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Cooling water conditioning in the future

Softening or desalination of make-up water for open cooling systems

TKI-Water technology project (P)

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Softening or desalination of the make-up water for cooling systems

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Clients

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Evides Industriewater, Pidpa

TKI Watertechnology program

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Summary

Introduction

Cooling systems dissipate excess low temperature heat from industrial processes to the environment and are therefore directly linked to primary industrial processes. Failure of cooling systems is undesirable. For this reason the industry (in general) puts a significant amount of effort in the optimal conditioning of cooling water. A good conditioning method simultaneously prevents corrosion, scaling and (microbiological) fouling of the cooling system. Classical conditioning programs based on the addition of a mixture of different chemicals - more or less tailored to the specific circumstances - to the make-up water are common practice. Such programs, however, may lead to high operational costs and a substantial impact of the cooling tower blowdown on the environment.

This desk study focusses on a change in paradigm from the classical "curative conditioning" to "preventive conditioning". The feasibility of alternative cooling water conditioning concerning fully or partially softened or desalinated make-up water was studied with regard to reduction of water, energy, chemicals use and costs. The feasibility studied the effects of alternative conditioning using the data from two existing industrial cooling systems. A spreadsheet tool was created to calculate operational effects and costs.

Project setup and results

Based on different criteria, of which the limited water loss of the unit process was the most important, the following combinations of technologies were selected for full or partial softening of make-up water of cooling systems:

- Scenario 1: Cation ion exchange (CIEX) – Anion ion exchange (AIEX)
- Scenario 2: Pellet softening – rapid sand filtration – CIEX
- Scenario 3: Pellet softening – rapid sand filtration – CIEX – AIEX

AIEX is introduced in scenario's 1 and 3 as a scavenger to remove nearly all organic material, which will have a beneficial effect on the microbiological growth in the cooling system.

Next a tool, Calculation Sheet Cooling Water (CaShCoW), was developed to determine the techno-economic feasibility of the proposed make-up water treatment scenarios in combination with an increase in the number of cycles of concentration for open recirculating cooling systems in comparison with the existing situation. The major aims of the tool are to calculate (1) the effect of the additional treatment on the make-up water quality and (2) the increase of cycles of concentration on the overall composition and scaling tendency of the blowdown. To give an indication about the scaling tendency the Langelier saturation index, the Puckorius Scaling Index and the Larson-Skold index are calculated in the tool. Another important part of the tool is to calculate the Capex and Opex of the alternative scenario's and compare them with the Opex of the existing situation. The most important restriction of the model is that it will give no indication of the actual corrosiveness or biofouling tendency of the water in the cooling system. Therefore in this study the calculated water composition was used separately to check corrosiveness of the water with PHREEQC-software.

The tool was applied using the data of two different cooling systems of the industrial partners involved in the project. One of the systems (SABIC-case) already has a high number of cycles of 9 while for the other system (Tata-case) this number is substantially lower (2.4).

For the SABIC-case all three alternative scenarios do not offer an economically beneficial alternative compared to the current situation. However, as regulations regarding, e.g. zinc discharge may change and limit the use of the current chemical conditioning program, scenario 1 may be a good alternative.

For the Tata-case an increase of the number of cycles from 2.4 to 5 results in a decrease in relative costs for all three scenarios. The calculations show that pellet softening leads to high depreciation and maintenance costs due to the high investment costs of the technology. The different indices give an indication that water is considered to be approximately at saturation equilibrium with calcium carbonate and therefore not indicating any scaling or corrosion tendency towards mild steel.

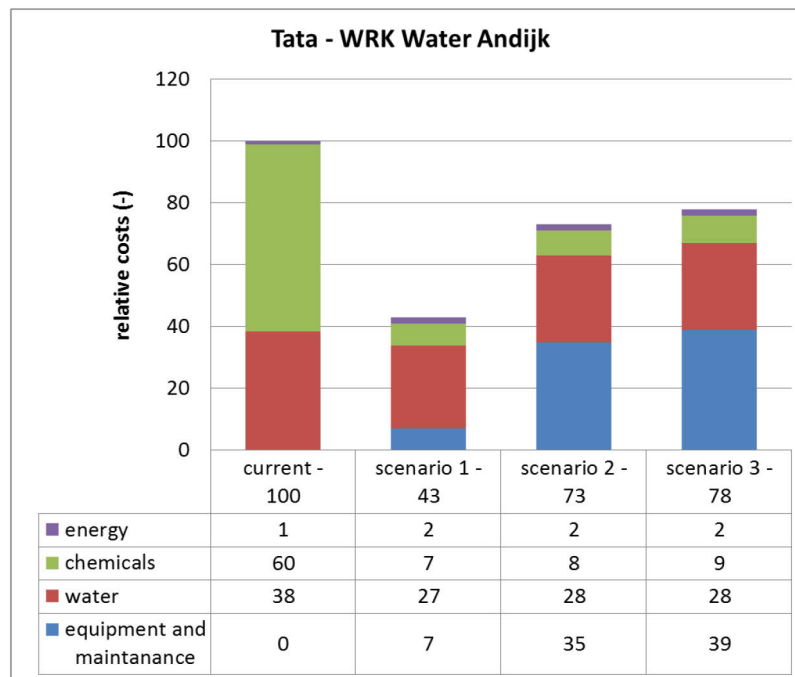


FIGURE S1: COSTS OF ALTERNATIVE SCENARIOS RELATIVE TO CURRENT SITUATION FOR TATA-CASUS USING WRK WATER FROM ANDIJK.

Conclusions

Model calculations in this study show that softening of make-up water for open cooling towers can lead to a reduction of water use and use of chemicals, as shown in the Tata case study. This is caused by the possibility to maintain a higher number of concentration cycles in the system and a phasing-out of traditional conditioning with proprietary chemicals. Complete softening is the preferred choice. Partial softening isn't realistic to prevent scale conditions later in the circulating cooling water.

Cooling water conditioning with complete softening of make-up water means a shift from complex conditioning chemicals to a conditioning system with only basic (bulk)chemicals such as sodium chloride, sodium hydroxide and sodium carbonate. In general this means that the environmental impact of cooling water blowdown will be strongly reduced. Furthermore this will lead to cost reductions on chemical consumption.

Model calculations in this study also show that especially owners of cooling systems with rather low numbers of cycles (< 5) and high costs for conditioning chemicals could have

benefits from an investment in partially softening of the make-up water. Local conditions with regard to water availability and water costs as well as energy costs will have substantial impact on the economic feasibility. The calculation tool can manage these specific local conditions.

Of the three scenarios for partial softening studied, the combination of CIEX/AIEX should be considered as most favourable due to the lowest operational costs. This is mainly caused by the relatively high investment costs and subsequently high depreciation costs for the two scenario's using pellet softening.

Recommendations

When developing and designing future cooling systems the option of (partial) softening of the make-up water should be part of the considerations as it might be a cheaper, more environmental friendly option and it will make the owner independent of water treatment companies that have a market monopoly.

The effects of partial softening of make-up water on corrosion and microbiological growth may look promising but they have to be confirmed under practical conditions. To study both phenomena at the same time performing a cooling water pilot test according to NEN-ISO 16784-2 would be strongly recommended. This specific standard describes a method for preliminary evaluation of the performance of treatment programmes for open recirculating cooling systems. It is based primarily on laboratory testing but the heat exchanger testing facility can also be used for on-site evaluation.

After confirmation of the positive effects of (partial) softening of make-up water on all three phenomena that form the virtual triangle of cooling water conditioning, the awareness of industries and water companies to change towards a more realistic environmental friendly type of cooling water conditioning should be stirred up by redefining the BREF (dating from 2001) for cooling water conditioning.

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1 Introduction

1.1 Project motivation

Cooling systems dissipate excess heat from industrial processes to the environment and are therefore directly linked to primary industrial processes. Failure of cooling systems is undesirable. For this reason the industry (in general) puts a significant amount of effort in the optimal conditioning of cooling water. A good conditioning method simultaneously prevents corrosion, scaling and (microbiological) fouling of the cooling system. Classical conditioning programs based on the addition of a mixture of different chemicals - more or less tailored to the specific circumstances - to the make-up water are common practice. Such programs, however, are sometimes complicated and may lead to high operational costs and a substantial impact of the cooling tower blowdown on the environment.

As part of their Joint Research Program for the Industry (OPIW) KWR performed - in subsequent projects (OPIW 24, 48 and 72) - a number of studies on alternative techniques to traditional chemical cooling water treatment. Industrial participants of these projects were Tata Steel, DOW, DSM/Sitech, EdeA and Shell, all companies that have to deal with the conditioning of their cooling systems. The study resulted in an overview of sustainable technologies for cooling water conditioning.

One of the alternative methods considered was the selective removal of salts from the make-up water of cooling systems. This can be realized by (partial or complete) softening or desalination of the make-up water. A lower salt content gives rise to a higher number of possible cycles of concentration (CoC) and this will subsequently lower the water and chemical demand of the system. In theory, every additional CoC would lead to less blowdown and therefore significantly reduce water and chemical consumption. This especially holds if a current cooling tower is operated at a low number of cycles, approximately up to 5. When the cooling water concentration factor is already higher (CoC > 5), the potential for additional water savings is substantially lower.

In the final update of project OPIW72, the innovative idea arose to apply full (precipitation) softening to the make-up water in such a way that most of the calcium (down to < 1 mg.L⁻¹), magnesium and silica is removed. This, in fact, would represent a change in paradigm from the classical "curative conditioning" to "preventive conditioning". Make-up water free of hardness and silica makes advanced chemical cooling water conditioning unnecessary: scaling by carbonates and silicates is excluded and corrosion control is easier because in an open cooling tower, after precipitation softening, the pH of the circulating cooling water will stabilize at a value of 9 or higher. Moreover, under these specific conditions - with a small dose of a (oxidizing) disinfecting agent like peroxides or ozone - the microbiology in the system can be effectively controlled without formation of undesirable by-products such as halogenated hydrocarbons. "Comfort" cooling systems, which operate under much less severe conditions as industrial cooling systems, already apply this type of conditioning regime successfully in the field for decades.

It is the line of thinking of make-up water treatment rather than cooling water treatment that has been furthered as part of the project described in this report.

1.2 Project targets

The main goal of the present project is to make a comparison based upon carbon footprint and water use between the following three alternative forms of cooling water conditioning:

- Curative conditioning (traditional cooling water treatment)
- Preventive conditioning (full softening of make-up water)
- Partial desalination/softening of make-up water (intermediate form)

Secondary goal of the project is the development of a spreadsheet tool. With this tool, the environmental and economic impact of alternative forms of cooling water conditioning can be calculated for any existing local cooling system based on the fixed correlation between investment, water, chemicals and energy usage of softening and desalination equipment.

1.3 Project description

This project gives information about the feasibility of alternative cooling water conditioning concerning fully or partially softened or desalinated make-up water with regard to reduction of water, energy, use of chemicals and costs.

The feasibility study focusses on the effects of alternative conditioning using data from two existing industrial cooling systems. A spreadsheet tool is created to calculate operational effects and costs. Furthermore, expert knowledge of the project team is used to assess the effects of alternative conditioning methods e.g. on cooling tower maintenance, shut down, replacement of specific cooling system parts and lifespan.

The following research questions are addressed:

- Does full or partial softening or desalination of make-up water of cooling towers lead to a reduction of water and chemicals use and a reduction of the carbon footprint?
- If so, how can these reductions be quantified, and how does alternative conditioning expressed in capital and operational costs compare to traditional cooling water conditioning?
- Does realisation of alternative cooling water conditioning lead to specific demands for the equipment in practice?
- Does realisation of alternative cooling require any specific type of process control, monitoring and/or automation?
- As this is a desk study, what uncertainties remain that need to be tested under practical circumstances and/or addressed in a pilot scale or full scale situation?

2 Theoretical basis for alternative cooling

2.1 Open cooling systems

This study focusses on open recirculating cooling systems that are fed by fresh water sources such as (treated) surface water. Because of the open character of these systems the circulating cooling water is in equilibrium with the gases in the cooling air.

Since e.g. the carbon dioxide gas pressure of cooling air is more or less constant (= 38 Pa), the dissolved carbon dioxide level in the open cooling water in agreement with Henry's Law also remains constant, independent of the pH of the cooling water. The concentration of bicarbonate and carbonate ions, however, varies considerably with the pH and the solubility of cations like iron and calcium varies accordingly.

2.2 Conventional treatment of water in open cooling water towers

2.2.1 Introduction

Cooling water is used as transport medium for the surplus of heat with low calorific value generated in production processes. The water is passed through heat exchangers in order to extract heat from the process. The increase in temperature makes cooling water streams highly susceptible to changes in water chemistry, resulting in (bio)-fouling, corrosion and scaling. Eventually, if insufficiently controlled, this will lead to a loss of heat exchange capacity and reliability.

To prevent this loss of heat exchange capacity, cooling water should be 'treated' or 'conditioned'. In general, suspended solids, organics, hardness salts and microbiological growth on surfaces (biofilm formation) can be considered as being (potentially) problematic. Pre-treatment is commonly applied to remove suspended solids from the make-up water. Traditionally, it concerns either a static sand filtration unit and/or a conventional coagulation/flocculation process.

However, hardness salts, some organics, nutrients and bacteria will pass these pre-treatment steps. Because these components tend to accumulate in open recirculating systems, controlling their behaviour inside the cooling system is essential to prevent problems. Traditionally, cooling water conditioning by means of chemical addition has been practised. This entails the controlled shifting of chemical equilibria within the water and inhibiting microbiological growth, scale growth and corrosion. These simultaneous threats to cooling systems are often graphically represented in the form of a (warning) triangle (see Figure 1).

