# Water in brewing

## M. Eumann, EUWA Water Treatment Plants, Germany

### 9.1 Introduction

## 9.1.1 Water as a raw material

Very often water is considered a utility in a brewery. As water is an important constituent of beer, though, making up more than 90% of the product, it is worth looking at water from a raw material perspective.

Historically the characteristics of different beer styles were influenced by the composition of the water used in their manufacture (see Table 9.1). To produce today's most prominent beer style, Lager or Pilsner beer (a bottom-fermented beer, light in colour and with a more or less pronounced hop flavour), it is necessary to treat the water used to make it, if the naturally available water source does not meet the composition accepted today as the standard.

Table 9.1 Different raw water compositions

		Munich	Dortmund	Vienna	Burton on-Trent	Pilsen
Total hardness	ppm CaCO <sub>3</sub>	264	737	689	980	28
m-alkalinity	ppm CaCO <sub>3</sub>	253	300	551	262	23
Non-carbonate						
hardness	ppm CaCO <sub>3</sub>	11	437	138	718	5
Ca	ppm CaCO <sub>3</sub>	189	655	407	880	18
Mg	ppm CaCO <sub>3</sub>	75	82	282	100	10
Residual alkalinity	°G	10.6	5.7	22.1	-0.2	0.9
Dry solids	ppm	284	1110	948		51

#### 9.1.2 Raw water sources

One can distinguish between surface water, which is water derived from lakes, rivers, man-made reservoirs or dams, and well water from underground. Surface water is more susceptible to seasonal changes due to rainfall or drought periods. It usually contains small quantities of minerals and high organic loads and is microbiologically contaminated. Well water from a suitable depth is usually protected from the surface and therefore its supply fluctuates far less. Depending on the hydrogeological situation, though, it can contain a lot of minerals. Its microbiological quality is usually good. Care has to be taken to use a well properly to prevent overuse which eventually can cause it to dry up.

#### 9.2 Water for use in breweries

#### 9.2.1 Water analysis and evaluation, definitions

Very often it is not acceptable to rely on a fluctuating water supply. Apart from obtaining hydrogeological data to determine whether water is sufficiently available, analysis should ideally also be carried out over at least a one-year period to determine seasonal fluctuations. But what should be analysed to evaluate the water composition? Table 9.2 lists the relevant components. Of course, the analysis is not confined to these parameters and specific site-related problems may require in-depth analysis. In most cases, though, analysing the parameters shown in Table 9.2 would be sufficient.

As an aside, total hardness of water is defined as the sum of all earth alkali ions, in this context  $\text{Ca}^{2^+} + \text{Mg}^{2^+}$ . Total hardness can be divided into carbonate and non-carbonate hardness, the former being  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  and the latter  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$  and  $\text{Mg}(\text{NO}_3)_2$ . Alternative terms used are temporary and permanent hardness, because a strong acid like HCl can make the  $\text{Ca}(\text{HCO}_3)_2$  disappear and form  $\text{CO}_2$ , whereas the HCl has no effect on the non-carbonate hardness and is thus permanent.

Depending on the system used, hardness and alkalinity can be defined as ppm CaCO<sub>3</sub>, °F (degree French hardness), °G (degree German hardness) or

Smell	Residual alkalinity
Taste	Na
Colour	Ca
Turbidity	Mg
Temperature	$HCO_3$
Conductivity	Cl
KMnO <sub>4</sub> consumption	$SO_4$
Fe	$NO_3$
Mn	$SiO_2$
As	$NO_2$
NH <sub>4</sub>	THMs

Table 9.2 Important water analysis parameters

**Table 9.3** Definition of hardness units

 $1^{\circ}F = 10 \text{ mg CaCO}_3/1$  $1^{\circ}G = 10 \text{ mg CaO/l}$  $1 \text{ meg/l} = 50 \text{ ppm as } CaCO_3$ 

meg/l. The SI measurement is mol/m<sup>3</sup>. See Table 9.3 for the definition of hardness units.

#### 9.2.2 Filtered water

The minimum requirement for water used in a brewery should be that it conforms to potable water standards such as the European drinking water regulations, WHO (World Health Organization) requirements, FDA (Federal Drug Administration) requirements or equivalent official standards. There are always two areas which need attention when deciding which type of water to use: firstly the process requirements, and secondly the integrity of materials in contact with the water, which are affected mainly by scaling and corrosion.

Filtered water of a suitable standard should be used for cleaning. If water is not heated, there is no risk of scaling. There are limitations, though, in the levels of chloride acceptable in filtered water. The chloride level should not exceed 100 ppm to avoid corrosion of stainless steel. Complete guidelines for the composition of filtered water are in Table 9.4.

Table 9.4	Guideline	for	filtered	water	quality

		Rang	ge
		Min.	Max.
Total hardness	ppm CaCO <sub>3</sub>		
Ca	mg/l		
Mg	mg/l	0	10
Na	mg/l	0	200
HCO <sub>3</sub>	ppm CaCO <sub>3</sub>		
Cl	mg/l	0	100
$SO_4$	mg/l	0	250
$NO_3$	mg/l	0	50
$SiO_2$	mg/l		
THM	$\mu$ g/l	0	10
Fe	mg/l	0	0.1
Mn	mg/l	0	0.05
NH <sub>4</sub>	mg/l	0	0.5
$NO_2$	mg/l	0	0.1
$BrO_3$	mg/l	0	0.01
$H_2S$	$\mu \mathrm{g/l}$	0	5

Other parameters according to WHO/EU drinking water guideline.

