# INDUSTRIAL WATER TREATMENT

## INTRODUCTION

Surprisingly, chemically pure water does not occur in the natural environment. The liquid that we know from our everyday lives under the term ”water’’ should be defined as a homogeneous solution containing a variety of organic and inorganic compounds such as salts, acids, and gases. In nature, water plays the role of a universal solvent that through various processes such as erosion of sedimentary rocks, seepage, and surface runoff from the soil, forms solutions (mainly of salts). The liquid with different concentrations of chemical compounds, e.g. freshwater salinity does not exceed $0.5\ g \times dm^{-3}$, and the salinity of seawater is much higher e.g. $6.0\ g \times dm^{-3}$ for the Atlantic Ocean.

### Chemical composition and properties of the freshwater

One of the most important water parameters is **pH** and the freshwater has a value of pH between 6.5 and 8.5.

The second significant parameter of freshwater for industrial use is **water hardness**, which can be simply defined as the amount of dissolved polyvalent metallic ions, mainly calcium and magnesium although iron, aluminum, and manganese salts can also contribute. In water processing, we can distinguish two types of water hardness: **permanent hardness** and **temporary (carbonate) hardness**. Temporary hardness is mainly caused by the presence of dissolved calcium and magnesium bicarbonates: $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ and can be easily eliminated by the boiling process of the water. Simultaneously, the permanent hardness of water is caused by the other dissoluble salts of polyvalent metals, mainly sulfates and chlorides.

Water hardness can be measured and is usually expressed in the total molar concentration of calcium and magnesium ions within the sample. The unit of water hardness is typically **$1\ mEq \times dm^{-3}$**, which means the number of milliequivalents per liter of solution. However, other historical units can be still in use depending on the country/region, e.g. German degrees (°n) defined with the following equation:

$$1°n = 10\ mg_{CaO} \times dm^{-3} \tag{1}$$

Detailed chemical composition of the water is always strongly dependent upon its source (geological and biological conditions within the water intake), however, besides the calcium and magnesium bicarbonates a few other chemical compounds can be often found in water:

- **Carbon dioxide** can be found in water in the free state as a dissolved gas from the atmosphere or in the bounded form in compounds such as bicarbonates and carbonates.
- **Iron** (especially iron (II)) is generally present in the water as bicarbonate or sulfate. Iron (II) cations dissolved in water can cause uncontrolled growth of the chemotrophic iron−oxidizing bacteria which produce insoluble reddish-brown biofilm and its accretion on the pipeline walls.
- **Chlorides and sulfates** are minerals that occur naturally in the surface and ground waters. High concentration of sulfates can lead to concrete corrosion (danger for hydraulic structures e.g. dams) and calcium sulfates also tends to form mineral deposits of **limescale.**

## Boiler feedwater problems

The main problem caused by the carbonate hardness in water is the formation of mineral deposits. This solid product is a result of processes of temperature conversion of dissoluble magnesium and calcium bicarbonates into insoluble carbonates or hydroxides that coat the surfaces of hot-water systems, clogging pipes and reducing heating efficiency. This phenomenon may be especially damaging in boiler feedwater, and the **boiler limescale** formation process is illustrated by the following reactions:

$$\mathrm{Ca(HCO_3)_2} \rightarrow \mathrm{CaCO_3} \downarrow + \mathrm{CO_2} + \mathrm{H_2O} \tag{2}$$

And

$$\mathrm{Mg(HCO_3)_2} \rightarrow \mathrm{MgCO_3} + \mathrm{CO_2} + \mathrm{H_2O} \tag{3}$$

Please, note that the magnesium carbonate that arises in reaction 3 is further converted to the insoluble magnesium hydroxide, according to the following equation:

$$\mathrm{MgCO_3} + \mathrm{H_2O} \rightarrow \mathrm{Mg(OH)_2} \downarrow + \mathrm{CO_2} \tag{4}$$

Depending on the chemical composition of the mineral deposit within the boiler or other heat exchange devices we can distinguish three types of limescale: **carbonate** (caused by calcium and magnesium bicarbonates), **sulfate** (caused by calcium sulfates), and **silicate** (of silica and calcium or magnesium silicates origin). Regardless of the type of limestone its deposition on the boiler walls reduces thermal conductivity within the device and disturbs the flow of the water which results in reduced heat exchange efficiency and in extreme cases may even cause critical failure. Therefore, for the heat exchange devices, feedwater should be previously processed to eliminate water hardness. Water softening may be achieved by various techniques which will be elaborated in the next section.

Another significant problem concerning feedwater for industrial use is its predisposition to form foam. Foaming is often caused by the high concentration of organic compounds, alkali, and overall salinity of the water. Foam within a heat exchange device (especially a steam turbine) causes a risk of steam contamination, reduces heat exchange efficiency, causes mineral deposits on turbine blades, and disturbs the steam flow within the power plant. Foaming can be prevented by removing organic compounds from the water (e.g. extraction) and maintaining the acceptable pH value of the feedwater.