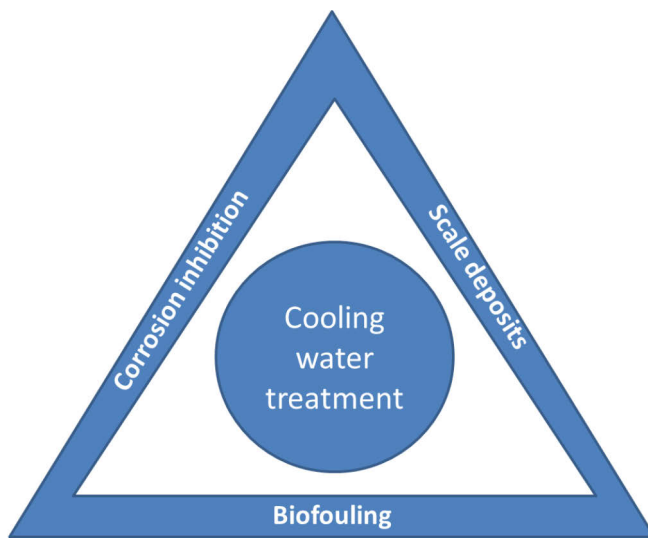


FIGURE 1: TRIANGLE OF COOLING WATER TREATMENT

2.2.2 Scaling prevention

To prevent scaling two principles are applied in conventional chemical conditioning. Hardness stabilisation hinders crystallization and further growth of carbonate crystals, due to the fact that certain stabilizers adsorb onto crystallization nuclei, thus blocking active crystallization sites and preventing the development of larger crystals. Sub-stoichiometric amounts of such stabilizers are required to disrupt the crystallization process, and their effect is commonly referred to as 'threshold inhibition'. Common chemicals used as stabilizers include phosphonates, poly-phosphates and organic poly-electrolytes.

In addition, dispersants (organic poly-electrolytes) can be applied to adsorb to particles and prevent their attachment to surfaces

2.2.3 Prevention of biofouling

In terms of biocides, both oxidizing and non-oxidizing chemicals are available. Oxidizing biocides oxidise the protein layer located on the exterior bacterial cell wall material, thus preventing further growth of micro-organisms. The most well-known and frequently used oxidizing chemical is chlorine in the form of sodium hypochlorite, also known as bleach. By contrast, non-oxidizing biocides target specific cell areas and interfere with vital processes such as cell duplication or cell metabolism. These types of biocides bind to microbial receptors and prevent the uptake of nutrients or denaturalise proteins or cytochromes. As a result, microbial inactivation occurs. However, as bacteria are highly adaptive, applying solely non-oxidizing chemicals will typically result in chemically resistant microbiology within a period of a few months

Chlorination gives rise to the formation of halogenated organic compounds, which form a threat to the environment. Therefore, the dosage of oxidizing biocides containing active chlorine is minimized. Thus, for instance, a treatment consisting of continuous low-level dosage of non-oxidizing biocides supported by periodic shock dosage of oxidizing biocides may be applied. The latter is specifically used to prevent the growth of biocide-resistant micro-organisms.

Micro-organisms will cluster and form biofilms which are more difficult to remove by ordinary biocides. A biodispersant is typically added in order to break down the biofilm and make the organisms more accessible for the biocide.

2.2.4 Corrosion prevention

Corrosion is the unwanted deterioration of metallic materials by oxidation of alloying elements over time. Although circulating cooling systems, including the distribution system, are preferably constructed from materials like glass fiber reinforced plastic pipes, heat exchangers are typically made from metal due to the desired heat transfer requirements. Depending on the specific choice of alloy and the composition of the water, corrosion can be a severe problem in cooling systems, either directly, because of leakages, or indirectly because of redeposition of corrosion products elsewhere in the system. There are several forms of corrosion, both uniform and non-uniform in nature. In most cases, a tailor-made conditioning approach is chosen to prevent corrosion depending on materials, water composition and temperature. Deposits from scaling of corrosion may also give rise to other corrosion phenomena due to the formation of a micro-environment underneath the deposits with a very different water composition (under-deposit corrosion). Deposits can also function as a substrate for micro-organisms causing microbiologically influenced corrosion (MIC).

To prevent corrosion so-called corrosion inhibitors are applied to prevent the dissolution of metals. These inhibitors function by interrupting the electrical circuit of the corrosion cell by forming a protective film by either an (oxidative) chemical reaction or adsorption. In the past chromate was also used to protect steel surfaces. When chromate was banned, a switch was made to other chemical programs based on the use of zinc and (poly)phosphate.

2.2.5 Scaling and corrosion indices

Several indices are used to predict the calcium carbonate scaling and corrosion potential of cooling water towards mild steel. Here only the Langelier Saturation Index, Puckorius Scaling Index and Larson-Skold index are described.

The Langelier Saturation Index or **LSI** is probably the most widely used indicator of (cooling) water scaling potential. It is purely an equilibrium index and deals only with the thermodynamic driving force for calcium carbonate scale formation and growth. It provides no indication of how much scale or calcium carbonate will actually precipitate to bring water to equilibrium. It does also not take into account any physico-chemical interactions between calcium and carbonate with other ions in the water, like reduction of 'available' calcium ion because of association with other anions like sulphate.

The LSI is calculated as follows:

$$\text{LSI} = \text{pH} - \text{pH}_s$$

in which pH is the measured water pH and pH_s is the pH at saturation of calcite or calcium carbonate under the prevailing conditions.

The LSI is interpreted as follows:

- If **LSI is negative**: No potential to scale, the water will dissolve CaCO_3
- If **LSI is close to zero**: Borderline scaling potential, water quality or changes in temperature, or evaporation could change the index
- If **LSI is positive**: Scale can form and CaCO_3 precipitation may occur

Water characterised by a negative LSI is also considered to be aggressive to metal, i.e. potentially corrosive.

The Puckorius Scaling index or Practical scaling index (**PSI**) attempts to quantify the relationship between saturation state and scale formation by incorporating an estimate of buffering capacity of the water into the index. For that purpose the equilibrium pH is used rather than the actual system pH to account for the buffering effects:

$$\text{PSI} = 2 (\text{pH}_s) - \text{pH}_{\text{eq}}$$

in which pH_s is the pH at saturation of calcite or calcium carbonate and pH_{eq} is the equilibrium pH, calculated as $1.465 \times \log^{10}[\text{Alkalinity; in mg/L as CaCO}_3] + 4.54$

The PSI is interpreted as follows:

- For **PSI < 6.5** water tends to be scale forming
- For **6.5 < PSI < 7** water is considered to be approximately at saturation equilibrium with respect to calcium carbonate
- For **PSI > 7** water is under saturated and, therefore, would tend to dissolve any existing solid CaCO_3 ; mild steel corrosion may become a problem.

Both LSI and PSI try to predict the formation tendency of a protective iron carbonate layer as a mechanism to prevent corrosion. However, there is some controversy concerning the correlation of these type of indices, particularly the LSI, with regard to the corrosiveness of water.

The Larson-Skold index describes the corrosiveness of water towards mild steel. The index is based on evaluation of in-situ corrosion of mild steel lines transporting Great Lakes waters. The index is the ratio of equivalents per million (epm) of sulphate (SO_4^{2-}) and chloride (Cl) to the epm of alkalinity in the form of bicarbonate plus carbonate:

$$\text{Larson-Skold index} = (\text{epm Cl} + \text{epm SO}_4^{2-}) / (\text{epm HCO}_3^- + \text{epm CO}_3^{2-})$$

{Please note that equivalents per million equals milli-equivalents per liter (meq.L⁻¹)}

The Larson-Skold index has been correlated to observed corrosion rates and to the type of attack in a study of Great Lakes waters. Extrapolation to other water qualities, such as those of low alkalinity or extreme alkalinity, goes beyond the range of the original data. The index has proven a useful tool in predicting the aggressiveness of once-through cooling waters in particular. It is especially interesting due to the preponderance of waters of composition similar to the Great Lakes waters and to its usefulness as an indicator of aggressiveness in reviewing the applicability of corrosion inhibition treatment programs that rely on the natural alkalinity and protective film forming capabilities of a cooling water.

The Larson-Skold index is interpreted as follows:

- **Index < 0.8:** chlorides and sulphate probably will not interfere with natural film formation
- **0.8 < index < 1.2:** chlorides and sulphates may interfere with natural film formation, higher than desired corrosion rates may occur.
- **Index > 1.2:** tendency towards high corrosion rates of a local type should be expected as the index increases

In a study dating from 2012 Sathish Kumar *et al.* studied the usefulness and applicability of the Langelier Saturation index, the Ryznar Stability Index (RSI)¹ and the Puckorius (or Practical) Scaling Index for predicting the corrosive/scaling forming tendency in open recirculating cooling towers (Kumar *et al.* 2012). The study is based on real corrosion and scale data for a period of almost 10 years carried out at a test reactor in India. They conclude that the LSI was always on the scaling side ($LSI > 0$) and could not indicate the observed high corrosion rates except for a few occasions. The other indices, PSI and RSI, were more helpful in indicating both corrosiveness and scale formation, and the PSI turned out to be better indicative than the RSI. Probably, the equilibrium pH and the empirical constants used for calculating the equilibrium pH make the PSI better represent the actual corrosive or scale forming tendencies than the actual pH utilised in LSI and RSI calculations.

2.3 Alternative treatment of cooling water

In current practice numerous so-called comfort cooling systems are operated with fully softened water. These relatively small cooling systems, mainly associated with heating, ventilation & air-conditioning (HVAC) systems located inside cities, mostly use the available potable water as make-up water. This water is commonly softened via ion exchange softening which can operate fully automatically based on a dual or triple system including water flow measurement and counter current mode to conserve on regeneration salt need.

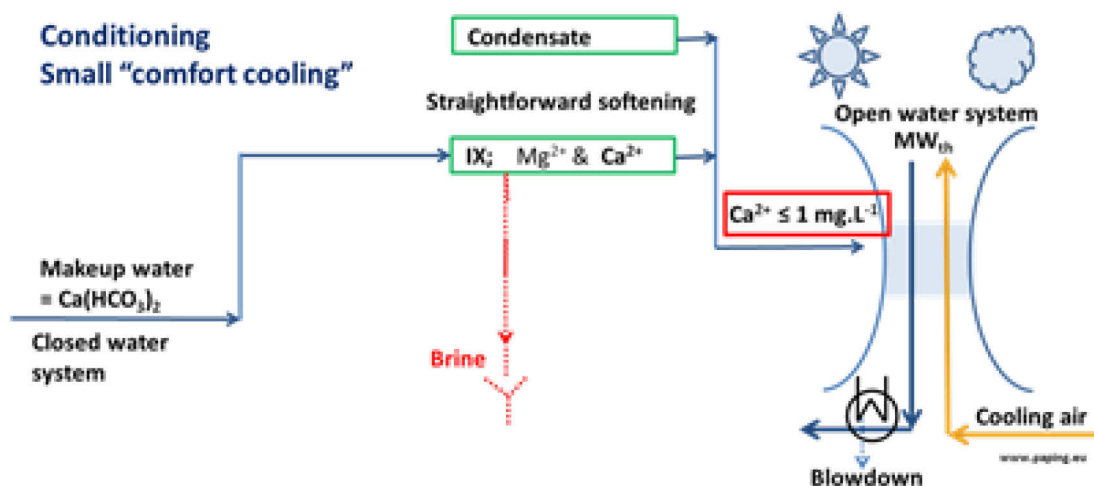


FIGURE 2: SCHEMATIC OF A SMALL SCALE COMFORT COOLING WITH FULL MAKE-UP WATER SOFTENING. (IEX = ION EXCHANGE)

The systems with this type of make-up water treatment do not need any additional chemical treatment of the circulating cooling water due to the absence of calcium. In all cases only a disinfectant must still be applied to control microbiological growth in this open system. The enhanced reliability and risk management control of these systems is not as easy to be addressed in numbers and are very site specific.

For bigger industrial cooling systems a new vision may be developed based on a shift towards more preventive rather than curative conditioning with chemical agents. This change in paradigm means in practical terms that curative conditioning in which chemicals are added to the cooling water is replaced by preventive conditioning in which the make-up water is treated using specific treatment equipment.

¹ The Ryznar Stability Index is calculated in a similar way as the Puckorius Stability Index, only the actual pH is used instead of the equilibrium pH

With respect to full softening of make-up water, ion exchange (IEX) is the preferred choice for fresh waters considering capital and operating costs as well as robustness. Nevertheless, IEX only removes hardness ions and creates a brine stream, while other technologies create less brine and are able to remove many other components that also have an impact on the cooling process. Therefore, other potential softening (and desalination) technologies are compared in this study to provide knowledge about the whole system, resulting in more elaborate/holistic treatment schemes (Figure 3).

Full softening should be considered as the limit of the removal of harness salts. This study not only considers the possibilities of full softening but also makes a comparison with partial softening and partial desalination as well. For this reason the study starts with an overview of technologies to achieve partial softening/desalination or full softening/desalination.