Table 9.5 Guideline for service water quality

		Rang	ge
		Min.	Max.
Total hardness Ca	ppm CaCO <sub>3</sub> mg/l	50	90
Mg Na HCO <sub>3</sub>	mg/l mg/l ppm CaCO <sub>3</sub>	0	200
Cl	mg/l	0	50
$SO_4$	mg/l	0	250
NO <sub>3</sub> SiO <sub>2</sub>	mg/l mg/l	0	50
THM	$\mu g/l$	0	10
Fe	mg/l	0	0.1
Mn	mg/l	0	0.05
$NH_4$	mg/l	0	0.5
$NO_2$	mg/l	0	0.1
$BrO_3$	mg/l	0	0.01
H <sub>2</sub> S	$\mu$ g/l	0	5

Other parameters according to WHO/EU drinking water guideline.

#### 9.2.3 Service water

This quality of water should be used whenever the water is heated but not used in the brewing process. Primary examples would be hot CIP (Clean In Place) and final rinse water for packaging applications. Table 9.5 outlines the composition of service water. It is important that hardness in this water is limited to prevent scaling, which can, for example, lead to the blockage of spray nozzles in the bottle washer. It is also important that the chloride content is limited to about 50 ppm. This is to avoid corrosion of stainless steel. If hot service water starts stainless steel corrosion in one place, the same water can also have an impact on other stainless steel parts of the brewery which come into contact with that water, even when it is no longer hot, because of the FE dissolved in the water. Furthermore, service water has to be free of microbiological contamination.

#### 9.2.4 Brewing water

As mentioned earlier, more than 90% of beer is water. Therefore it is of utmost importance that the quality of the brew water is high. A very important ion in brew water is calcium. During mashing it reacts with the phosphate buffer from the malt, influencing the pH level. In order for the enzymes to work properly, a pH of 5.2-5.4 is optimal. More than 100 years ago Kolbach came up with an empirical formula to determine whether the pH will rise or fall. This is called residual alkalinity and is defined according to the formula in equation 9.1:

$$RA = m - \frac{Ca + 0.5Mg}{3.5}$$
 (9.1)

where RA = residual alkalinity, ppm CaCO<sub>3</sub>

m = m-alkalinity, ppm CaCO<sub>3</sub>

 $Ca = calcium concentration, ppm CaCO_3$ 

Mg = magnesium concentration, ppm MgCO<sub>3</sub>

A residual alkalinity of zero means that there is no pH influence. A positive residual alkalinity will lead to an increased pH, and a negative residual alkalinity will decrease the pH. Today in many cases artificial acidification by addition of lactic acid or mineral acid (mostly phosphoric acid) is used to adjust the pH. The calcium content during mashing and sparging can be influenced by dosing with calcium chloride and/or calcium sulphate.

Another important reason why calcium is required in the brew water is for oxalate precipitation. It is necessary to have sufficient calcium in the water to facilitate oxalate precipitation, which of course is also aided by low temperatures in storage vessels. If not removed, oxalate crystals can cause gushing in the finished product, but brewing with water of the correct composition will prevent this being an issue. Therefore it is worth aiming at a negative residual alkalinity in the brew water and sufficient calcium content.

Magnesium ions, although important for human health, are not necessarily a sufficiently positive influence on pH in the concentrations usually present in brew water. Because magnesium phosphates are more soluble than calcium phosphates, about twice the amount of magnesium is required to achieve the same effect as is achieved with calcium. Further, for reasons of taste the use of high levels of magnesium salts is not encouraged.

Because sodium salts are very soluble they do not cause the phosphates to precipitate. As there is no interaction with the phosphate buffer, subsequently there is no pH change.

On the anion side, chloride is a factor that influences the corrosivity of the water, though this does not happen when the water is already mixed with the wort. Exactly why this is the case cannot be clearly determined, but this is of advantage to breweries. Beer containing predominantly chloride anions has a milder flavour.

Having sulphate ions in the brew water is of no disadvantage. It is even reported that elevated levels of sulphate can facilitate sulphite formation. Sulphite acts as an oxygen scavenger and thus increases the ageing potential of a beer. A pronounced bitterness is associated with higher sulphate contents in the beer.

Nitrate can be reduced in anaerobic conditions to  $NO_2^-$ , which poisons cells and therefore destroys the brewing and fermentation process. Therefore levels of  $NO_2^-$  in brew water have to be very low.

Bicarbonate increases the pH of water as it absorbs acidity. Nearly all water contains a certain natural level of bound CO<sub>2</sub> and bicarbonate. Bicarbonate buffers any acidity, for example that caused by CO<sub>2</sub> or other acids like lactic or phosphoric acid. Before the artificial acid can bring down the pH, the bicarbonate has to be destroyed first. Bicarbonate, though, can also be responsible for

Table 9.6 Guideline for brewing water quality

		Range		Target	
		Min.	Max.		
pH		5	9.5		
Ca	mg/l	70	90	80	
Mg	mg/l	0	10		
Na	mg/l	0	20		
HCO <sub>3</sub>	ppm CaCO <sub>3</sub>	10	50	25	
Cl	mg/l	30	80	50	
$SO_4$	mg/l	30	150	100	
$NO_3$	mg/l	0	25		
$SiO_2$	mg/l	0	25		
Residual alkalinity	ppm CaCO <sub>3</sub>		20	<0	
THM	$\mu$ g/l	0	10		
Fe	mg/l	0	0.1		
Mn	mg/l	0	0.05		
$NH_4$	mg/l	0	0.5		
$NO_2$	mg/l	0	0.1		
$BrO_3$	mg/l	0	0.01		
$H_2S$	$\mu$ g/l	0	5		
Turbidity	NTU	0	0.5		

Other parameters according to WHO/EU drinking water guideline.

formation of a layer of lime on mild steel piping which protects the piping from corrosion. This is of less importance nowadays, though, as stainless steel is the preferred material in today's brewery environment. It also should be noted that when water comes into contact with mild steel in the form of pipelines, reservoirs or vessels, free aggressive  $\rm CO_2$  has to be removed beforehand by a  $\rm CO_2$ -trickler and the so-called +p (phenolphthalein) alkalinity (pH > 8.2) has to be adjusted.

