a modest oxygen content. Furthermore, the corrosion will be most vigorous in the upper part of the tanks with softened water that has not been deoxidized.

Further corrosion has been detected at the tank bottom, where there have been sedimentations. In connection with such sedimentations, it can be a question of bacteriological corrosion. Recommendations as to corrosion prevention when constructing holding tanks are as mentioned under the below items. Furthermore, the tanks must be constructed in accordance with the Danish norm for steel tanks, DS 417, as to inspection access, railings, and ladders, etc. Manhole in the top should be minimum 600 mm in diameter.

### 10.2.1 Steam cushions

Unpressurized tanks are often protected against air penetration trough the vent pipe by water trap and steam cushion over the water surface. Usually, the pressure in the steam cushion is 300 mmVS (unit of pressure: millimetres, water gauge). On small plants, the steam cushion is often made with an electric immersion heater in the tank for production of the steam and maintenance of the steam cushion. When using an electric steam generator or immersion heater, make sure that the capacity is sufficient in case of quick and protracted temperature changes in the water, so that the steam cushion does not collapse and air penetrates via the water trap or the pressure and vacuum valve.

Use of steam cushion can only be recommended where sufficient steam capacity is available to maintain the steam pressure under all conditions. A greater steam capacity can be obtained from an oil or natural-gas fired steam boiler or steam generator. The steam cushion pressure should be equipped with constant monitoring and registration via a SCADA plant.

In principle, the water treatment chemicals should be steam volatile when using steam cushions, so that the oxygen binding potential and the pH-value are retained in the steam and especially in the condensate, which runs down the tank sides over the water surface. In large transit systems that typically are separated from the distribution net, conditioning with ammonia is used. In plants, in which ammonia is not recommended and sodium hydroxide is used, the requirement cannot be met and therefore the use of nitrogen cushion is recommended. Ammonia is recommended, but amines are also a possibility.

### 10.2.2 Nitrogen cushions

Instead of steam cushion, the unpressurized tanks can be protected against air penetration by means of a nitrogen cushion ($N_2$) over the water surface in the tank.

Nitrogen cushions are recommended in preference to steam cushions in holding tanks in the district heating systems. Likewise, nitrogen cushions are recommended for pressure storage tanks and other tanks with free water surface.

In principle, nitrogen cushion can be established and maintained in two ways. Either by means of a tank plant/bottle battery or by means of a nitrogen generator. Both types of plants can be equipped with nitrogen recovery and buffer tank, so that plant and operating economy are optimized to the current plant. When using nitrogen generator, make sure that it produces nitrogen of the required purity.

Nitrogen from nitrogen generators can be produced with a purity of from 99 % to 99.9 % pure $N_2$. Nitrogen on bottles is available with different purities of 99 % pure $N_2$ and 99.96 % pure $N_2$.

The requirement for purity is linked with the nitrogen consumption, since it is the total volume of oxygen supplied that is decisive. A large nitrogen consumption requires large purity, whereas a small consumption is less demanding as to purity.

The nitrogen cushion is relatively indifferent to temperature fluctuations in the water and shall primarily be dimensioned based on the expected water surface changes in the tank.

The water's uptake of nitrogen is limited by diffusion in the stagnant water. Henry's law governs the solubility in the upper water layer, cf. *section 4.3: Degassing.*

### 10.2.3 Sand blasting and degreasing

Sand blasting and internal degreasing of tanks are recommended before commissioning and also very thorough inside cleaning of the tank before water filling.

An alternative to sand blasting on site is to use sand-blasted and shop-primed steel plates. Sand-blasted and shop-primed plates are a normal commodity.

When using shop-primed plates, all welding seams and other worked surfaces must be finished to the same surface standard as the plates. The same applies to all welded piping and branches, etc. as well as the central pipe.

Iron scales, grease deposits, and impurities on tank walls and in the tank bottom can increase the risk of covered corrosion.

### 10.2.4 Internal surface treatment

Inside surface treatment of holding tanks is not recommended. If inside surface treatment is applied, make sure that the surface treatment can sustain the many and quick temperature changes without formation of cracks. Also, make sure that the surface treatment is absolutely without pinholes. Formation of pores and cracks can cause very concentrated corrosion attacks.

### 10.2.5 Use of high-strength steel

In general, high-strength steel should not be used for holding tanks. Steel with enhanced strength should only be applied if documented data are available on the material's sensitivity to corrosion and fatigue in boiler and district heating systems. Thus, it must be documented that a local rusting through or a local crack formation does not cause a running fracture or collapse of the tank.

### 10.2.6 Possibility of better water quality

When the holding tank is separated from the district heating system by a heat exchanger, it is expedient to maintain a better water quality in the holding tank than in the rest of the plant.