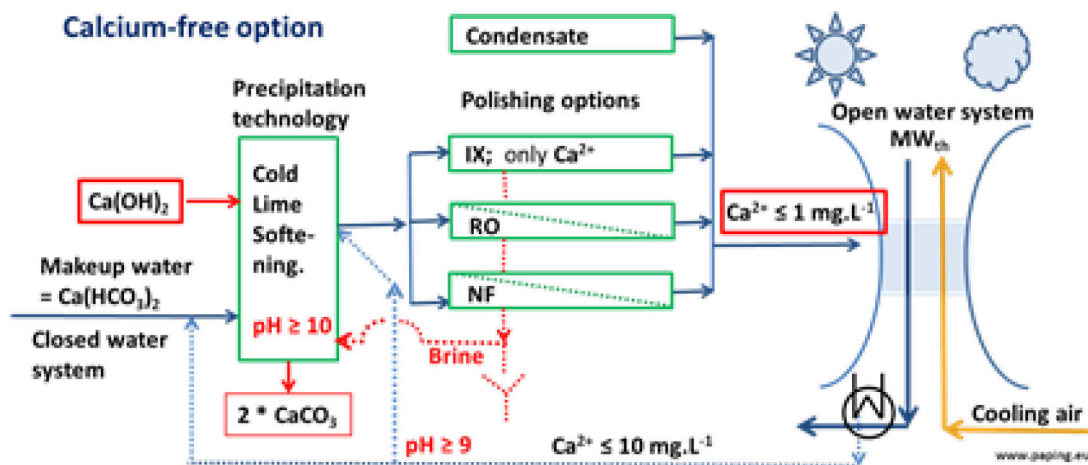


FIGURE 3: OTHER OPTIONS FOR FULL SOFTENING IN COOLING SYSTEMS

In the case of full softening the application of cold lime softening only removes calcium hardness at a specific pH, in most cases in the 9.8 to 10 range. At slightly higher pH values of 10.3 to 10.5 also most of the magnesium and silica is removed. Current pellet reactor technology produces an effluent with around 10 mg.L⁻¹ Ca. For cooling water application the calcium concentration should remain below 1 mg.L⁻¹ to achieve at least ten cycles of concentration in the cooling tower². Additional polishing technology is necessary to reach that level.

In the open circulating cooling system a pH around 9 to 9.5 will install. No hardness precipitation takes place due to the very low calcium residual attained by full softening of the make-up water. The cooling air in the open system buffers the whole matrix of alkalinities and metal solubilities as well as the pH. The pH 9-9.5 range is expected to offer adequate protection against corrosion as the solubility of notably iron carbonate is extremely low under these alkaline circumstances³. Indeed, at a pH of 9 in an open system, the expected carbonate level amount to 0.25 mmol.L⁻¹, so iron solubility drops to one tenth of a μmol.L⁻¹. In case the cooling water pH becomes half a log-point higher, the carbonate

² At a pH of 10 in the circulation cooling water the natural solubility of calcium is in the magnitude of 10 mg.L⁻¹ so at ten cycles of concentration, the make-up water should contain less than 1 mg.L⁻¹ calcium. A target of at least ten cycles due to the softening technology is driven to make a difference with the current practise of only a few cycles that then results in more blowdown.

³ Due to the elevated pH together with abandoning any acid dosage, the ratio of (bi)carbonate to chlorides and sulphates in the circulating cooling water will significantly increase, so corrosion rates are expected to be reduced.

level increases ten times and the iron solubility decreases by a factor of ten again. It is anticipated that this results in the formation of a protective iron carbonate layer on mild steel. Due to a lack of calcium hardness, under-deposit corrosion is not expected to take place under the prevailing alkaline conditions.

With regard to the corrosion protection at elevated pH explained above, it is important to keep in mind that this only holds for iron (steel). Other metallic materials such as aluminium alloys behave amphoteric and have a higher solubility at elevated pH. In the current curative conditioning regime natural traces of zinc give some cathodic corrosion inhibition. The softening of the make-up water, besides hardness also removes these natural traces of zinc.

Water savings are one of the few easily measurable benefits of the proposed alternative treatment method. Other savings like less maintenance of heat exchangers, better heat transfer, lower process temperatures and process pressure and higher levels of safety, plant reliability and availability are harder to quantify in the field as well as to prove over a short time period. The new vision on cooling water treatment will only be applied if enough savings can be demonstrated. These may be quantified as (costs) for water intake, blowdown discharge, chemicals or energy. Other advantages need to be shown through comparative pilot studies.

3 Overview of technologies

3.1 Introduction

This chapter starts with an overview of technologies for softening and desalination in general. Based on different criteria a selection is then made of suitable technologies for treating make-up water of cooling systems. The following criteria are used:

- Residual hardness
- Removal of other salts (besides hardness salts)
- Removal of silica
- Water loss
- Energy consumption
- Chemical consumption
- Investment costs (CAPEX)
- Operational costs (OPEX)
- Waste production

Removal of silica can be relevant for example when a technology preferentially removes calcium and as a consequence magnesium silicate scaling can occur.

Water loss of a technology is relevant as a relatively high water loss conflicts with the intention to increase the number of cooling cycles.

3.2 Technologies for softening

The most common method for removing water hardness relies on ion exchange (IEX) resins (sorptive technology). Other approaches include chemical precipitation processes, membrane filtration (nanofiltration or reverse osmosis), electro dialysis or combinations of these technologies.

3.2.1 Sorptive technology

In conventional water softening "hardness ions" in the water - mainly Ca^{2+} and Mg^{2+} - are exchanged against sodium ions released from cationic ion exchange resin. Ion exchange (IEX) resins are organic polymers containing anionic functional groups to which multivalent cations bind more strongly than monovalent cations. When nearly all the available Na^+ ions have been replaced with calcium or magnesium ions, the resin must be regenerated-charged by eluting the Ca^{2+} and Mg^{2+} ions using a solution of sodium chloride. The spent regenerant, containing the unwanted calcium and magnesium salts, is typically discharged to the sewage system.

3.2.2 Chemical precipitation processes

Chemical precipitation softening is a type of water treatment used for water softening which uses the addition of a.o. sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and/or calcium hydroxide (Ca(OH)_2) to remove hardness (calcium and magnesium) ions by precipitation. As a result of the addition of the chemicals the pH is raised and the equilibrium of carbonate species in the water is shifted. Dissolved carbon dioxide (CO_2) is converted into bicarbonate (HCO_3^-) and then carbonate (CO_3^{2-}). This causes calcium carbonate (and to an extent magnesium hydroxide and/or carbonate) to precipitate as their respective solubility products are exceeded. The precipitates are then removed by conventional processes of coagulation/flocculation, sedimentation and filtration. In precipitation softening,

there is a substantial reduction in total dissolved solids (TDS) whereas this is not the case with IEX softening.

There are different types of precipitation processes:

- Cold lime softening
- Hot lime softening
- Electrochemical precipitation
- Pellet softening

In **cold lime** and **hot lime softening** and in **pellet softening** precipitation is a result of the dosage of a base into the water. In **electrochemical softening** the pH of the water is increased by OH⁻-ions formed/generated at the cathode in an electrolyser cell.

Cold and hot lime softening and **electrochemical softening** produce large volumes of a mixture of calcium carbonate and magnesium hydroxide in a very finely divided white precipitate which may also contain some organic matter flocculated out of the raw water. Processing or disposal of this material may be a cost to the process. With **pellet softening** calcium carbonate will crystallize at the surface of sand or calcite seed material present in a fluidized bed. The particles are allowed to grow into pellets of approximately 1 mm in diameter. Pellets are periodically extracted from the fluidized bed and new seed material is added.

3.2.3 Membrane softening

Nanofiltration (NF) and reverse osmosis (RO) are driven by hydrostatic pressure gradients across a semi-permeable membrane. The membrane can transport water, but will retain hardness ions such as Ca²⁺ and Mg²⁺ to a certain extent – these are flushed away by excess water into the concentrate. This concentrate is typically discharged to a sewage system. The resulting soft water supply is free of hardness ions without any other ions being added to replace them.

3.3 Desalination technologies

Desalination technologies can be divided into electrically driven membrane processes, pressure driven membrane processes, adsorptive technologies and thermal processes. Some processes are combinations of those.

3.3.1 Electrically driven membrane processes

In electrically driven membrane processes dissolved ions are transported across an IEX membrane driven by an electrical potential. The water depleted from salts is called the diluate and the water stream with the concentrated ions is called the concentrate.

The following electrically driven membrane processes can be distinguished:

- Electro dialysis (ED)
- Capacitive deionisation (CDI)
- Radial deionisation (RDI)
- Electro deionisation (EDI)

Electro dialysis (ED) is used to transport salt ions from one solution to another through IEX membranes driven by an applied electric potential difference. This is done in an ED cell, consisting of a feed/diluate compartment and a concentrate compartment formed by alternating anion exchange membranes and cation exchange membranes between two electrodes. In an ED stack, the feed/diluate stream and the concentrate stream are allowed to flow through the appropriate cell compartments formed by the IEX membranes. Under the

influence of an electrical potential difference, negatively charged ions (e.g. chloride) in the feed/diluate stream migrate towards the positively charged anode. These ions pass through the positively charged anion exchange membrane, but are prevented from further migration toward the anode by the negatively charged cation exchange membrane and therefore report to the concentrate stream, which becomes concentrated with the anions. Positively charged species (e.g. sodium) in the feed/diluate stream migrate towards the negatively charged cathode and pass through the negatively charged cation exchange membrane. These cations also report to the concentrate, prevented from further migration toward the cathode by the positively charged anion exchange membrane. As a result of the anion and cation migration, electric current flows between the cathode and anode. Only an equal number of anion and cation charge equivalents are transferred from the feed/diluate stream into the concentrate stream and so the charge balance is maintained in each stream. The overall result of the ED process is an ion concentration increase in the concentrate stream with an equivalent depletion of ions in the feed/diluate stream.

Capacitive deionization (CDI) is a technology to deionize water by applying an electrical potential difference over two porous carbon electrodes. Anions are removed from the water and are stored in the positively polarized electrode. Likewise, cations are stored in the cathode, which is the negatively polarized electrode. Today, CDI is mainly used for the desalination of brackish water, which is water with a low or moderate salt concentration (below 10 g.L⁻¹). Compared to RO and distillation, CDI is considered to be an energy efficient technology for brackish water desalination. This is mainly because CDI removes salinity from the water, while the other two technologies extract water from the salt solution.

The operation of a CDI system cycles through two phases: an adsorption phase during which is desalinated and a desorption phase in the course of which the electrodes are regenerated. During the adsorption phase, a potential difference over two electrodes is applied and ions are adsorbed from the water. The ions are transported through interparticle pores of the porous carbon electrode to intraparticle pores, whereby the ions are electrosorbed in the so-called electrical double layers (EDLs) of the electrodes. After the electrodes become saturated with ions, the adsorbed ions are released for regeneration of the electrodes by reversing or reducing the potential difference between electrodes. In this way, ions leave the electrode pores and can be flushed out of the CDI cell resulting in an effluent stream with a high salt concentration, the so-called concentrate. Part of the energy input required during the adsorption phase can be recovered during this desorption step.

Radial deionisation (RDI™) is a proprietary form of capacitive deionisation (Atlantis 2016). According to the website radial deionisation significantly differs from previous generations of capacitive deionisation techniques. The design allows for water to flow across 1 to 10 meters of continuous supercapacitor material as opposed to the current state-of-the-art CDI which only allows for flow across 10 cm of material, or 1/100th of the distance. The long distance with RDI™ allows for greater TDS reduction and for processing of very high TDS streams and flowrates. The RDI™ Desalination System also incorporates proprietary operating techniques that enable fouling resistance, energy conservation, brine concentration, and backwashing. Moreover, the RDI™ Desalination System's supercapacitors incorporate the latest generation materials, allowing for extremely high capacity for salts.

Electro-deionisation (EDI) comprises the use of two separation technologies, membranes and ion exchange, combined into one sealed, self-contained unit. The primary use of EDI has focussed on production of ultra-pure water by polishing of RO permeate. Indeed, EDI has found its way into industry as a final polisher technology replacing traditional IEX units liked mixed bed ion exchange columns, which require chemical regeneration using basic and

acidic reagents. The lack of chemical usage makes EDI an attractive technology for use in a wide range of industries, ranging from pharmaceutical to power generation.

Within an EDI cell the water is split into 2 streams, a diluate and a concentrate. The electrical current applied to the EDI cell causes ions present in the diluate stream to migrate across a “bridge” of ion exchange resin beads until they pass through a semi-permeable membrane into the concentrate department. The concentrate stream typically represents around 10% of the EDI feed water and is recycled to the preceding RO plant. The diluate quality expressed in terms of resistivity is commonly $> 12 \text{ M}\Omega\cdot\text{cm}^{-1}$. The electrical current generated within the EDI cell creates H^+ and OH^- ions, which bring about continuous regeneration of the ion exchange resin within the dilute compartment. As a result continuous operation can be achieved – there is no need for downtime to regenerate the resins.

3.3.2 Pressure driven membrane processes

In pressure driven membrane processes (a.o. reverse osmosis, nanofiltration, ultrafiltration and microfiltration) a pressure exerted on the solution at one side of a semi-permeable membrane serves as the driving force for separation of solution into a permeate and a concentrate. Separation takes place based on molecular size or ionic radius. The permeate is usually pure water, whereas the concentrate is a concentrated solution that must be disposed of or treated by other methods.

The following pressure driven membrane processes can be applied for (partial) desalination of water:

- Nanofiltration (NF)
- Reverse osmosis low pressure (RO-LP)
- Reverse Osmosis high retention (RO-HR)

Nanofiltration membranes have a nominal pore size of approximately 0.001 microns and a molecular weight cut-off (MWCO) of 1,000 to 100,000 daltons (Da). In order to push water through such small membrane pores a certain pressure is required. Operating pressures are usually near 600 kPa and can be as high as 1,000 kPa. Nanofiltration can remove virtually all cysts, bacteria, viruses and humic materials. NF also removes hardness (and other bi- and trivalent ions) from water, which is why NF membranes are sometimes being referred to as “softening membranes”. NF membranes have a moderate retention (depending on manufacturer 20–80%) for univalent salts.