Another component worth looking at in brew water is silica. Silica also has limited solubility in water and therefore should be removed to levels below 25 ppm. It goes without saying that oxidizing agents like chlorine in its various forms or ozone should not be present in the brewing liquor. THMs (Tri Halo Methanes) are also substances of concern in the brew water stream and should be removed to as great an extent as possible, preferably to below 10 ppb. Table 9.6 describes brew water.

#### 9.2.5 Dilution water

It is important that the calcium content of dilution water is not higher than the calcium content of the concentrated beer to be diluted, in order to avoid oxalate precipitation. There are also strict requirements regarding oxygen content, which should mainly be less than 20 ppb, and THM levels are also of great importance. Some breweries distinguish between brewing liquor and dilution liquor in terms

Table 9.7 Guideline for dilution water quality

		Range		Target	
		Min.	Max.		
pН		5	9.5		
Ca	mg/l	20	40	30	
Mg	mg/l	0	10		
Na	mg/l	0	20		
HCO <sub>3</sub>	ppm CaCO <sub>3</sub>	10	50	25	
Cl	mg/l	0	50		
$SO_4$	mg/l	0	50		
$NO_3$	mg/l	0	25		
$SiO_2$	mg/l	0	25		
Residual alkalinity	ppm CaCO <sub>3</sub>		20	<0	
THM	$\mu$ g/l	0	10		
Fe	mg/l	0	0.02		
Mn	mg/l	0	0.02		
$NH_4$	mg/l	0	0.5		
$NO_2$	mg/l	0	0.1		
$BrO_3$	mg/l	0	0.01		
$H_2S$	$\mu$ g/l	0	5		
Turbidity	NTU	0	0.5		

Other parameters according to WHO/EU drinking water guideline.

of levels of THMs permitted, though others do not. The microbiological composition of the dilution water is very important as this water is not necessarily boiled. Treatment with a proper disinfection system and a UV (ultraviolet) system prior to use is indispensable (see Table 9.7).

#### 9.2.6 Boiler feed water

For the boiler house it is necessary that the feed water is of adequate quality and free of hardness. The cheapest method to obtain good boiler feed water is to recover as much condensate as possible, as the condensate usually contains very low levels of minerals and thus virtually no hardness. It is important that the feed water contains HCO<sub>3</sub> at a level of less than 50 ppm (expressed as CaCO<sub>3</sub>), otherwise the intense heat in the boiler leads to the formation of NaOH and CO<sub>2</sub> from NaHCO<sub>3</sub>. The CO<sub>2</sub> will be corrosive and eventually destroy the boiler. The mineralization of the boiler feed water also impacts on the frequency of blowdown and thus the energy efficiency of the boiler. Hot brew water can be used as a source of boiler feed water, if appropriately treated for hardness, as this can help to provide water of the correct alkalinity and save energy.

Boiler feed water must also be thoroughly deaerated to achieve an oxygen content ideally of less than 20 ppb. It should also be conditioned properly with caustic to adjust the pH, with phosphate for hardness scaling prevention and with sodium bisulphite for oxygen scavenging.

**Table 9.8** Guideline for boiler and boiler make-up water quality

		Boiler feed water		Boiler water for ≤10 bar boilers	
		Min.	Max.	Min.	Max.
Total hardness	ppm CaCO <sub>3</sub>	0	2		
Conductivity	$\mu$ S/cm			0	5000
рН	,			10.5	12
HCO <sub>3</sub>	ppm CaCO <sub>3</sub>	0	50		
$SiO_2$	mg/l	0	20		
Fe	mg/l	0	0.1		
Mn	mg/l	0	0.5		
$PO_4$	mg/l PO <sub>4</sub>			10	20
KMnO <sub>4</sub> index	mg/l KMnO <sub>4</sub>			0	10
$SO_3$	mg/l			4	10
p-alkalinity	meq/l			1	12

For energy efficiency it is also worth exploring the possibilities of a closed condensate system which is operated under pressure, as considerable energy savings can be achieved. A frequent boiler water analysis must be executed as well. Table 9.8 provides guidelines for boiler feed and boiler water. It should be noted that the correct composition of the boiler and boiler feed water also depends on the pressure and the size of the boiler.

## 9.3 Treatment technologies

Water treatment in the brewery differs from treatment of other components used in the brewing process, as it is completely site related. The treatment process cannot easily be standardized unless breweries have a common water source. There are always several options to achieve the desired water quality. It is very important to have a good analytical data pool prior to designing a water treatment plant.

Several of the technologies described in the following sections can give similar results and therefore the choice of which technology to use should be driven by economics and constraints of space. There is no such thing as the ideal water treatment system and every brewery is unique. This is also reflected in the fact that different water treatment companies are likely to offer different solutions to problems and it is not easy for the one-off purchaser of a treatment system to see the pros and cons of each solution.