Feedwater highly saturated with gases such as carbon dioxide and oxygen is an accelerator of electrochemical corrosion. To reduce the risk of uncontrolled decay of the steel components within the installation, additional pretreatment of the feedwater such as decarbonization, deoxygenation, and pH adjustment should be applied.

## Boiler feedwater treatment

The first stage of water treatment should be always proper filtration. Boiler feedwater is no exception therefore its pretreatment consists of two main steps. First is the filtration of the organic and inorganic residues that are usually separated gravitationally in the settling tanks (large and heavy particles) and later by the sorption on a variety of filters e.g. pressure filter. The second step of water pretreatment is the removal of organic and mineral oils which can create organic-metallic compounds that can accelerate electrochemical corrosion of the hot-water pipelines. Oils are usually separated on the active carbon filters.

The third stage of water treatment should be water softening and this may be achieved by various techniques. On a large scale, the lime-soda process is preferred. Calcium may be removed from water efficiently also by the addition of sodium hydroxide or orthophosphate. Possible alternatives are the use of thermal methods, ion-exchange processes, or distillation.

- **Lime-soda process**; Hard water is treated with calcium hydroxide $Ca(OH)_2$ which causes precipitation of calcium/magnesium carbonates, other residual salts are removed afterward by the addition of sodium carbonate $Na_2CO_3$. In this process following reactions occur.
  First step for calcium bicarbonate:

$$\mathrm{Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O} \quad (5)$$

Similarly first step for magnesium salts:

$$\mathrm{Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow MgCO_3 + CaCO_3 \downarrow + H_2O} \quad (6)$$

Since magnesium carbonate is relatively well soluble in water it continues to react with an excess of the calcium hydroxide:

$$\mathrm{MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow} \quad (7)$$

The second step of this process is realized by adding sodium carbonate as the source of carbonate ions therefore it can be described by the overall ionic reactions:

$$\mathrm{Ca^{+2} + CO_3^{2-} \rightarrow CaCO_3 \downarrow} \quad (8)$$

$$\mathrm{Mg^{+2} + CO_3^{2-} \rightarrow MgCO_3} \quad (9)$$

- **Sodium hydroxide process**; In the water softening by the addition of NaOH the following reactions may occur:

$$\mathrm{CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O} \quad (10)$$

$$\mathrm{Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3 \downarrow + Na_2CO_3 + 2H_2O} \quad (11)$$

$$\mathrm{Mg(HCO_3)_2 + 4NaOH \rightarrow Mg(OH)_2 \downarrow + 2Na_2CO_3 + 2H_2O} \quad (12)$$

$$\mathrm{MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 \downarrow + Na_2CO_3} \quad (13)$$

- **Orthophosphate salts process**; in the water softening by addition of $Na_3PO_4$ the following reactions may occur.

  For calcium salts:

$$\mathrm{3Ca(HCO_3)_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_3)_2 \downarrow + 6NaHCO_3} \quad (14)$$

$$\mathrm{3CaSO_4 + 2Na_3PO_4 \rightarrow Ca_3(PO_3)_2 \downarrow + 3Na_2SO_4} \quad (15)$$

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_3)_2\downarrow + 6NaCl \qquad (16)$$

Analogous reactions for magnesium salts also occur.

- **Thermal treatment**; Water softening may be carried out by simply boiling the feedwater. In this process only calcium and magnesium bicarbonate salts are removed (reactions 2-4).
- **The ion exchange process** could be defined as the reversible transfer of ions between an aqueous solution and a solid material capable of bonding ions. This technology is an effective and economical technique widely used for industrial and domestic water treatment. Several materials have ion-exchanging properties e.g. zeolites (of natural origin), however, in modern ion-exchange technology the synthetic **ion-exchange resins** composed of organic polymers with attached functional groups are dominant. These compounds are insoluble in water and the functional groups allow them to selectively exchange ions. Ion-exchange resins depending on their ability to exchange anions or cations may be divided into two main groups: cation-exchange resins (**cation exchangers**) with acidic properties and anion-exchange resins (**anion exchangers**) featuring properties of a chemical base.

  Cation-exchange resins are typically composed of acidic functional groups or their salts e.g. $-SO_3H$, $-COOH$, $-OH$, and anion-exchange resins contain alkaline functional groups or their salts e.g. $-NH_3^+OH^-$, $= NH_2^+OH^-$, $\equiv NH^+OH^-$.

  Macromolecules of the ion-exchange resins are usually schematically presented as follows: R—$SO_3H$, R—COOH, R—OH, R—$NH_3OH$, etc., where R represents the polymer macromolecule that hosts functional groups.

  Ion-exchange softening of the water is possible thanks to the electrolytic dissociation of the functional groups (equations 17 and 18) after the ion-exchange resin is immersed in the solution.

  e.g. dissociation of the cation-exchanger

$$R - SO_3H \rightleftarrows R - SO_3^- + H^+ \qquad (17)$$

  e.g. dissociation of the anion-exchanger

$$R = NH_2^+OH^- \rightleftarrows R = NH_2^+ + H^+ \qquad (18)$$

  For example, water containing $Ca^{2+}$ and $SO_4^{2-}$ ions after passing through the column with an anion exchanger and cation exchanger, respectively, will be completely free of calcium and sulfate (VI) ions, and the $H^+$ and $OH^-$ ions released during the process will form a water molecule.