Compared to NF, **reverse osmosis** membranes have a lower MWCO ($< 200 \text{ Da}$), resulting in much higher retention of dissolved salts. Operating pressures can range from 1,000 kPa (for desalination of low TDS water) up to 8,400 kPa (for desalination of seawater). **Low pressure reverse osmosis** (RO-LP) membranes have a high salt retention (approx. 99%) at a relatively low feed pressure. **High retention reverse osmosis** (RO-HR) membranes offer improved retention (up to 99.8%), but require higher feed pressures to achieve that performance.

3.3.3 Adsorptive technologies

Ion exchange (IEX) is a process used to remove dissolved ions from a solution by electrostatic sorption onto and into IEX materials (typically resins). The removed ions are replaced with equivalent amounts of other ions of the same charge, usually H^+ or Na^+ for positive charge ions and OH^- or Cl^- for negative charged ions. IEX is most commonly used for purification purposes, but is also widely implemented for the separation and extraction of valuable substances. IEX resins are organic polymers containing functional groups to which cations and anions bind more strongly than the counter ion present in the resin. When the exchange capacity of the resin is exhausted, the resin must be regenerated by eluting the

adsorbed ions using a diluted acid solution or a concentrated salt solution (to regenerate cationic exchange resins) and a diluted base or concentrated salt solution (to regenerate anionic exchange resins). The wastewaters eluted from the IEX columns, containing the removed ions, are typically discharged to the sewage system.

The following adsorptive processes can be applied for (partial) desalination of water:

- Ion exchange (IEX)
- Ion exchange scavenger (AIEX)

Typically, **desalination of water with ion exchange (IEX)** is performed through a number of treatment steps. First, water passes a column filled with cationic (ion) exchange resin (CIEX) in which positively charged cations are exchanged against H^+ ions. Due to the resulting decrease of the pH, bicarbonate ions react with the H^+ ions, which gives an increase of the CO_2 concentration in the water. In most cases, CO_2 is subsequently stripped from the water in a degassifier. Next, the degassed water passes a column filled with anionic (ion) exchange resin (AIEX) in which negatively charged anions are exchanged with OH^- ions. Surplus H^+ ions react with OH^- ions to water.

An **ion exchange scavenger** is a specific form of an AIEX. Besides removing dissolved anions this type of resin is also capable of adsorbing organic matter (dissolved organic carbon, a.o. humic acids) which has beneficial effects on the required disinfection of cooling systems.

3.3.4 Thermal processes

Thermal desalination processes are widely used desalination techniques all over the world. With thermal desalination a specific amount of heat is provided to the water, so that the water starts boiling. Salt-free water vapour escapes from the liquid water and is recovered in condensers. With thermal desalination a high quality distillate can be produced, normally with TDS concentrations of less than 5 mg.L^{-1} .

There are different thermal desalination processes:

- Multi-stage flash distillation (MSF)
- Multi-effect-distillation (MED)
- Mechanical or thermo vapour compression distillation (MVC or TVC)
- Membrane distillation (MD)

Multi-stage flash distillation (MSF) is a water desalination process whereby seawater is distilled by flashing of a portion of the water into steam in multiple stages which essentially consist of counter current heat exchangers. An MSF plant comprises a number of stages, each containing a heat exchanger and a condensate collector. The sequence has a cold end and a hot end while intermediate stages have intermediate temperatures. The stages have different pressures corresponding to the respective boiling points of water at the stage temperatures. The vessel after the hot end is called the brine heater.

When the plant is operating at steady state, feed water at the cold inlet temperature flows, or is pumped, through the heat exchangers in the various stages and warms up. When it reaches the brine heater it already has nearly reached the maximum temperature. In the brine heater, additional heating takes place. After the heater, the water flows through valves back into the stages with progressively lower pressure and temperature. The water is now called brine, to distinguish it from the inlet water. In each stage, as the brine enters, its temperature is above the boiling point at the pressure of the stage, and a small fraction of the brine water boils off ("flashes"). This steam generation reduces the temperature until an equilibrium is reached. The steam is a little hotter than the feed water to the heat exchanger.

The steam cools and condenses against the heat exchanger tubes, thereby heating the feed water as described earlier.

Multi-effect-distillation (MED) consists of multiple stages or "effects". In each stage the feed water is heated by steam in tubes. Some of the water evaporates, and the steam flows into the tubes of the next stage, heating and evaporating more water. Each stage essentially reuses the energy from the previous stage. The tubes can be submerged in the water, but more typically the feed water is sprayed on the top of a bank of horizontal tubes, and then drips from tube to tube until it is collected at the bottom of the stage.

Vapour compression desalination refers to a distillation process where the evaporation of sea or saline water is obtained by the application of heat delivered by compressed vapour. Since compression of the vapour increases both the pressure and temperature of the vapour, it is possible to use the latent heat rejected during condensation to generate additional vapour. Water vapour can be compressed via two methods:

- The first method utilizes an ejector system driven by steam at manometric pressure from an external source in order to recycle vapour from the desalination process. It is referred to as ejector or thermo vapour compression (TVC).
- The second method employs a mechanical device, electrically driven in most cases. This form is designated mechanical vapour compression (MVC). There are two variations to MVC: vapour compression (VC) and vacuum vapour compression (VVC). VC designates those systems in which the evaporation effect takes place at manometric pressure, and VVC the systems in which evaporation takes place at sub-atmospheric pressures (under vacuum).

Compression is mechanically carried out using equipment such as a compression turbine. As vapour is generated, it is passed over to a condenser which returns vapour to water. The resulting fresh water is moved to storage while the heat removed during condensation is transmitted to the remaining feedstock. The VVC process is the more efficient distillation process available in the market today in terms of energy consumption and water recovery ratio. As the system is electrically driven, it is considered a "clean" process. It is stated to be highly reliable and simple to operate and maintain.

Membrane distillation is a thermally driven separation technology in which separation is enabled by phase change. A hydrophobic membrane forms a barrier for the liquid phase, allowing solely the vapour phase (water vapour) to pass through the membrane's pores. The driving force for the process is the partial vapour pressure difference commonly triggered by a temperature difference. In some system vacuum is applied to the permeate side of the membrane in order to increase the vapour transport through the pores of the hydrophobic membrane.

3.3.5 Resume desalination technologies

In Table 1 an overview is given of desalination technologies considered to treat cooling tower make-up water. Only the technologies that are potentially suitable for the treatment of cooling tower make-up water (see final column in Table 1) are selected for the technology matrix described in the following paragraph.

TABLE 1: OVERVIEW OF DESALINATION TECHNOLOGIES CONSIDERED AS PRETREATMENT OF COOLING WATER MAKE-UP WATER

Technology	Principle	Materials	Raw Water (type) ¹⁾	Unit/Commercial size ²⁾	Product TDS (mg.L ⁻¹) or EC (µS.cm ⁻¹)	Suitable for industrial cooling towers
ED(R)	Potential difference	Membranes	Fresh/Brackish water	Modular, up to 18 m ³ .h ⁻¹ .stack	<10 mg.L ⁻¹ TDS	Yes
CDI		Membranes	Fresh/Brackish water	Modular, up to 11 m ³ .h ⁻¹ .stack	50-95% TDS reduction	Yes
RDI		Membranes	Brackish/Sea water	Modular, up to 22 m ³ .h ⁻¹ .stack	50-95% TDS reduction	Yes
EDI		Membranes & Resins	RO product/Demin water	Modular, up to 19 m ³ .h ⁻¹ .stack	< 16 MΩ.cm ⁻¹	No
NF	Pressure difference	Membranes	Brackish/Sea water	Modular, up to 1 m ³ .h ⁻¹ .module (8 inch)	90-95% hardness reduction	Yes
RO-LP		Membranes	Brackish/Sea water	Modular, up to 1 m ³ .h ⁻¹ .module (8 inch)	95-99% TDS reduction	Yes
RO-HP		Membranes	Brackish/Sea water	Modular, up to 1 m ³ .h ⁻¹ .module (8 inch)	98-99.5% TDS reduction	Yes
IEX	Electrostatic attraction	Resins	Fresh/Brackish water	Engineered systems, from 1 up to 1,000 m ³ .h ⁻¹	< 1 µS.cm ⁻¹	Yes
AIEX		Resins	Fresh/Brackish water	Engineered systems, from 1 up to 1,000 m ³ .h ⁻¹	TOC reduction	Yes
MSF	Temperature difference	Multiple staged	Sea water	Engineered systems, up to 3,000 m ³ .h ⁻¹ .unit	5-10 mg.L ⁻¹ TDS	No
MED		Multiple staged	Sea water	Engineered systems, up to 1,600 m ³ .h ⁻¹ .unit	5-10 mg.L ⁻¹ TDS	No
MVC/TVC		Multiple staged	Sea water	Engineered systems, up to 125 m ³ .h ⁻¹ .unit	1-10 mg.L ⁻¹ TDS	No
MD		Membranes	Brackish/Sea water	Modular, up to 0.31 m ³ .h ⁻¹ .stack	1-10 mg.L ⁻¹ TDS	No

1) Fresh/Brackish water typically <100 – 15,000 mg.L⁻¹ TDS
 Brackish/Seawater typically from 1,000 up to 60,000 mg.L⁻¹ TDS
 RO product/Demin water typically from < 1 up to 50 mg.L⁻¹ TDS
 Seawater typically from 30,000 up to 60,000 mg.L⁻¹ TDS

2) Modular systems contain multiple stacks/modules in parallel and in series to obtain larger capacities, e.g. largest CDI plant: 5,000 m³.h⁻¹, largest seawater RO plant: 26,000 m³.h⁻¹
 Engineered systems contain multiple filters/vessels in series to obtain larger capacities, e.g. largest MSF & MED plants: 19.000 m³.h⁻¹, largest MVC plant: 720 m³.h⁻¹

3.4 Technology matrix

In a technology matrix (see Table 2) different desalination and/or softening technologies were checked against a number of criteria to assess their suitability for alternative conditioning of cooling systems. These criteria are, in order of relevance:

- Partial softening of water instead of full softening
- Low percentage of water loss (< 5 %), in order to compete with the expected difference between the current and future cooling tower blowdown
- Low or moderate energy consumption (< 0.2 kWh.m⁻³)
- Low or moderate capital and operational costs
- Commercially available in medium to large scale systems (> 10 m³.h⁻¹)

TABLE 2: TECHNOLOGY MATRIX WITH AN OVERVIEW OF TECHNOLOGIES FOR PARTIAL SOFTENING AND DESALINATION OF WATER

Technology Selection Table for partial and total softening of Cooling Tower Make Up Water													
Technology		Residual Hardness		Other Salts	SiO2	Water Loss	Consumption		Capex	Opex	Remarks	Selection Criteria	
		Ca mg/l	Mg %	removal %	removal %	%	Energy	Chemical					
Chemical Precipitative Processes	Cold lime softening	pH ~10,3 pH > 11	10 10	80 60	HCO ₃	10	2 - 4	low	high	moderate	moderate	sludge dewatering upto 60% sludge dewatering upto 20-25%	Sludge production & handling
	Hot lime softening	pH ~10,3 pH > 11	5 5	25 5	HCO ₃	80 - 90	2 - 4	high (heating)	high	moderate	moderate	SiO ₂ adsorbes on Mg(OH) ₂ precipitate	Sludge production & handling
	Pellet Softening	pH ~10,3	10	100	HCO ₃	10	0,5	low	moderate	moderate	moderate	Proven Technology Drinking Water Treatment No Sludge, but reusable pellets	No sludge production
	Electro Chemical Precipitation		10	Approx 25% of Ca removal	HCO ₃	?	?	high	na	?	high	Limited performance sludge production	Sludge production & handling
Electrical Driven Membr. Processes	Capacitive Deionisation (Voltea)		50	50	50	0	10 - 15	moderate	na	moderate	moderate	Proven Technology	Chemical free operation
	Radial Deionizing (Atlantis)		50	50	50	0	10 - 15	moderate	na	?	moderate	Relative new, Super capacitor Manufacturer claims lower CAPEX compared to Voltea	Relative new product
	Electro Dialysis - single stage double stage		50 75	50 75	50 75	0 0	5 - 10 5 - 10	moderate high	low (AS)	moderate high	moderate moderate	Proven technology	Anti scalant required
Pressure Driven Membr. Processes	Nanofiltration (NF)		5 - 10	5 - 10	40 - 70	80	15 - 20	moderate	low (AS)	high	moderate	Little difference in operating conditions compared to RO-LP	Lower hardness removal compared to RO-LP at approx same Opex
	Reverse Osmosis Low Pressure (RO-LP)		1 - 2	1 - 2	90 - 95	99	15 - 20	moderate	low (AS)	high	moderate	Little difference in operating conditions compared to NF	High hardness removal with moderate opex
	Reverse Osmosis High Retention (RO-HF)		0,5 - 1	0,5 - 1	95 - 99	99,5	20 - 25	high	low (AS)	high	high	Higher TH removal at higher Opex compared to RO-LP	Only slightly higher TH removal at higher Opex compared to RO-LP
Adsorptive Processes	Ion Exchange Softening (CIEX)		< 0,1	< 0,1	0	0	1 - 2	low	moderate (NaCl)	low	low	Only removal of multi-valent cations	Complete hardness removal at lower Capex & Opex compared to IEX
	Ion Exchange Scavenger (AIEX)				SO ₄ PO ₄	0	1 - 2	low	moderate (NaCl)	low	low	Only removal of multi-valent anions	NOM removal
	Ion Exchange Desalination (IEX)		< 0,1	< 0,1	99,99	99,5	3 - 4	low	moderate (Acid & Base)	moderate	low	Complete demineralisation	Higher Capex & Opex compared to CIEX
Selected Processes for Hardness & NOM Removal	CIEX + AIEX		< 0,1	< 0,1	SO ₄ & PO ₄	0	2	low	moderate (NaCl)	low	moderate		
	Pellet Softening + (RSF) + CIEX		< 0,1	< 0,1	HCO ₃ & PO ₄	10	3,5	moderate	moderate (NaOH + NaCl)	moderate	moderate		
	Pelletsoftening + (RSF) + CIEX + AIEX		< 0,1	< 0,1	HCO ₃ , SO ₄ & PO ₄	10	4	moderate	moderate (NaOH + NaCl)	moderate	moderate		

The relatively high water loss associated most electrically and pressure driven membrane processes makes these uninteresting with perspective to water savings in cooling water make-up treatment. The most interesting processes in line with this project’s selection criteria are ion exchange processes and pellet softening.