#### 9.3.1 Disinfection

Depending on the source, water is likely to be microbiologically contaminated to differing degrees and surface water is far more likely to be affected. However, to

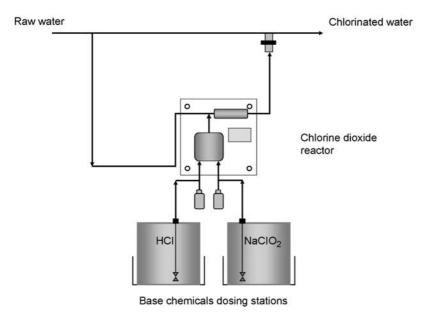


Fig. 9.1 ClO<sub>2</sub> plant based on the acid-chlorite process.

avoid any risk it should be the norm to disinfect all water coming on site. Even if the water is already treated by the municipality and thus most likely to have been exposed to some sort of disinfection process, the piping systems are often in such a poor state that a reliable and constant level of disinfectant cannot be detected all the time. The preferred disinfection method is chlorine dioxide (ClO<sub>2</sub>). It works according to the following principle:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$$
 (9.2)

The layout of a ClO<sub>2</sub> plant is as shown in Fig. 9.1. The advantages of ClO<sub>2</sub> plants are that they are easy and safe to use and virtually no by-products (THMs) are formed. Disinfection with sodium hypochlorite or chlorine gas is far more hazardous and unwanted by-products are created. It is usually too expensive only to use ozonization as a disinfection method. This method should be used only in cases where oxidation is required as well. It should also be noted that UV and ozone do not deposit anything in the water but do not possess any residual disinfection ability, so recontamination is possible.

#### 9.3.2 Oxidation/aeration

For the removal of certain components, especially iron and manganese, oxidation is necessary. Furthermore, aeration might be necessary to strip out odours like H<sub>2</sub>S.

In most cases, a simple injection of air with a static mixer is enough to supply sufficient oxygen to facilitate the reaction. To remove H<sub>2</sub>S, though, or correct a

low pH due to excess  $CO_2$ , open aeration is necessary. It has to be considered that an intensive aerator without filling material is much easier to clean than a trickler column, as the oxidized components might readily precipitate. It is beneficial to design the aeration system so it can be cleaned in place. It is also possible to use ozone as an oxidizing agent as mentioned in the previous section. However, it is quite expensive and therefore its application in this way is usually confined to special cases.

Only low levels of chlorine are allowed legally, therefore oxidation by chlorination is in most cases not possible because the amount of chlorine required exceeds the legal limit.

Should the water contain too much ammonia, it is necessary to provide enough oxygen for nitrate to form. Oxidation to form nitrate requires the presence of the bacteria *Nitrosomonas* and *Nitrobacter*, and therefore it can only be performed in conjunction with a carrier material like a sand filter. This is a rather slow reaction and pilot tests have to be carried out in many cases for this route to be followed. Alternatives to this process are strongly acidic cation exchange and reverse osmosis.

#### 9.3.3 Particle filtration

Particle filters are used to remove suspended solids. These solids either originate from pipelines or have been created by the previous oxidation process or by a flocculation or precipitation process (e.g. lime softening). The most common filter is the sand filter in which different grades of sand and gravel are layered within a mild steel-coated vessel.

It might also be necessary to install a precipitation reactor prior to filtration, if for instance iron levels are very high. A flocculant, in most cases PAC (Poly-Aluminium-Chloride), is beneficial for the flocculation process. It might also be possible to use lime, as use of this compound both raises pH and serves as a crystallization point for flocs. It has been noted that chlorine has an inhibiting influence on floc formation. Figure 9.2 shows a sand filter plant.

Apart from sand filters, multilayer filters consisting of different grades of sand, gravel and anthracite are also used. Anthracite is a coal-based black material which allows in-depth filtration, so that particles are removed not only from the surface but also from within the bed. When anthracite is used, the removal capacity is higher and the backwash is less frequent. However, it must be ensured that all filtration devices can be backwashed with air. Sand filters are backwashed with air and water at the same time. Multilayer filters work separately, first with air, then water. They also facilitate the removal of H<sub>2</sub>S.

If arsenic is present, it can be removed in GEH (Granulated Ferric Hydroxide) filters. GEH is a filter material based on synthetic granular ferric hydroxide. It is an adsorbent with a high porosity and a large inner surface. The material is rather expensive and has to be replaced or regenerated when exhausted. It should not be used for particle filtration, therefore, as this would reduce its adsorption capacity.

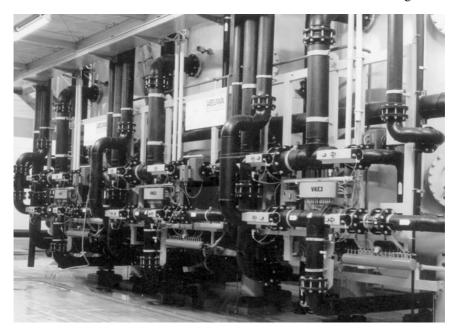


Fig. 9.2 Sand filter plant (Source: EUWA).

The alternative to classic sand and multilayer filters is ultrafiltration technology. Hollow fibre membranes made out of poly(ether)sulphone or cellulose triacetate are used in dead-end or crossflow filtration. The filtered water quality is quite good, but issues with wastewater and investment costs have so far prevented widespread use of this technology in breweries.

In many cases it is worth exploring the opportunity to recycle the backwash water from filtration. This will be described in more detail in Section 9.4.