Demineralized water can be a relevant choice for holding tanks that are separated from the plant irrespective of whether softened water or partially demineralized water is used in the distribution net.

The water quality in holding tanks separated from the plant shall be monitored to register and correct deviations from the required quality.

## 10.3 Motor cooling systems

Water treatment for cooling water circuits on motors and turbines, etc. is not covered by this guide. Such treatment must be carried out in accordance with the instructions of the manufacturer using the products recommended by the manufacturer. There are differences in requirements and needs varying from motor type to motor type, even within the same make of motors.

For make-up water to cooling circuits, the purest water available should be used. As an absolute minimum, the use of softened water is recommended, but because of the risk of sedimentation and the high conductivity, which can cause galvanic corrosion, demineralized make-up water should be used instead. Untreated drinking water should not be used as make-up water for cooling systems. Here it must be emphasized that the suppliers of plants not always have the necessary knowledge of the use of demineralized water and therefore do not recommend this.

The conditioning of make-up water usually comprises addition of corrosion inhibitors and perhaps antifreeze agents in accordance with the instructions of the manufacturer. Antifreeze additives influence the heat conductivity and the specific heat capacity as well as the boiling point of the antifreeze.

There is a relation between density and the concentration of glycol and thus the frost protection temperature. Control of bulk density should therefore be done to make sure that the system is protected against frost. Be aware of the type of antifreeze in question, since the bulk density varies. Usually, ethylene glycol and propylene glycol are used. The latter is more common because it is more environmentally acceptable.

Maintenance and renewal of water in the cooling water circuits must comply with the instructions of the motor manufacturers and the antifreeze suppliers. As a minimum, the inhibitor concentration and functioning should be checked once a year.

## 10.4 Cooling systems with frost protection

In solar heating systems and in heat pumps working at low temperatures, it is necessary to add substances, which lower the freezing point. Salts are out of the question because of corrosion, but glycol systems have shown to be most effective. Glycol can however result in corrosion in the system, the use of deoxidized water is recommended to make the system as tight as possible.

Throughout the ages, ethylene glycol and propylene glycol have usually been used. Because of the less hazardous effect of propylene glycol, this substance is now typically used. There is always risk of corrosion in the systems and often many different materials are used so that the added corrosion inhibitors must cover a very broad spectrum. Furthermore, the product also contains sodium hydroxide to increase pH and thereby reduce the corrosion risk. Glycol will always be gradually decomposed forming breakdown products like lactic acid, oxalic acid, formic acid, or acetic acid. In case of surplus of sodium hydroxide, the breakdown products will be neutralized.

Furthermore, the corrosion inhibitors have a certain risk of precipitating on the surface and thus not giving the necessary protection.

# 11 ENVIRONMENTAL CONDITIONS

District heating is an environmentally sound heating form with a green profile, therefore we must make sure that the water treatment and the corrosion prevention also live up to this. The large plants over 50 MW are comprised by the regulation on large firing, whereas smaller plants belong under the following items:

### G. Power and heat production

G 201. Power producing plants, heat producing plants, gas turbine plants, and motor plants with a total nominal thermal output of firing between 5 and 50 MW.

G 202. Power producing plants, heat producing plants, gas turbine plants, and motor plants based on solid bio fuels or biogas, with a total nominal thermal output of firing between 1 MW and 5 MW.

The obligation of approval comprises plants in which chemicals are handled that should be stated in the application. Below a number of the conditions are stated, which should be allowed for in connection with use and handling of chemicals for water treatment and corrosion prevention.

## 11.1 Chemical storage

Special requirements for storage, handling, and transport shall appear from the labelling or from the documents supplied with the product.

Chemicals must be stored in original packaging until they are used and they must only be filled into dosing tanks labelled in the same way as the original packaging. Chemicals shall be stored on a tight bottom without outlet to drain. The storage area shall be protected against fall of rain or snow and shall have collection in a reservoir, so that at least a quantity corresponding to the largest packaging can be retained in case of spillage or leakage. The storage room must be separate, locked, and well ventilated.

Handling of chemicals must comply with the rules laid down in the working environment legislation and as described in the plant's work site evaluation.

Transport of chemicals outside own premises is subject to the regulations for “Road transport of hazardous goods”, which set up special requirements for transport documents, transport vehicle, and driver of the vehicle.

Caustic substances like acids and lye are classified as hazardous goods class 8.

The national regulations governing the area stipulate a free quantity of maximum 100 kg that can be transported without complying with the special requirements. Chemicals must always be labelled and packaged as laid down in the regulations.

The chemical storage should be treated in the contingency plan of the district heating plant, if such a plan has been prepared.