3.5 Make-up treatment scenarios

The following combinations of technologies were selected from the technology matrix in paragraph 3.4 (see bottom rows of Table 2):

- Scenario 1: CIEX – AIEX
- Scenario 2: Pellet softening – rapid sand filtration (RSF) – CIEX
- Scenario 3: Pellet softening – RSF – CIEX – AIEX

These make-up treatment scenarios (graphically shown in Figure 4) form the basis of the Excel tool described in Chapter 4.

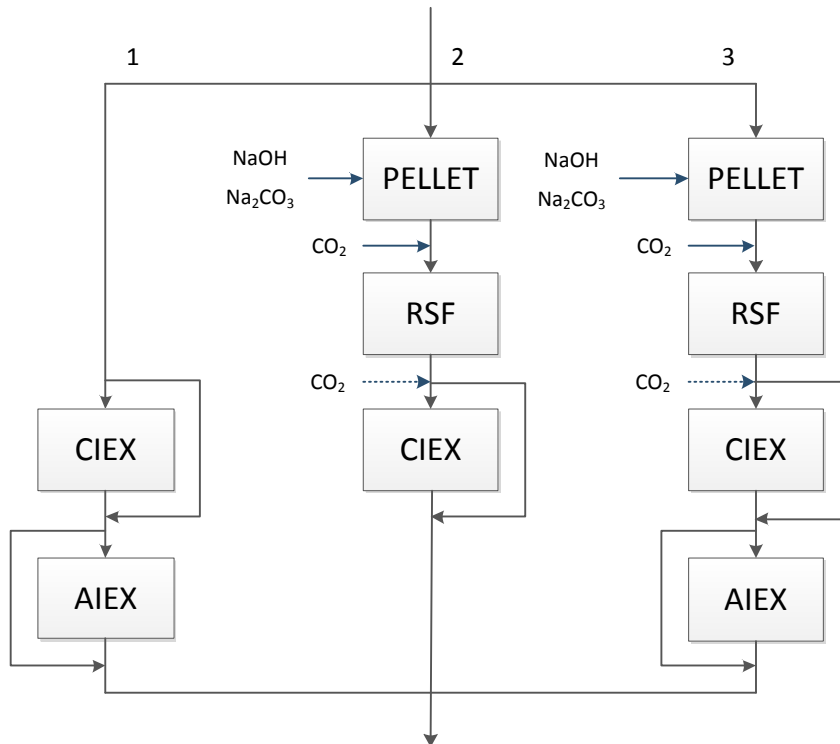


FIGURE 4. SELECTION OF THREE SCHEMES WITH PARTIAL SOFTENING FOR THE MODEL CALCULATIONS

With all of the selected scenarios multivalent cations will be removed from the cooling system make-up water, as these are considered to be the cause for scaling problems. Although no full desalination takes place the threat of under-deposit corrosion in the cooling water is taken away when no scaling can form.

In the first scenario, CIEX is incorporated to reduce the hardness of the raw water. Normally all hardness is removed by CIEX, but with a bypass of raw water the residual hardness can be tailored to the desired value in the make-up water.

The second and third scenario both start with pellet softening. Pellet softening will reduce the calcium concentration to 0.25 mmol.L^{-1} (10 mg.L^{-1}). The effluent of pellet softening is supersaturated with calcium carbonate. To prevent further precipitation CO_2 is dosed to it. There is some flexibility with the location of the CO_2 addition – this may either be before or after the sand filter. After pellet softening a (static) rapid sand filter (RSF) is necessary for the removal of suspended solids from the water and/or carry-over from the pellet softener. In the RSF, organics and microorganisms will be partly removed. This is beneficial for the prevention of biofilm growth in the cooling tower and will probably also somewhat reduce

the consumption of biodispersant. After the RSF the water is treated by CIEX down to the desired hardness in the make-up water to the cooling system.

AIEX is introduced in scenarios 1 and 3 as a scavenger to remove nearly all organic material. This is expected to have a significant favourable effect on disinfection in the cooling system in terms of biocide and biodispersant use.

The CIEX as well as the AIEX will be regenerated with sodium chloride.

4 Model set-up and description

4.1 Introduction

The Excel based calculation tool developed as part of this project is called the **Calculation Sheet Cooling Water (CaShCoW)**. The purpose of the tool is to determine the techno-economic feasibility of the selected make-up water treatment scenarios in combination with an increase in the number of cycles of concentration for open recirculating cooling systems. Reference is the existing situation.

In an open recirculating cooling system water circulates through process heat exchangers and cooling tower. Due to evaporation the dissolved solids concentration in the water will increase, thus increasing corrosion and deposition tendencies. In addition, relatively high temperatures significantly increase the corrosion potential and biological growth.

The major aims of the tool are to calculate (1) the effect of treatment on make-up water quality and (2) the increase of cycles of concentration on the overall composition and scaling tendency of the blowdown. For the latter an indication of corrosiveness the Langelier Saturation Index, the Puckorius Scaling Index and the Larson-Skold index are also computed.

Another important goal of the tool is to calculate the CAPEX and OPEX of the treatment scenarios and to compare these with the costs of the existing situation.

The most important limitation of the model is that it does not give any quantitative information on the corrosiveness or biofouling tendency of the water in the cooling system. Additional insights in this regard may be obtained using other software – as part of this study, for instance, selected calculations were performed using PHREEQC freeware.

4.2 Set-up of Excel spreadsheet

As mentioned before, the tool has been developed as an Excel spreadsheet. In the spreadsheet the major calculations are incorporated in the following worksheets:

- Description of the existing cooling tower system, including
 - Size of the cooling tower system (in sheet 1)
 - Raw water composition (in sheet 2)
 - Existing conditioning program (in sheet 4)
- Determination of the basic design parameters for the make-up treatment (sheet 6)
- Calculation of the CAPEX & OPEX of the make-up treatment (sheet 7)
- Calculation of the composition of the blowdown (sheet 8)

The data from these worksheets enhance the local specific chemical and physical characteristics and circumstances.

Besides the above worksheets the calculation tool also has a number of auxiliary worksheets:

- Disclaimer (sheet 0.1)
- Manual (sheet 0.2)
- Input chemical costs (sheet 3)
- Input energy & water costs (sheet 5)
- Input of the basic design & costs data of the selected make-up treatment processes (sheet 9)

The data from these worksheets enhance the local specific financial characteristics and circumstances.

4.3 General instructions for input of data

In the calculation tool cell formatting is used to indicate which cells require data input:

- Yellow colouring indicates that the values in these cells can be changed, other cells are for information or calculation results
- Some yellow cells contain dropdown menus, which are opened by clicking the cell followed by clicking the small triangle to the right of the selected cell (see Figure 5)
- After making the selection additional data input cells will appear

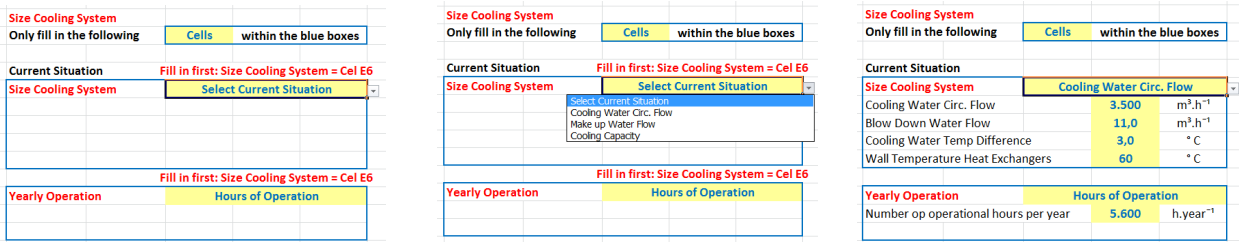


FIGURE 5. EXAMPLE OF INPUT OPTIONS BY DROPDOWN MENUS

- Some worksheets also contain slide bars (see Figure 6) with which costs for chemicals can be given. Another option is to directly input the costs in the cell to the right of the slide bar.

Future Make-up Treatment						
Raw material costs & concentrations				Raw material price		Point of dosage
	Chemical	Conc. w/w		Costs	Unit	
Generic Chemicals						
Base 1	Caustic (NaOH)	50 %	◀ ▶	€ 450	€.tonne-1	Future CT Conditioning
Base 2	Soda ash (Na2CO3)	100 %	◀ ▶	€ 260	€.tonne-1	Future CT Conditioning
Acid 1	Carbon Dioxide (CO2)	100 %	◀ ▶	€ 200	€.tonne-1	Future CT Conditioning
Disinfectant 1	Bleach (NaOCl)	12,5 %	◀ ▶	€ 180	€.tonne-1	Future CT Conditioning
Disinfectant 2	Not used		◀ ▶			
Salt	Sodium Chloride (NaCl)	100 %	◀ ▶	€ 80	€.tonne-1	Future CT Conditioning

FIGURE 6. EXAMPLE OF INPUT OPTIONS BY SLIDE BARS

4.4 Required data to perform the calculations

The tool contains a lot of information about the processes in a cooling tower and alternative treatment processes. To perform the calculations, specific data for each local case are required.

The following is given as an example of the required input:

- The size of the cooling system (worksheet 1, see Figure 7, left part) is determined by a number of parameters: this can be water volumes (make-up and blowdown), cooling capacity (MWth) and/or cooling water temperature difference. The tool will calculate the corresponding current number of cycles.
- Desired future situation (also worksheet 1, see Figure 7, right part). Input as required blowdown or number of cycles: by choosing different numbers the tool will determine the effect of the number of cycles on both water use, blowdown quality and costs for the alternative treatment scenarios.

Current Situation			
Size Cooling System		Cooling Water Circ. Flow	
Cooling Water Circ. Flow	3,500	m ³ .h ⁻¹	
Blow Down Water Flow	11,0	m ³ .h ⁻¹	
Cooling Water Temp Difference	3,0	° C	
Wall Temperature Heat Exchangers	60	° C	
Yearly Operation		Hours of Operation	
Number op operational hours per year	5.600	h.year ⁻¹	
<i>data to be used further:</i>			
Output: Cooling Capacity			
Cooling Power as heat loss in time	12,2	MWth	
Output: Water flows existing situation			
Make up Water Flow	26	m ³ .h ⁻¹	
Blow Down Water Flow	11	m ³ .h ⁻¹	
Evaporation	15	m ³ .h ⁻¹	
Cycles of Conc. of Make-up	2,4	[-]	
Number op operational hours per year	5.600	h.year ⁻¹	
Volume of Make Up Water	145.600	m ³ .year ⁻¹	
Volume of Blow Down Water	61.600	m ³ .year ⁻¹	

Future situation			
Blowdown or Cycles		Cycles of Conc. desired	
Cycles of Conc. desired	5,0	[-]	
<i>data to be used further:</i>			
Output: Blowdown or Cycles			
Blowdown desired	3,8	m ³ .h ⁻¹	
Cycles of Conc. desired	5,0	[-]	
Volume of Make Up Water	105.000	m ³ .year ⁻¹	
Volume of Blow Down Water	21.000	m ³ .year ⁻¹	

FIGURE 7. INPUT DATA FOR DETERMINATION OF THE SIZE OF A COOLING SYSTEM

- Raw water analysis (worksheet 2, see Figure 8). A detailed and especially accurate raw water analysis is required for a proper calculation. Input of the data can be in many units, like mg.L⁻¹, ppm as CaCO₃, meq.L⁻¹, mmol.L⁻¹, deg D, deg F and P- and M-number. The input is converted to meq.L⁻¹ and electro-neutrality of the input is checked.

Input Raw Water Analysis		
Only fill in the following	Cells	within the blue boxes
Cations	Unit	Input
Calcium	mg.L-1	68,7
Magnesium	mg.L-1	10,7
Sodium	mg.L-1	42,924
Potassium	mg.L-1	4,3
Barium	mg.L-1	0,072
Strontium	mg.L-1	0,45
Iron (soluble)		
Iron (insoluble)	mg.L-1	0,005
Manganese	mg.L-1	0,005
Aluminium	mg.L-1	0,005
Zinc	mg.L-1	0,016
Copper	mg.L-1	0,0034
Nickel	mg.L-1	0,0021
Ammonium	mg.L-1	0,1
Comp. c1		
Comp. c2		
Comp. c3		

FIGURE 8. INPUT RAW WATER COMPOSITION (ONLY CATION PART SHOWN)

- Costs of chemicals (worksheet 3, see Figure 9). For the existing cooling tower system there is an extensive list of possible chemicals, including proprietary chemicals. For the future situation only a limited number of basic chemicals are incorporated. There are different options for chemicals (selection of common chemicals made), concentrations (available on market for selected chemicals) and chemical costs (with slide bar, different units can be chosen). There is a list of suggested market prizes (May 2016) given for some commonly available chemicals.