#### 9.3.4 Activated carbon filters

Activated carbon filters are used for dechlorination, adsorption and H<sub>2</sub>S removal. Dechlorination is a very rapid process in which activated carbon causes free chlorine to be converted into chloride. The reaction happens within seconds so probably takes place in the top 10 cm of the bed. It has been reported that chlorine dioxide cannot be removed by activated carbon filters, but this is not the case. Using activated carbon filters is a safe and reliable method to dechlorinate water containing chlorine dioxide as well as water containing free chlorine.

To adsorb (and therefore remove) substances such as THM or odours and colours from water, the activated carbon filter acts as a chromatographic bed. The time taken to adsorb contaminants depends on the concentration and polarity of the components to be removed and the way they interact with each other. The contact time, though, is usually 10-20 minutes.

Recently, activated carbon plants equipped with steam-stripping devices have been constructed. The steam-stripping devices use high temperatures of 140°C to strip out volatile components from the carbon filters and therefore the lifespan of the carbon is extended up to five-fold. Whether or not a steamstripping device is in use, it is important in any case to construct the activated carbon filter plant in such a way that it can be sterilized properly with either hot water (min. 95°C) or steam (up to 140°C). The only material from which the plant can be made is stainless steel, the grade depending on the chloride content of the water. A strainer plate for a proper distribution of water and steam also needs to be in place and the strainer nozzles must be covered with gravel. Steam sterilization should happen at least once a week, or when microbiological conditions deteriorate. The corresponding flow diagram is shown in Fig. 9.3. If there are several carbon filters in use, they should be run in parallel and taken offline only for sterilization and/or backwashing, as continuous operation is the best method to prevent premature microbiological growth on the carbon.

In some cases also, organic scavengers in the form of polystyrene resins are used for adsorption. These can be regenerated, for example with caustic soda among other substances. Using organic scavengers, however, is a rather expensive method and is used only in special cases. Figure 9.4 shows an activated carbon filter plant installation.

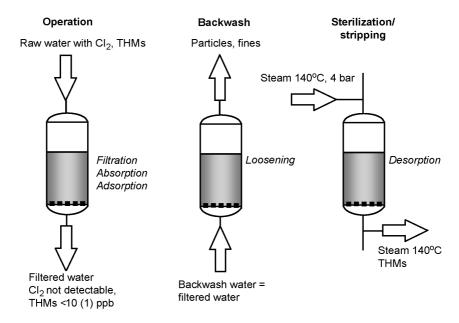


Fig. 9.3 Activated carbon filter – process steps (Source: EUWA).



**Fig. 9.4** Activated carbon filter plant (Source: EUWA).

#### 9.3.5 Lime precipitation

Lime precipitation is the oldest method commonly used for water treatment in breweries. Although some consider this method old-fashioned, it has not lost its appeal. It remains an attractive method even today if it is carried out properly. It is used for waters containing mainly carbonate hardness. By the addition of Ca(OH)<sub>2</sub>, either as saturated lime water in smaller plants or as lime milk in larger plants, most of the carbonate hardness is precipitated. The corresponding equation is as follows:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$
 (9.3)

Open lime softening (also called one-stage lime softening) and lime precipitation under pressure are two different lime precipitation processes used in breweries. In a one-stage lime softening plant, the reaction takes place in a cylindroconical tank, whereas in lime precipitation under pressure, CaCO<sub>3</sub> is precipitated at so-called reactor sand, through which water and lime Ca(OH)<sub>2</sub> are run. It is worth mentioning that iron and manganese are removed as well when carrying out one-stage lime softening, whereas when using the lime precipitation under pressure method, these components need to be treated beforehand.

It is important to take into account the ratio of magnesium to non-carbonate hardness for successful decarbonization. FeCl<sub>3</sub> will react with carbonate hardness and increase the non-carbonate hardness, thus influencing the ratio between

Two-stage lime softening plant, Morgenstern system, to reduce magnesium and calcium

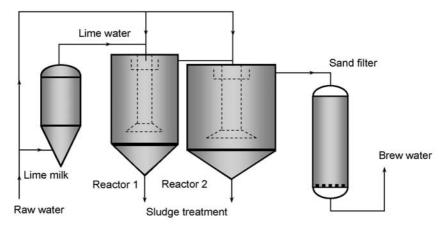


Fig. 9.5 Lime softening process steps.

Mg and non-carbonate hardness. If Mg(HCO<sub>3</sub>)<sub>2</sub> needs to be removed, it is necessary to use a two-stage lime softening plant with reactor and refiner following the Morgenstern system (Fig. 9.5). As can be seen from the following equation, the amount of Ca(OH)<sub>2</sub> doubles, as magnesium has to be precipitated as hydroxide and not as bicarbonate. Figure 9.5 shows a flow diagram of this process.

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$
 (9.4)

Open lime softening can also be used for the treatment of water containing humic acids, to increase the pH and to flocculate organic water components. The pH of the water is relatively high, but this is not a matter of great concern, since the water's buffer capacity is considerably reduced by lime softening, in some cases to a *m*-alkalinity of <25 ppm as CaCO<sub>3</sub>. This is usually <50 ppm as CaCO<sub>3</sub>.

After lime softening, the water always passes through a sand or multilayer filter for the removal of insoluble matter and further dealkalization at the sand surface. By adding a rinse water recycling system to recycle filtration water and by dewatering sludge or treating it in chamber filter presses, the percentage of water wasted can be reduced to <1%.

The operating costs of lime softening plants are very low and the systems are very robust. A disadvantage of this method is the large floor space required for a lime softening plant and the fact that automation is relatively costly. The limitations of the quality of the raw water to be treated also need to be considered.