## 11.2 Chemical spillage

Any person who causes substantial contamination with chemicals or who finds such contamination shall immediately inform the local environmental authorities. In the event of a major acute accident, an alarm call must immediately be made.

In case of chemical spillage, the responsibility lies with the heating plant of taking the necessary preventive measures on own initiative or according to the instructions of the environmental authorities. In the event of spillage of water treatment chemicals, this will above all be barring of the sewer, so that the contamination does not spread to the local sewage system. Spillage on earth must be collected as soon as possible so that percolation is avoided.

## 11.3 Circuit water

All chemicals for water treatment and corrosion prevention must be labelled cf. *section 6.13:* Labelling of chemicals and must be accompanied by an environmental declaration cf. *section 6.12: Requirement specification for environmental declarations*.

When choosing water treatment system, the district heating plant should attach great importance to the environmental declaration and choose the system causing minimum environmental stress.

The chemical content in the circuit water is part of this environmental stress, because water loss is conducted to nature either through direct percolation into the soil or via drain and sewage systems.

The environmental evaluation of the circuit water must comprise an attitude to the consequence of the following items:

- Hot service water contaminated by circuit water.
- Percolation of circuit water into the soil.
- Circuit water in the drain systems.
- Circuit water in the sewage system.

### Environmental screening

When a plant is to be approved, an environmental screening could be required to assess the risk in case of leakage and major accidents on the plant.

Usually, the temperature poses the greatest risk of damage on the surroundings. Even if a high pH of 9.8 ± 0.2 in the district heating water has a potential risk of damage, the temperature is the worst. The pH-value will quickly be set off, if the water gets into contact with water of another quality, especially if this is demineralized water, in which the buffer capacity is smaller than water from the surroundings.

If other additives are used, the supplier of these chemicals is responsible for stating the risk.

Sodium hydroxide has so high a purity that there is no risk of influence from heavy metals.

## 11.4 Wastewater discharge from water treatment plants

An important point in the environmental approval of the plant is the wastewater discharge from the water treatment plant. The discharge is subject to “Connection of industrial wastewater to municipal wastewater works”. Notice No. 501 of June 21, 1999, on wastewater approvals, etc. according to sections 3 and 4 in the environmental protection law.

Limit values are only guideline values and they must be determined based on what is technically and financially possible in the actual environmental approval. Thus, the local authority can stipulate discharge limits in the environmental approval in consideration of the functioning and the discharge of the wastewater treatment plant.

## 11.5 Degassing from water treatment plants

Degassing from water treatment plants is subject to the requirement for environmental approval. Account must be given of gasses and volumes that are released and degassed. Degassing of ammonia from make-up water from power plants or from transmission systems must be described separately and the degassing must be approved in connection with the environmental approval.

The degassing is subject to the Environmental Protection Agency's Guide No. 2, 2001 “Guide on air“. Limitation of air contamination from businesses”.

## 11.6 Chemical waste

All chemical waste is subject to the Environmental Protection Agency's notice No. 619 of 27 June 2000, which in section 9 stipulates regulations for hazardous waste including chemical waste.

Exhausted filtering media (ion exchangers) from for example softening plants and demineralization plants are classified as hazardous waste and are subject to the duty to notify in accordance with § 50 in the notice and the requirement for municipal refuse collection. As an alternative and after approval by the municipal authority, the filtering media can be sent back to the supplier for reuse or the media can be handed over to an approved firm for disposal through incineration. The important question is whether the ion exchangers contain toxic substances. Ion exchangers used for treatment of drinking water are usually unproblematic.

## 11.7 Green accounting and environmental certification of district heating plants

District heating plants larger than 50 MW are subject to requirements for preparation of yearly green accounting pursuant to Danish legislation on environmental protection, notice No. 210 of 3.03.2010 on certain businesses' submission of environmental information – G101 businesses.

A number of small district heating plants prepares green accounting on their own initiative. Consumption of make-up water, water treatment chemicals, and discharge of wastewater from the water treatment plant as well as toxicity and environmental load resulting from this are elements in green accounting and should be minimized as much as possible.

In connection with environmental certification of district heating plants, on which a few plants have begun, a complete account of the used substances and their environmental load throughout the entire life cycle of the product is required.

## Total survey of legislation

Survey of current Danish legislation

Notice on approval of listed businesses (list of hazardous substances)
Notice No. 482 of 07-05-2013
Notice on certain businesses' submission of environmental information
Notice No. 210 of 03-03-2010
Guide on air
Guide No. 12415 of 01-01-2001
Guide on classification, etc. of chemical substances and products
Guide No. 9580 of 20-10-2004
Notice on wastewater approvals, etc. acc. to section 3 and 4 in the environmental protection law
Notice No. 1448 of 11-12-2007
Guide on wastewater approvals
Guide from MST No. 5, 1999