Input Raw Materials & Costs					
Only fill in the following		Cells	within the blue boxes		
Existing CT-conditioning					
Raw material costs & concentrations				Raw material price	
Chemical	Conc.		Costs	Unit	Point of dosage
Generic Chemicals					
Base 1	Caustic (NaOH)	50,0%			Existing CT Conditioning
Base 2	Quick Lime (CaO)	50,0%			Existing CT Conditioning
Base 3	Soda ash (Na ₂ CO ₃)	100,0%			Existing CT Conditioning
Acid 1	Carbon Dioxide (CO ₂)	96,0%			Existing CT Conditioning
Acid 2	Hydrochloric acid (HCl)	85,0%			Existing CT Conditioning
Acid 3	Sulphuric acid (H ₂ SO ₄)	100,0%			Existing CT Conditioning
Disinfectant 1	Bleach (NaOCl)	12,5%	€ 180	€.tonne-1	Existing CT Conditioning
Disinfectant 2	Hydrogen Peroxide (H ₂ O ₂)	12,5%		€.m-3	Existing CT Conditioning
Salt	Sodium Chloride (NaCl)	100,0%			Existing CT Conditioning
Corrosion inhibitor	Zinc Chloride (ZnCl ₂)	98,0%			Existing CT Conditioning
Scale inhibitor	Organic Phosphonates	100,0%			Existing CT Conditioning
Dispersant	Dispersant xx	20,0%			Existing CT Conditioning
Proprietary Chemical Mixtures					
Chem 1	Mixture 1 Proprietary produ	100,0%	€ 5.000	€.tonne-1	Existing CT Conditioning
Chem 2	Mixture 2 biodetergent	100,0%			Existing CT Conditioning
Chem 3	Mixture 3 corrosion inhibitor	100,0%			Existing CT Conditioning
Chem 4	Mixture 4 Proprietary product	100,0%			Existing CT Conditioning
Chem 5	specify product				

FIGURE 9. INPUT CHEMICAL COSTS (ONLY EXISTING CT-CHEMICALS SHOWN)

- Current chemical dosage in circulation cooling water (sheet 4). In this sheet the actual usage of chemicals has to be given. The tool uses this information to calculate the OPEX of the existing cooling system.
- Costs of energy, water and wastewater discharge (worksheet 5). Energy cost can be given based on the production from oil, gas, coal or as electricity from the grid. The tool converts the input to energy cost in € per GJe. This value is used to calculate energy costs of the existing and the future cooling system.

For operation of the alternative treatment scenarios, some design choices have to be made as well:

- Calcium Hardness in recirculating cooling water. In some cases, the client requires a minimum calcium hardness in the recirculating cooling water. The tool calculates the corresponding maximum allowable calcium concentration in the make-up water.
- CIEX and AIEX runtime and bed height (typical values are default).
- AIEX bypass ratio

The above is only an indication of the required input. In the manual (sheet 0.2 of the tool) a more elaborate description of the requirements is given.

4.5 Calculation method for water quality and quantity

Calculation of the water composition after the treatment processes (worksheet 8), for most ions, is based on mass balance calculations and the additions related to the used cooling water conditioning chemicals.

For the ion exchange processes (CIEX and AIEX) the amount of multivalent cations and anions (expressed as meq.L⁻¹) is replaced with an equivalent amount of sodium and chloride ions, respectively.

Calculation of the alkalinity and the CO₂-HCO₃⁻-CO₃²⁻ equilibrium after pellet softening and of the recirculating cooling water is based on carbon dioxide - carbonic acid equilibrium constants from literature.

4.6 Cost calculation method

The CAPEX of the water treatment options is calculated using cost functions based on literature data, cost functions from the RoyalHaskoning/DHV Kostenstandaard and budget quotations. The resulting equipment costs are multiplied with an investment factor, which is adjustable by the end-user depending on specific site conditions.

In the OPEX calculation the following items are included:

- Depreciation of the CAPEX
- Operation and maintenance costs
- Energy costs
- Chemical costs
- Raw water and waste water costs

5 Case descriptions

During the project kick-off meeting in April 2015 a selection was made of two cooling systems, one for each industrial partner, as the starting point for this study. For operational reasons, Tata Steel proposed another cooling system in July 2015.

The present study centers on the following two reference systems:

- For SABIC, the cooling system of the main cracker on the Chemelot site in Geleen, with a cooling capacity of 200 MWth (165 MWth + 35 MWth), a cooling water pumping rate of 18,000 m³.h⁻¹, conditioned with a zinc/phosphonate program and fed with flocculated surface water (River Meuse water through the Juliana Canal). It is operated continuously (8,760 h.yr⁻¹).
- For Tata Steel, the indirect cooling system of the Direct Sheet Plant (tunnel furnace) in IJmuiden, with a capacity of 13 MWth, a cooling water pumping rate of 3,500 m³.h⁻¹ and an all organic conditioning program. It is in operation around 5,600 h.yr⁻¹.

At this moment, the indirect cooling system still has an unintentional (not yet identified) open connection with the direct cooling system. However, in the future this will be separated completely. The current connection results in a chloride limitation in the system of 600 mg.L⁻¹ due to operational demands of the direct cooling system, resulting in a limited concentration factor of the circulating cooling water in the indirect system. In the future this limit may disappear when the two cooling systems are completely separated - Tata has no discharge limit for chloride.

Tata can receive two types of water through the WRK (Watertransportmaatschappij Rijn-Kennemerland) system. Both are surface waters. The first is water from Lake IJssel that has been pretreated in Andijk and then transported to Velsen where it supplies the industry with fresh water. This water has a relatively low hardness. The second source is water from the river Lek in Nieuwegein, which is also piped to Velsen. This water has a higher calcium concentration and higher alkalinity than the water from Lake IJssel. Excel tool calculations are performed with both types of water.

Detailed information of both systems including technical and economic data can be found in the appendix.

6 Results calculations case studies

6.1 Introduction

In this chapter the results of Excel tool calculations are presented using the case descriptions in chapter 5 and Appendix I as the starting point.

Tool calculations were performed looking at water quality aspects and economics to find out what treatment scenario from paragraph 3.5 would be most suitable for each case and to investigate if the new approach would be economically attractive.

6.2 Results case study 1 (SABIC)

The current situation in the SABIC case uses 238 m³.h⁻¹ of raw water, resulting in a blowdown of 27.5 m³.h⁻¹. So, the system operates at a concentration factor of 9, which is already high in comparison to similar systems. Moreover, costs for water are low, resulting in relatively low operational costs for this cooling system.

To decide what scenario would still be potentially beneficial to the SABIC case, a few choices are made followed by a sensitivity analysis of the effect of the amount of cycles, costs for chemicals, water and energy, and the effect of variations in operations on raw water use and costs.

Chosen parameters:

- Desired number of cycles 10 (based on current cycles of 9)
- Calcium hardness in recirculating cooling water: 0.1 mmol.L⁻¹ (requirement given by client)
- Cation ion exchange softening: runtime 12 hours, bed height 2 m (typical value)
- Anion exchange dissolved organic carbon (DOC) removal: bypass 0%, runtime 12 hours, bed height 2 m (typical values)

The effect of increased costs for chemicals, energy and, water on the total costs of the scenarios is also determined. As energy and water prices may fluctuate in future, this is something to be considered as well.

TABLE 3: RAW WATER USE AND RELATIVE COSTS FOR THE CURRENT SITUATION AND THREE ALTERNATIVE SCENARIOS.

		Current Situation	Scenario 1	Scenario 2	Scenario 3
Raw water capacity	m ³ .h ⁻¹	238	237	240	241
Make-up water capacity	m ³ .h ⁻¹		234	234	234
Water losses make-up water treatment	m ³ .h ⁻¹		3	7	7
Relative costs	%	100	160	271	309

Figure 10 shows the breakdown of costs for the current situation and the three treatment scenarios at a concentration factor of 10.

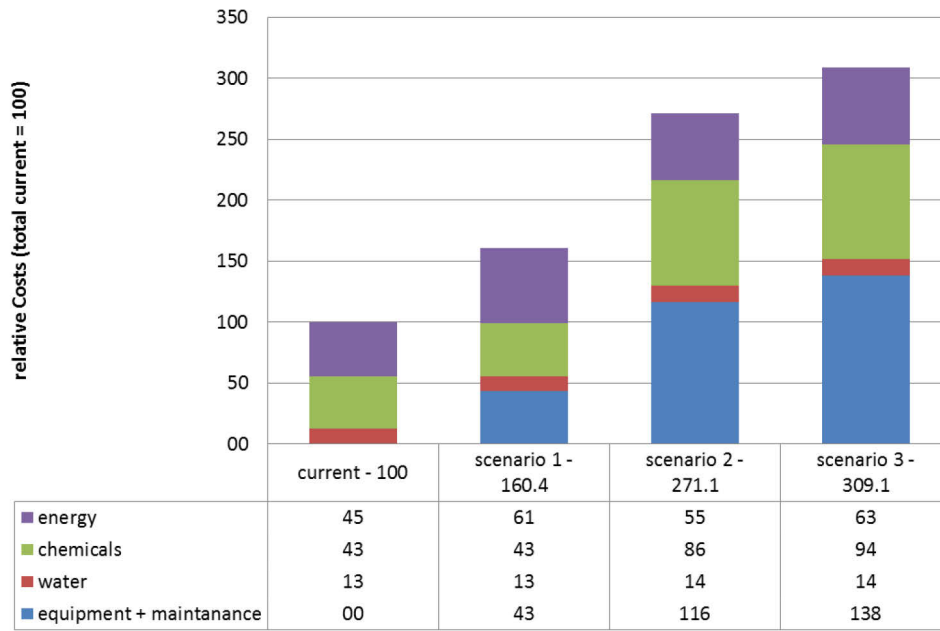


FIGURE 10: COSTS OF TREATMENT SCENARIO'S DIVIDED BY TYPE. THE CURRENT COSTS ARE A RELATIVE TOTAL OF 100. THE OTHER SCENARIOS SHOW THEIR COSTS RELATIVE TO CURRENT.

Both in Table 3 and Figure 10 the total costs of the current situation are normalized to 100. The relative costs of the other scenarios are shown. As can be seen, the total costs of the other scenarios are higher than for the current situation. The dominant costs in the current situation are for energy and chemicals while in the new scenarios the new equipment also takes a major part of the total costs, as can be expected as additional equipment has to be installed. The part 'equipment and maintenance' applies only to additional equipment and not to equipment such as pumps, dosing stations etc., that are already present and will most likely still be required when installing the additional equipment.

6.2.1 Cycles

It can be expected from the above calculations that an increase in costs for water, or water savings by increasing the concentration factor, would not have a major effect on the total costs. Especially as the concentration factor is already 9, not much water can be saved.

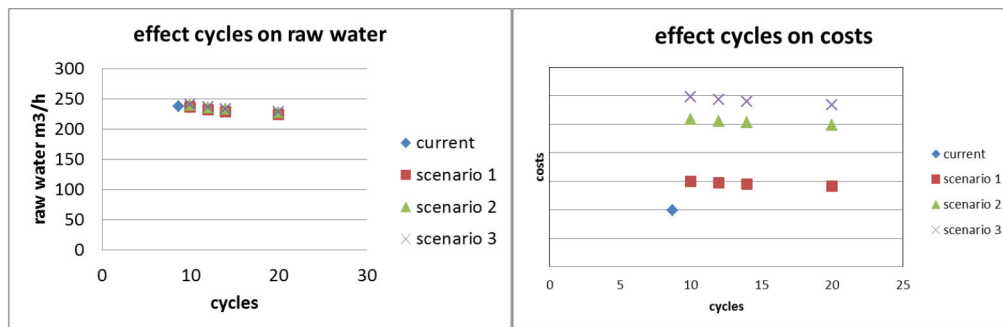


FIGURE 11: THE EFFECT OF THE NUMBER OF CYCLES ON THE RAW WATER USE AND COSTS FOR THE CURRENT AND ALTERNATIVE TREATMENT SCENARIOS FOR THE COOLING TOWER OF SABIC.

When the number of cycles (concentration factor) is increased from 10 to 20, raw water use decreases from 236-241 m³.h⁻¹ (scenario 1-3) to 224-228 m³.h⁻¹ (scenario 1-3 respectively).

The costs also decrease but for all scenarios would be significantly higher than in the current situation.

6.2.2 Costs of chemicals, water and energy

In the current system a zinc/phosphonate conditioning program is applied using proprietary chemicals from a specific supplier. In the proposed alternatives this program is replaced by a low-chemical program, using only commodity chemicals. Depending on supplier pricing, there is a tipping point at which one of the make-up water treatment alternatives would become economically more attractive. Calculations show that this point would be reached if the price of the current chemicals would increase by a factor 3.2 with the cost for the other chemicals remaining the same. This is, however, unlikely to happen in the near future.

The cost of water is only a minor part of the total costs. As the number of cycles is already high, not much more water can be saved. The alternative treatments require approximately the same amount of water. An increase in costs of raw water, or for discharge water, does not benefit the does not make the three alternatives economically look more favourable compared to the current situation.

Energy is another major cost factor. A change in energy costs would have an effect on all 4 situations (1 current, 3 alternative treatments). If the cost of energy increases, the total costs increase for all situations, and the three alternative treatments would always be more expensive than the current situation.

6.2.3 Variations in operation

In scenario 1 and 3 an anion exchanger is applied. It is possible to decide to have a bypass over the AIEX. This results in a smaller system and lower costs for regeneration. However, even when the AIEX is bypassed completely (100% bypass, nothing going through the AIEX) the total costs of the treatment would still be much higher than in the current situation.

6.2.4 Water quality of blowdown water

The amount of raw water required is similar for all three alternative treatment options. However, the composition of the blowdown is different for each.

As the composition and effect of the added chemicals (proprietary chemicals) on the ions present is not known, it is not possible to provide the scaling or corrosion tendency for the current situation. The equilibrium pH and concentration of selected ions with the three scenarios are given in Table 4 and Figure 12.