There are several exciting new applications of lime softening plants. One of these combines a lime softening plant with a reverse osmosis plant, for example to remove nitrate. The quantity of wastewater is reduced using this technology to <5%. If lime softening plants are connected to Ca-addition systems, the water quality achieved improves considerably. Figure 9.6 shows a lime softening plant with 150 m³/h throughput.



Fig. 9.6 Lime softening plant (Source: EUWA).

## 9.3.6 Ion exchange

Ion exchange is a very suitable method of changing the composition of the water. It can be applied specifically and can be used to convert a wide range of substances.

## Weakly acidic cation exchanger

Following this method,  $Ca^{2+}$  and  $Mg^{2+}$  ions bound to  $HCO_3^-$  are removed (dealkalization). The advantages of this method are its high capacity and the fact that it uses regeneration chemicals very efficiently. Regeneration is carried out with HCl or  $H_2SO_4$  in counter-current, and backwash in the vessel is possible. A disadvantage is that it is not possible to monitor this process satisfactorily. There is also a danger of over- or under-regeneration.

## Strongly acidic cation exchanger

Following this method, all cations are exchanged with  $H^+$  ions (using HCl or  $H_2SO_4$  for regeneration) or with  $Na^+$  ions (using NaCl for regeneration). When

an acid is used for regeneration, one advantage is the possibility of monitoring by differential conductivity. Conductivity is measured before and after the safety zone and transmitted to an instrument where the differential conductivity is displayed. Hence the exact exhaustion point can be determined. The regeneration should be effected in counter-current, in order to achieve a constant high water quality combined with a low chemical requirement and low wastewater production. This can be achieved with a special design which integrates quality monitoring with differential conductivity measuring. This design is also the only counter-current system which enables backwash within the vessel, as it does not require an upper nozzle plate.

If the water contains carbonate- and non-carbonate hardness, using a socalled layer bed exchanger is the optimal solution. When a layer bed exchanger is used, strongly and weakly acid exchange material is layered in a vessel. This system therefore combines the advantages of weakly and strongly acidic exchangers. Figure 9.7 shows, from left to right, a weak exchanger, a layer bed exchanger and a strong exchanger

By regenerating strongly acidic cation exchangers with NaCl in countercurrent, savings of >40% compared to conventional systems are achievable.

## Weakly basic anion exchanger

Following this method, anions of strong acids are removed and replaced with OH<sup>-</sup> ions. A strongly acidic cation exchanger always has to be installed in front of a weakly basic anion exchanger, and in that combination demineralization can be achieved. The advantages of this method are its high capacity and efficient use of chemicals. Monitoring is by conductivity measurement, and regeneration uses NaOH.

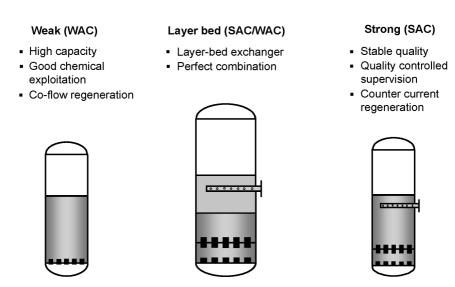


Fig. 9.7 Ion exchange principles – weak, layer bed and strong exchangers.

## Strongly basic anion exchanger

Anions from strong as well as weak acids (especially silica and carbonic acid) are removed by this exchanger, which is regenerated with NaOH. The regeneration is effected in counter-current, and is similar to the regeneration of strongly acidic cation exchangers. For the NaCl regeneration the ion exchange is conducted in a  $Cl^-$  cycle. In addition, specific nitrate exchangers are available which remove nitrate. These can be combined with strongly acidic cation exchangers, using the anion of the acid for regeneration. When using HCl and  $H_2SO_4$  for regeneration, the  $Cl/SO_4$  ratio can be adjusted in the treated water.

In all ion exchange systems, calcium is usually added to neutralize the acidity. The calcium levels are always adjusted back to the required level.  $\rm CO_2$  removal is really only necessary if the corrosivity of the water is a problem for mild steel piping reservoirs and vessels. Only food-grade resin should be used in all brewery applications, except, of course, in the boiler house where non-food-grade resin can be used.

An ion exchanger installation can be seen in Fig. 9.8.



**Fig. 9.8** Ion exchange plant (Source: EUWA).

## 9.3.7 Membrane technology

Apart from the ultrafiltration process described earlier, nanofiltration and especially RO (reverse osmosis) have gained a significant market share in water treatment. RO is the best available filtration method. In reverse osmosis, in order to overcome the osmotic pressure of an aqueous solution, a pressure is applied to a semi-permeable membrane. Therefore, most of the molecules and ions will be rejected, whereas pure water can pass through the membrane. The saline solution is called the concentrate, whereas the demineralized portion is called the permeate. The ratio between permeate and feed water is called the recovery rate. The higher this value is, the less wastewater is produced.

The efficiency of the membranes can be affected by fouling or scaling. Fouling is the term used to describe the presence of organic deposits on the membrane, which can be at least partly removed from the membrane surface by a suitable cleaning regime. In this context the Silt Density Index (SDI) serves as an indicator. Scaling is the precipitation of inorganic salts at the membrane surface. A suitable selection of cleaning agents can be used to reverse this effect if they are applied before too much scale has formed.

For the operation of a reverse osmosis plant to be trouble-free, it is essential to pretreat the water sufficiently. The water should be free of particles, which can be guaranteed by installing polishing filters, and the amount of organic substances should also not be too high. Furthermore – due to the organic polymer structure of membranes – oxidants (e.g.  $\text{Cl}_2$  or  $\text{O}_3$ ) must not be present, as their presence can lead to irreversible damage of the membrane. Therefore, in most cases at least sand filters and often also activated carbon filters are used to pretreat the water.