Water after the softening process is often subjected to other treatments (depending on the final application). One of the most frequently implemented treatments is **desilication** which removes dissolved silica derivatives from water by precipitating it with calcium hydroxide, according to the following reaction:

$$SiO_3^{2-} + Ca(OH)_2 \rightarrow CaSiO_3 + 2OH^- \qquad (19)$$

## OBJECTIVE OF THE TASK

This experiment aims to determine the effectiveness of various methods of softening water from public supply systems (by boiling the water, distillation, and ion exchange process).

## APPARATUS

- Burette with stand.
- Column with anion exchanger.
- Column with cation exchanger.
- Electric kettle.

## LAB GLASS

- Beaker 100 ml — 1 pcs.
- Beaker 75 ml — 1 pcs.
- Erlenmeyer flask **(only for titration)** 125 ml — 3 pcs.
- Laboratory spatula — 1 pcs.
- Measuring cylinder 10 ml — 1 pcs.
- Pipette 50 ml — 1 pcs.
- Pipette 10 ml — 1 pcs.
- Polyethylene funnel — 1 pcs.

## CHEMICALS

- Ammonium buffer solution (pH = 10).
- Solution of EDTA — 0.05 mol × dm$^{-3}$ (0.1 Eq × dm$^{-3}$).
- Eriochrome Black T (powder) mixed with NaCl. Titration indicator

## EXPERIMENT PROCEDURES

### Sample preparation

Four following water samples should be prepared for analysis:

a) 200 ml of mains water directly from the public supply system (reference sample).

b) 200 ml of boiled water (thermal method). Water should be boiled 2 times in the electric kettle with an open cover.

**WARNING! Please, beware of the hot steam!**

c) 200 ml of water after the ion-exchange process. Raw water from the public supply system should be first filtered through the column with an anion exchanger and next through the column with a cation exchanger.

**WARNING! The water level in both columns should be ALWAYS higher than the level of the solid ion exchanger!**

d) 200 ml of distilled water from the laboratory supplies.

### Analysis

Using a pipette introduce 50 ml of tested water into the Erlenmeyer flask. Then add 5 ml of ammonia buffer (use measuring cylinder and funnel) and a pinch of Eriochrome Black T powder (use spatula). The prepared analysis should be then titrated with 0.05 mol × $dm^{-3}$ (0.1 Eq × $dm^{-3}$) solution of EDTA (while stirring) till the initial purple (mauve) color of the solution turns into a blue at the endpoint.

**Each water sample should be analyzed three times. Take the average as a result.**

## PREPARATION OF RESULTS

Calculate the water hardness of each sample using the titration results and compare the effectiveness of applied water-softening methods.

### Complexometric titration mechanism

In the water hardness determination, EDTA is used as the titrant that complexes $Ca^{2+}$ and $Mg^{2+}$ ions. Although neither the EDTA titrant nor its calcium and magnesium complexes are colored, the endpoint of the titration can be visually detected by adding a metallochromic indicator to the water sample. A color change occurs when the indicator goes from its metal ion-bound form to the unbound form. This color change signals the endpoint, as it takes place when the EDTA, after complexing all of the unbound $Ca^{2+}$ and $Mg^{2+}$ ions, removes the $Mg^{2+}$ ion bound to the indicator. This removal is only possible because the EDTA complexes $Mg^{2+}$ more strongly than the indicator.

### Calculations

The concentration of the $Ca^{2+}$ and $Mg^{2+}$ ions in the sample can be calculated knowing that at the end of the titration process, each of the $Ca^{2+}$ or $Mg^{2+}$ ions was complexed by one particle of the EDTA. Therefore:

$$\mathrm{N_{H_2O}} = \frac{\mathrm{N_{EDTA}} \times \mathrm{V_{EDTA}} \times 1000}{50} = 20 \times \mathrm{N_{EDTA}} \times \mathrm{V_{EDTA}} \tag{20}$$

Where:

$\mathrm{N_{H_2O}}$ — equivalent concentration of ions within the solution (water hardness) / mEq × $dm^{-3}$.
$\mathrm{N_{EDTA}}$ — equivalent concentration of the EDTA solution / Eq × $dm^{-3}$.
$\mathrm{V_{EDTA}}$ — volume of the EDTA solution used titration of the sample /ml.

Poznan, 08.09.2023

Template of the table and draft of the study

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| ……………………………..<br>*Wydział*<br>……………………………….<br>*Kierunek*<br>*Studia stacjonarne/niestacjonarne* | ……………………………………………….<br>*Imię i Nazwisko studenta* | …………………………………...<br>*Data wykonywania ćwiczenia:* |
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