TABLE 4: pH OF BLOWDOWN AT EQUILIBRIUM, SABIC

Scenario	Equilibrium pH open system
1	9.6
2	9.4
3	9.4

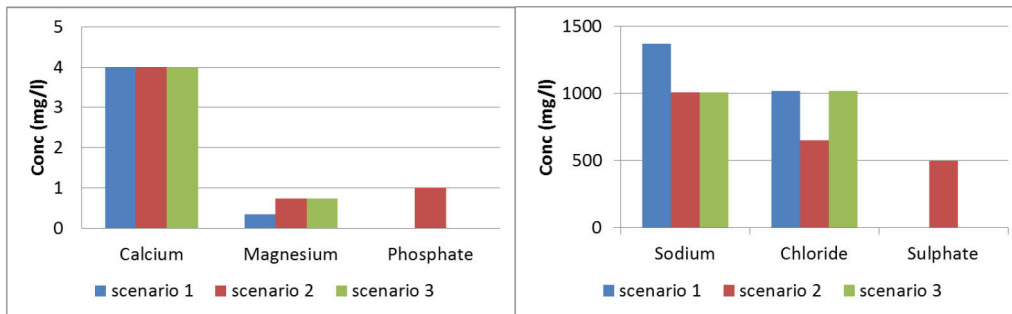


FIGURE 12: CONCENTRATIONS OF SOME IONS IN THE BLOWDOWN AFTER TREATMENT ACCORDING TO SCENARIO 1, 2 OR 3.

The maximum film temperature in the current system is 60 °C. The Langelier saturation index, the Larson-Skold index and the Puckorius Scaling Index are calculated for each alternative scenario. As the composition of the currently used proprietary chemicals is not exactly known, it is not possible to calculate a value for the indices in the current situation. However, it is expected that the currently used chemicals are dosed with the goal to prevent both corrosion and scaling. The indices for the alternative scenarios are given in Table 5:

TABLE 5: SCALING INDICES FOR THE THREE ALTERNATIVE SCENARIOS, SABIC

	Scenario 1	Scenario 2	Scenario 3
Langelier Saturation Index @ 60 °C	2.35	1.8	1.8
Larson-Skold Index	1.00	2.0	2.0
Puckorius Scaling Index	5.19	6.3	6.3

The Langelier Saturation Index predicts that CaCO_3 scale formation may be problematic with all scenarios. When the calcium concentration in the blowdown is decreased to $2 \mu\text{mol.L}^{-1}$ the LSI is around zero for scenario 2 and 3. To eliminate the risk of scaling with scenario 1, the calcium concentration in the blowdown would have to be decreased to $<1 \mu\text{mol.L}^{-1}$. However, it is assumed that the cation exchanger cannot achieve a concentration below $1 \mu\text{mol.L}^{-1}$ and with a concentration factor of 10 this would result in a calcium concentration of $10 \mu\text{mol.L}^{-1}$ in the blowdown. Therefore the Langelier Index cannot reach values around zero for the SABIC case.

The Larson-Skold Index predicts no scaling nor corrosion for scenario 1, while higher corrosion rates than desired can be expected at scenario 2 and 3. This is contradictory to the Langelier saturation index.

The Puckorius Scaling Index predicts limited scaling under the chosen conditions with all scenarios. Lowering the calcium concentration in the blowdown to $44 \mu\text{mol.L}^{-1}$ would result in a $\text{PSI}=7$ (no scaling) for scenario 2 and 3. Lowering the calcium concentration in the blowdown to $12 \mu\text{mol.L}^{-1}$ would result in a $\text{PSI}=7$ for scenario 1.

Concerning the working range of the indices, the PSI may be most reliable (in comparison with LSI as Sathish Kumar et al. stated and in comparison to the Larson-Skold Index that was not developed for this pH range). If so, this gives an indication that neither scaling nor corrosion can be expected for the three scenario's. However, it may be reasonable to lower the calcium concentration a bit more than was assumed in previous calculations, to 0.05 mmol.L^{-1} or lower. This increases the costs by 0.5 to 1% compared to the costs

calculated for 0.1 mmol.L^{-1} Ca in the blowdown, while the scaling tendency may be further reduced.

6.2.5 Choice for alternative scenario

All three alternative scenarios do not offer an economically beneficial alternative compared to the current situation. However, as regulations regarding, e.g. zinc discharge may change and limit the use of the current chemical conditioning program, scenario 1 may be a good alternative. This increases costs by about 60% compared to the current situation but is the cheapest alternative providing a cooling water quality that prevents corrosion and scaling.

6.3 Results casus 2 (Tata Steel)

The current situation in the Tata case uses $26 \text{ m}^3\text{.h}^{-1}$ of raw water, resulting in $11 \text{ m}^3\text{.h}^{-1}$ blowdown. This system has a concentration factor of 2.4, which is not very high compared to e.g. the SABIC cooling system.

To decide what scenario would be most suitable for the Tata Steel case, a few choices are made and then a sensitivity analysis of a few parameters are shown as the effect of this parameter on the raw water use and on the costs.

Chosen parameters:

- Desired nr of cycles 5 (based on current cycles of 2.4)
- Calcium Hardness in Recirculating Cooling Water: 0.1 mmol.L^{-1} (required by client)
- Cation ion exchange softening: runtime 12 hours, bed height 2m (typical value)
- Anion exchange DOC removal: bypass 0%, runtime 12 hours, bed height 2m (typical value)

TABLE 6: WATER DEMAND OF THE CURRENT AND ALTERNATIVE TREATMENT SCENARIOS FOR WRK WATER FROM ANDIJK.

		Current Situation	Scenario 1	Scenario 2	Scenario 3
Raw water capacity	$\text{m}^3\text{.h}^{-1}$	26	19	19	19
Make-up water capacity	$\text{m}^3\text{.h}^{-1}$		19	19	19
Water losses make-up water treatment	$\text{m}^3\text{.h}^{-1}$		0.35	0.48	0.54
Relative costs	%	100	43	73	78

The chart below shows the breakdown of costs for the current situation and the situation at a desired concentration factor of 5, for three treatment scenarios using WRK water from Andijk (treated Lake IJssel water).

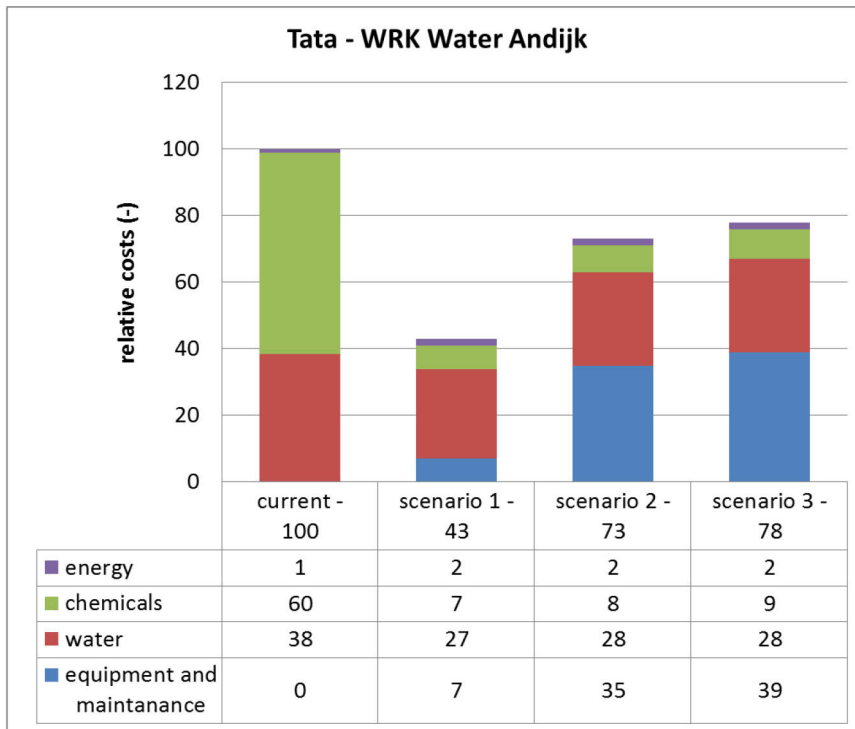


FIGURE 13: COSTS OF ALTERNATIVE SCENARIOS RELATIVE TO CURRENT SITUATION FOR WRK WATER FROM ANDIJK.

The WRK water from Nieuwegein is higher in calcium concentration, lower in sodium concentration and the alkalinity is higher (see appendix 1, Table 14). Other components have similar values as the WRK water from Andijk. The effect of this is that the costs are about 2% higher for the scenarios compared to the current situation than when water from Andijk is used. It has a negligible effect on the raw water use for all scenarios.

TABLE 7: RELATIVE COSTS OF TREATMENT FOR WRK WATER FROM NIEUWEGEIN

		Current Situation	Scenario 1	Scenario 2	Scenario 3
Relative costs	%	100	45	75	80

6.3.1 Cycles

The current system has 2.4 cycles. The number of cycles is limited by the chloride concentration as the direct and indirect cooling system are in contact with each other and a too high chloride concentration would result in pitting on the roll surface that are cooled by the direct cooling system. It is assumed however, that the cooling systems will be uncoupled and the chloride limitation is discarded in the indirect cooling system. Therefore the number of cycles can be increased. This will result in a major decrease in raw water use. Raw water intake decreases from 26 m³.h⁻¹ at 2.4 cycles, to 19 m³.h⁻¹ at 5 cycles, and to 17 m³.h⁻¹ at 10 cycles, for WRK water from Andijk. Costs also decrease when increasing the number of cycles. As the costs for water are significant part of the total costs, a reduction in water use will result in a reduction of costs.

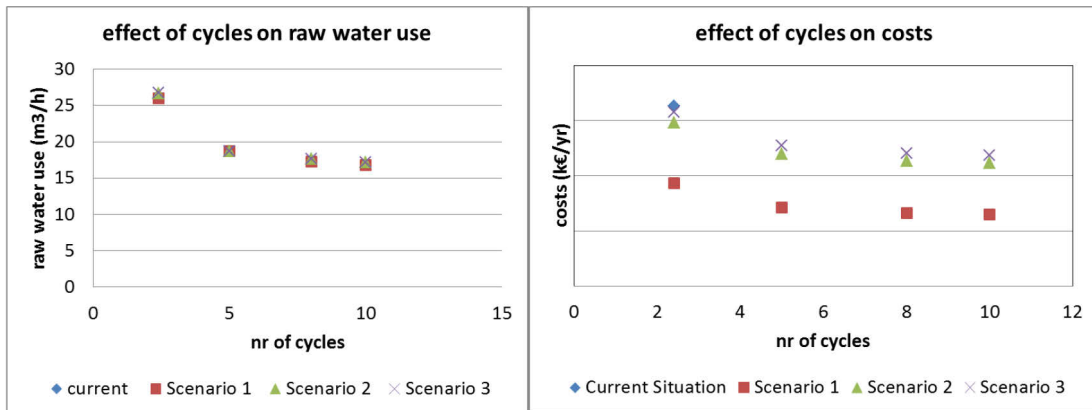


FIGURE 14: EFFECT OF CYCLES ON RAW WATER USE AND COSTS FOR TREATMENT FOR TATA USING ANDIJK WRK WATER.

6.3.2 Costs of chemicals, water and energy

The current costs of chemicals is quite high. When the supplier decides to reduce the costs by e.g. 50% (which is not likely), scenario 2 and 3 are as expensive as the current situation. The current costs for chemicals have to be omitted completely for the current scenario to costs same as scenario 1.

Much water can be saved as the number of cycles is low at this moment. When the price of water is decreased all scenarios benefit and become cheaper. The alternative scenarios remain more cost effective than the current scenario, even when the price is reduced. Even when the price of water is omitted completely the alternative scenarios are cheaper. When the water price doubles, this has more effect on the current situation than on the alternative scenarios as the total cost for water is currently higher than in the alternatives.

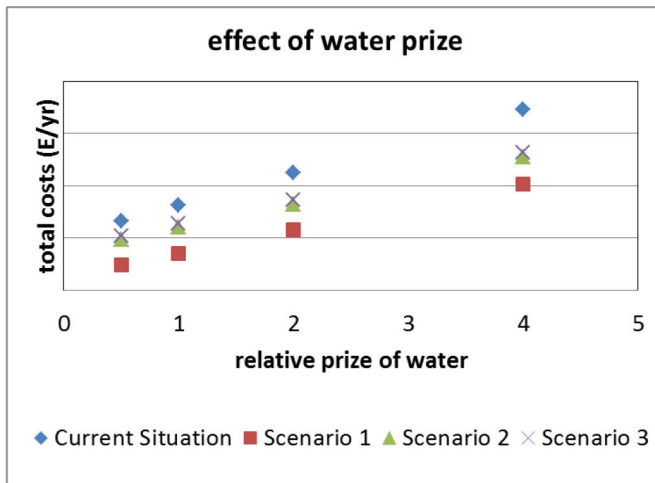


FIGURE 15: EFFECT OF WATER PRICE ON THE TREATMENT SCENARIOS FOR WRK WATER FROM ANDIJK AT 2.4 CYCLES CURRENTLY AND 5 CYCLES FOR SCENARIO 1,2 AND 3.

Energy contributes only for a small part to the total costs of the current system as well as for the alternative scenarios as the prize that Tata pays for electrical energy is very low. A change in energy prize does not affect the total costs significantly.

6.3.3 Variations in operation

The costs for scenario 1 and 3 are calculated without a bypass in the anion exchanger. However, one can choose to have a bypass here and not remove all sulphate and DOC. It has a negligible effect on the scaling potential of the water. The costs for scenario 1 and 3 would decrease slightly as the AEX can be designed a little smaller.

The TOC in the raw water is only 1.2 mg.L⁻¹. The anion exchanger would decrease this, assuming part of the TOC is negatively charged dissolved organic matter, such as humic acids. When this is not removed the TOC level in the tower will be approximately 6 mg.L⁻¹. Microorganisms use TOC to grow. Decreasing TOC levels will enhance the control of microorganisms but it is not possible to prevent biological growth completely.