In order to minimize the wastewater, the recovery rate should be as high as possible. To achieve this, anti-scalants or scale inhibitors are used. They prevent crystallization although the solubility limit of salts has been exceeded so that a remarkable reduction in operating costs can be achieved. Furthermore, adding mineral acid or carbon dioxide can lead to a better recovery rate. However, the recovery rate always depends on the quality of the raw water available. Usually the recovery rate is 80–90%, but in some cases it can be increased up to 95%. Figure 9.9 is a flow diagram of the reverse osmosis process.

Technological developments have also reduced the necessary pressure to less than 13 bar, or in some cases even to less than 10 bar. Nanofiltration requires even less pressure. Since more porous membranes are used in nanofiltration, however, ions, such as smaller monovalent ions, e.g. sodium and chloride, can pass through the membrane and it is therefore not ideally suited for brewing applications. Nanofiltration can theoretically be used to soften water, but the technology is still expensive compared to an ion exchange system with a strongly acidic cation exchanger regenerated with sodium chloride. For special cases such as ion exchange wastewater recycling, nanofiltration can be used successfully.

Reverse osmosis plants should also be built in conjunction with calcium addition systems, as the mineral content of the water produced is minimal. The

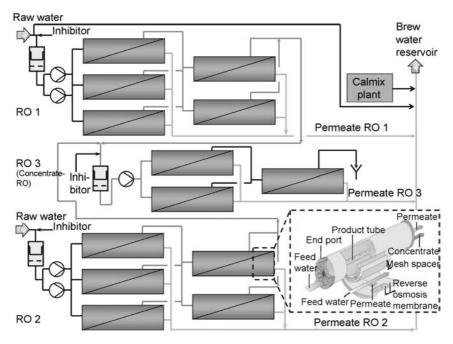


Fig. 9.9 Reverse osmosis flow diagram.

advantage of RO is that from very fluctuating raw water conditions a very stable so-called permeate is produced, therefore variability in water quality from the beer production process is no longer such an issue.

Figure 9.10 shows a reverse osmosis plant with 80 m<sup>3</sup>/h permeate capacity.



Fig. 9.10 Reverse osmosis plant (Source: EUWA).

#### 9.3.8 Calcium blending

Various forms of calcium blending are possible. The presence of calcium ions is a decisive factor in the brewing process. They are required both for mashing and sparging to influence the pH via the phosphate buffer of the mash and also for precipitation of oxalates to avoid gushing. There are different ways in which calcium can be added.

If the water comes from an ion exchanger, for example a strongly acidic cation exchanger, then clear lime water produced from lime powder or lime milk in a lime saturator is used to neutralize mineral acids. CaCl<sub>2</sub> and CaSO<sub>4</sub> are formed according to the following equations:

$$2HC1 + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O \tag{9.5}$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$$

$$(9.6)$$

In a second step, the carbonate hardness can be adjusted to the desired value, though a surplus of CO<sub>2</sub> remains in the water:

$$3CO_2 + Ca(OH)_2 \rightarrow Ca(HCO_3)_2 + CO_2 \tag{9.7}$$

If free  $CO_2$  cannot be tolerated due to its corrosive nature, the system can be combined with a  $CO_2$  trickler. For this purpose the pH has to be adjusted to >8.2 (+p value).

If the mineral acidic salinity of the water is not sufficient, if the water is very soft or if only demineralized water (from reverse osmosis or ion exchange) is available, the addition of hydrochloric acid and/or sulphuric acid is recommended to solve the problem and ensure that enough calcium is produced. This can be done both before and after the lime saturation process.

It is also possible to mix lime milk, hydrochloric acid and/or sulphuric acid with the main brew water flow. Lime milk is added first, then HCl and/or H<sub>2</sub>SO<sub>4</sub>, before the mixture goes through the reactor and is then mixed with the main brew water flow. When this method is followed, CaCl<sub>2</sub> and CaSO<sub>4</sub> can be added separately. This water can then be used directly for mashing and sparging or can be added into the wort. Figure 9.11 is a flow diagram demonstrating this process. The advantage of this process compared to conventional CaCl<sub>2</sub> and CaSO<sub>4</sub> dosing is its complete automation. No manual interference is required, which helps to ensure that the water quality is stable and reproducible.

Because of the positive influence of this process on the pH of the water, less lactic or mineral acid is then required to be added in the brewhouse. Furthermore, it is worth noting that because of its low solubility CaSO<sub>4</sub> cannot be dosed in a liquid and completely dissolved form except when following the system described above. This, of course, also influences the effectiveness and economics of the application of CaSO<sub>4</sub>. This novel process opens up new possibilities of tailoring the water quality according to the requirement of specific beer brands and beer types. Since nowadays it is the norm rather than the exception to produce a wide range of products with different characteristics, variable and flexible treatment processes that meet these demands are indispensable. Figure 9.12 shows a picture of such a system for a 500,000 hl/year brewery.

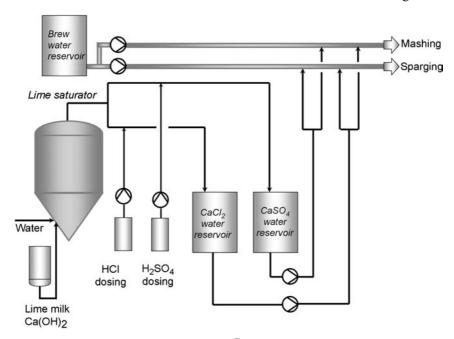


Fig. 9.11 Calmix<sup>®</sup> flow diagram.

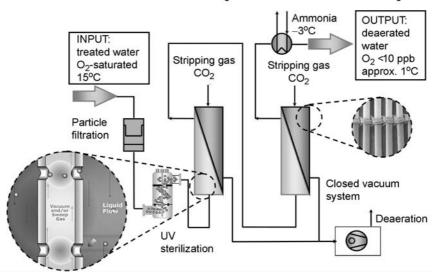


Fig. 9.12 Calmix® plant (Source: EUWA).

#### 9.3.9 Deaeration

Deaeration of water is necessary for various applications. Especially when using a high-gravity brewing process, a very low oxygen level is required. Originally deaeration was achieved by applying a vacuum and using a stripping gas ( $CO_2$ ). The residual oxygen levels achievable with this method are no longer sufficient for today's requirements (<10 ppb). The hot deaeration process is a different method which uses a raised operating temperature. The process design features are the same as described above, but the  $O_2$  levels achieved are lower. This process, though, has a much higher energy requirement. A further possibility is a packed bed column, which can be used either at ambient temperatures with a higher residual  $O_2$  content or hot with a lower residual  $O_2$  level. The risk of precipitation increases if the hot process is used.

A membrane deaeration system is another approach used. At its core are hollow fibre membrane modules, which have a large surface area. The membranes are semi-permeable, i.e. permeable to gas but not to water. By using a stripping gas ( $CO_2$  or  $N_2$ ) and applying a vacuum, nearly complete oxygen removal at ambient temperatures can be achieved. The water flows upstream, whereas the stripping gas is led downstream through the membrane by the vacuum pump. Due to the modular setup, the capacity of a membrane deaeration system can easily be expanded. The membranes can be used in parallel and/or in series. It is essential to integrate a disinfection as well as a filtration unit into the membrane treatment system. The deaerated water will also need to be cooled down to <1°C. Compared to other systems, the membrane system offers lower operating costs, precipitation is avoided and the plant size is compact. Figure



EROX -- deaeration: flowsheet of two-stage membrane deaeration with cooling

Fig. 9.13 Membrane deaeration system flow diagram.



Fig. 9.14 Erox deaeration plant (Source: EUWA).

9.13 shows a flow diagram of this process and a picture of the plant can be found in Fig. 9.14.

There has also been debate on whether to use deaerated water for mashing and sparging as well, processes in which deaerated water is not usually used. This possibility has not yet been explored fully and therefore the benefits compared to the costs involved have not been evaluated on a full-scale basis.

## 9.4 Recycling

As water can be a scarce commodity, recycling is becoming more and more important. To treat the whole effluent stream of a brewery so that it can be recycled as potable water requires major efforts and the efficiency of the process will inevitably be low. It is more sensible to focus on specific areas where the contents of the water are clearly defined and can be tackled more specifically. However, further developments in membrane technology will certainly widen recycling possibilities.

One area that produces relatively large amounts of wastewater is the water treatment plant itself. Therefore it is worth considering recycling backwash water from particle filtration systems. Some recycling systems are shown in Fig. 9.15. It is also worth considering dewatering the sludge from lime softening systems. In ion exchange systems nanofiltration of the regenerant effluent from

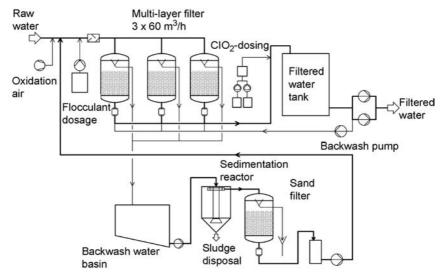


Fig. 9.15 Backwash water recycling.

weakly acidic cation exchangers can be worthwhile. Recycling systems in bottle washers are already widely used, but there is not always a balance between the cost of the extra equipment required and the savings achieved.

There have been attempts at recycling some of the wastewater created during reverse osmosis. To do this, the efficiency of RO is kept artificially low, and then the concentrate stream can be used in other applications in the brewery. This, however, requires very balanced, integrated water reticulation within the brewery and large reservoirs to buffer water fluctuations. Therefore this system has not been adopted in many breweries.

#### 9.5 Future trends

Brewery water treatment systems of the future will be very flexible, allowing breweries to tailor-make their water for different products. At the same time, these future water treatment systems will aim to achieve optimum efficiency in terms of operating cost and especially wastewater produced. The advances in analysis techniques will inevitably lead to further challenges, as it will be possible to detect certain components that are not an issue today but will then need to be removed. It will also continue to be vital for brewers to pay attention to their water supply to avoid surprising and unexpected quality defects in the finished product.

## 9.6 Sources of further information

WZW Forschungszentrum Weihenstephan für Brau- und Lebensmittelqualität; Alte Akademie 3, D-85354 Weihenstephan, contact: Dr Karl Glas (k.glas@wzw.tum.de).

- IBD The Institute of Brewing & Distilling, 33 Clarges Street, London W1J 7EE (www.ibd.org.uk).
- VLB Berlin Research and Teaching Institute for Brewing in Berlin, Seestrasse 13, D-13353 Berlin, contact: Dr Alfons Ahrens (ahrens@ylb-berlin.org).
- MBAA Master Brewers' Association of the Americas, 3340 Pilot Knob Road, St Paul, MN 55121-2097 (www.mbaa.com).
- EUWA H.H. Eumann GmbH Water Treatment Plants, Daimlerstrasse 2-10, D-71116 Gaertringen (web: www.euwa.com, e-mail: info@euwa.com).

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