6.3.4 Water quality of blowdown water

The amount of raw water required is similar for all three scenarios. However the composition of the three blowdowns is different due to the different treatments.

As the composition and effect of the added chemicals (proprietary chemicals) on the ions present is not quantified, it is not possible to provide the scaling or corrosion tendency for the current situation. The equilibrium pH and concentration of selected ions with the three scenarios are given in Table 8 and Figure 16.

TABLE 8: pH OF BLOWDOWN AT EQUILIBRIUM, TATA STEEL – WATER FROM ANDIJK

Scenario	Equilibrium pH in open system
1	9.3
2	9.2
3	9.2

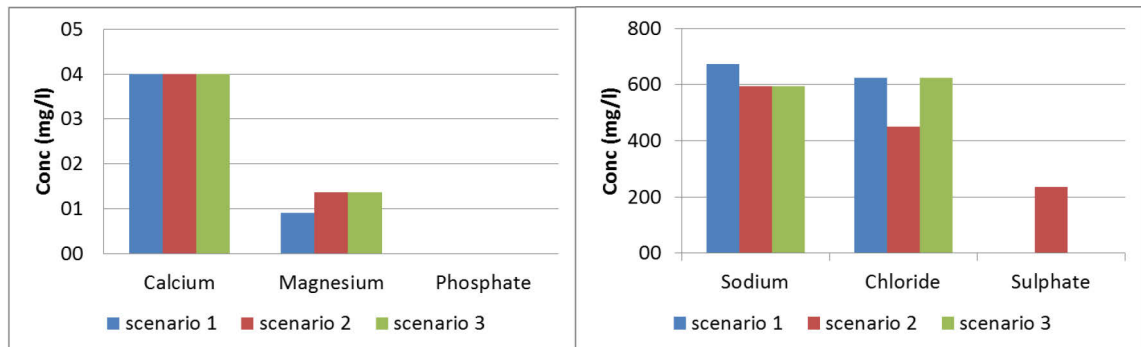


FIGURE 16: CONCENTRATIONS OF SELECTED IONS IN THE BLOWDOWN AFTER TREATING THE WRK WATER FROM ANDIJK FOLLOWING SCENARIO 1, 2 OR 3.

As can be seen from Figure 16 the concentrations of the ions do not vary much between the three scenarios. The Langelier saturation index, the Larson-Skold index and the Puckorius Scaling Index are calculated for each scenario in Table 9:

TABLE 9: SCALING INDICES FOR THE THREE ALTERNATIVE TREATMENT SCENARIOS, TATA STEEL – WATER ANDIJK

	Scenario 1	Scenario 2	Scenario 3
Langelier Saturation Index @ 60 °C	1.7	1.4	1.4
Larson-Skold Index	1.5	2.0	2.0
Puckorius Scaling Index	6.5	7.0	7.0

The Langelier Index gives positive values for all three cases, indicating that there is tendency for scaling. To reach a LSI of zero (borderline of scaling) for scenario 1 the calcium concentration would have to be brought down to $2 \mu\text{mol.L}^{-1}$ in the blowdown, indicating a required calcium concentration in the make-up water of $0.4 \mu\text{mol.L}^{-1}$. This is not possible to reach with the current set up. To bring the LSI to zero for scenario 2 and 3 the calcium concentration has to be maximum $3.6 \mu\text{mol.L}^{-1}$, requiring a concentration of $0.7 \mu\text{mol.L}^{-1}$ Ca in the make-up, which is also not possible.

The Larson-Skold Index indicates no corrosion (scenario 1) or a higher than desired corrosion rate, meaning no scaling (scenario 2 and 3).

The PSI indicates an equilibrium for CaCO_3 saturation. This means that a slight increase of calcium scaling would be observed but under the current conditions it is not expected to observe scaling.

Again looking at the working range of the indices, the PSI may be most reliable in a pH-range of 9.2 (scenario 2 and 3) to 9.3 (scenario 1), If so, this gives an indication that water is considered to be approximately at saturation equilibrium with calcium carbonate and therefore not indicating any scaling or corrosion tendency. However for scenario's 2 and 3 the upper limit (7) of the equilibrium range is reached, indicating that mild steel corrosion could become a problem.

6.4 Results PHREEQC-calculations

To compare the results of the model with a commercially available module, as proposed by the project team, the calculated composition of the blowdown water of both SABIC and Tata (WRK water Andijk) were entered in the online PHREEQC software available on the website Aquatic Chemistry for Engineers (http://ac4e.omnisis.nl/?page_id=30). This software calculates the scaling tendency of water with a certain composition. However some remarks have to be made with regard to this calculation. The total inorganic carbon concentration that is used for the calculation, differs from the one entered into the program. This affects the equilibrium pH that is calculated in PHREEQC. The pH given in Table 4 and Table 8 are the equilibrium pH's that will be present in the cooling towers based on the equilibrium of CO_2 in the outside air with the conditions in the cooling tower. A different pH as calculated with PHREEQC will lead to a different scaling potential.

The program also gives an imbalance in anions/cations while the calculation in the tool is based on a balanced cation and anion charge, resulting in a certain division of carbonate and bicarbonate, based on the TIC and pH. The main information from this program is the calcite precipitation potential. Waters tend to precipitate CaCO_3 when oversaturated with respect to CaCO_3 and tend to dissolve CaCO_3 if undersaturated with respect to CaCO_3 . SI values of 0 indicate equilibrium.

The calculated calcite precipitation potential for the **SABIC case**:

			Scenario 1	Scenario 2	Scenario 3
SI (calcite)	SI-c	-	0.93	0.78	0.80
Equilibrium-pH (pH _s or pH-Langelier)	pH-L	-	8.67	8.62	8.60
Calcite Precipitation Potential	CPP	mmol.kgw ⁻¹	0.09	0.08	0.08
Calcite Precipitation Potential at 60 °C	CPP-60	mmol.kgw ⁻¹	0.09	0.08	0.08
Calcite Precipitation Potential at 90 °C	CPP-90	mmol.kgw ⁻¹	0.09	0.08	0.08
Calcite Precipitation Potential at 100 °C	CPP-100	mmol.kgw ⁻¹	0.09	0.08	0.08

The calculated calcite precipitation potential for the **Tata case**:

			Scenario 1	Scenario 2	Scenario 3
SI (calcite)	SI-c	-	0.85	0.74	0.77
Equilibrium-pH (pH _s or pH-Langelier)	pH-L	-	8.45	8.46	8.43
Calcite Precipitation Potential	CPP	mmol.kgw ⁻¹	0.09	0.08	0.08
Calcite Precipitation Potential at 60 °C	CPP-60	mmol.kgw ⁻¹	0.09	0.08	0.08
Calcite Precipitation Potential at 90 °C	CPP-90	mmol.kgw ⁻¹	0.08	0.08	0.08
Calcite Precipitation Potential at 100 °C	CPP-100	mmol.kgw ⁻¹	0.09	0.08	0.08

The SI in all cases and scenarios is positive. This indicates that calcite scaling has to be expected. However the number is slightly different than one can expect as the equilibrium pH that PHREEQC calculates is lower than predicted by the tool.

Feedback from the designer of the calculation toolbox on the website Aquatic Chemistry for Engineers learned that the specific calculation model used, is not meant for industrial cooling water with pH-values above 9. Therefore the calculation for scenario 3 of the SABIC case was repeated using PHREEQC-software (version 2, 1999) from KWR. As the results from this calculation show calcite precipitation potentials that only differ slightly from those shown above (0.09 instead of 0.08), it is assumed that the latter can be regarded as indicative enough. Furthermore the recalculation also revealed that certain magnesium silicates (such as chrysotile and talc) show very high saturation indices (SI > 6).

7 Discussion, conclusions and recommendations

7.1 Discussion

In this study a calculation tool in Excel was developed to calculate the water quality of the recirculating water in a cooling system on the basis of different treatment scenario's for make-up water. These treatment scenarios were selected based on following criteria:

- Partial softening of the water instead of full softening
- Low percentage of water loss
- Low or moderate energy consumption
- Low or moderate capital and operational costs.

Scenarios were either based on cation ion exchange (CIEX) or a combination of CIEX and pellet softening. Anion ion exchange was added as a scavenger for organics.

To perform the calculation, the following data from a case study is required: size of the cooling system in volume or in cooling capacity (MWth), hours of operation, current and desired number of cycles of concentration (CoC), raw water analysis, costs of used chemicals, current chemical dosage in circulation cooling water and costs for energy, water and wastewater discharge.

The results of the study show that production of 'calcium free' make-up water is feasible and could theoretically lead to a situation in which the number of CoC can be increased substantially and in which conventional chemical conditioning of the water is no longer necessary with regard to scaling problems, as shown in the two case studies. PHREEQC calculations indicate high saturation indices for calcium carbonate and certain magnesium silicates. The calculations also show a low precipitation potential for calcium carbonate due to very low calcium concentrations. However for magnesium silicates no precipitation potential was calculated. As in all three water treatment scenario's for make-up water cation ion exchange (CIEX) is used, either as main treatment or as a polishing step, also magnesium (besides calcium) will be effectively removed. For that reason it is also unlikely that the positive saturation indices for magnesium silicates will result in actual scaling.

Only basic chemicals are needed for the production of the make-up water (i.e. sodium hydroxide, sodium carbonate and carbon dioxide). This study shows that the feasibility of the production of 'calcium free' make-up water increases when existing cooling systems have a low number of concentration cycles and/or high chemical cost for the existing conditioning program. The Excel-tool gives direct information on economic feasibility.

No specific process control, measuring or automation is needed to maintain the gain of 'calcium free' make-up water under practical conditions. The make-up water treatment system should provide a constant and guaranteed water quality with regard to the hardness parameters. In practice this can be easily controlled by using bypass facilities and in-line hardness measurement. In fact, for most industries softening of process water is a common practice.

This study is inconclusive with regard to the tendency of corrosion of (mild) steel in cooling systems when using 'calcium free' make-up water. The corrosion indices that were calculated in both case studies may show good results. However as the use of these indices to predict corrosion is already doubtful in a general sense (see paragraph 2.2), in this situation it is particularly questionable if the indices can be used under the specific circumstances at high pH and high alkalinity. Nevertheless, the high pH and relatively high carbonate concentrations in circulating water of the cooling system suggest good corrosion protection due to the formation of a protective FeCO_3 layer. So hypothetically, the softening of make-up water will lead to favourable conditions in the recirculation cooling water with respect to corrosion. Nevertheless, corrosion tests with the actual cooling water should confirm this hypothesis. At least coupon tests should be performed to determine the weight loss per unit of time. Preferably the polarization resistance of mild steel is measured in an accelerated corrosion test (e.g. according to or similar to ASTM G59) as this gives quick answers to whether the metal can be applied safely under the specific conditions in the cooling system. It is recommended to perform extensive research in a cooling water pilot plant (e.g. according to NEN-ISO 16784-2) in which the whole cooling water process can be simulated and the actual effects on heat exchanger pipes can be monitored including scaling, corrosion and microbiological effects.

It is important to keep in mind that corrosion protection at elevated pH-levels as discussed here only applies to iron (steel). Other metallic materials, like aluminium, may show opposite behaviour, i.e. increasing solubility at elevated pH (amphoteric). It is therefore essential to make a thorough inventory of metals or alloys applied in the cooling system as a whole including pumps, other accessories and their internals before alternative conditioning with fully softened make-up water is considered.

As can be expected the Excel-tool is also inconclusive with regard to microbiological effects in the cooling systems. In general high pH-values ($\text{pH} > 8$) will suppress microbiological growth as most bacteria prefer neutral pH. Bacteria not adapted to high pH may have a low growth rate and may be washed out of the cooling tower. Furthermore the application of ALEX as part of two treatment scenario's for make-up water will scavenge organic material and therefore reduce the biofilm forming tendency of the water. This will have a positive contribution to microbiological control in the cooling system. It also reduces the phosphate concentration, also resulting in limited microbiological growth. Due to the alkaline conditions in the cooling water the hypothesis is that even a small dose of a (oxidizing) disinfecting agent like peroxides or ozone should be enough to produce sufficient hydroxyl radicals to control the microbiology in the system effectively without formation of undesirable by-products such as halogenated hydrocarbons. This hypothesis has to be proven under practical conditions.

7.2 Conclusions

Model calculations in this study show that softening of make-up water for open cooling towers can lead to a reduction of water use and use of chemicals, as shown in the Tata case study. This is caused by the possibility to maintain a higher number of concentration cycles in the system and a phasing-out of traditional conditioning with proprietary chemicals.

Cooling water conditioning with (partial) softening of make-up water means a shift from complex conditioning chemicals to a conditioning system with only basic (bulk)chemicals such as sodium chloride, sodium or calcium hydroxide and sodium carbonate. In general this means that the environmental impact of cooling water blowdown will be strongly reduced. Furthermore this will lead to cost reductions on chemical consumption.

Model calculations in this study also show that especially owners of cooling systems with rather low numbers of cycles (< 5) and high costs for conditioning chemicals and service costs could have benefits from an investment in (partially) softening of the make-up water. Local conditions with regard to water availability and water costs as well as energy costs will have substantial impact on the economic feasibility.

Of the three scenarios for partial softening studied, the combination of CIEX/AIEX should be considered as most favourable due to the lowest operational and capital costs. This is mainly caused by the relatively high investment costs and subsequently high depreciation costs for the two scenario's using pellet softening.

For an existing cooling system with a capacity of 12.2 MWth the model calculations show that partial softening of the make-up water could lead to a reduction of operational costs of at least 22% (scenario 3) to 56% (scenario 1) on a yearly basis due to an increase of the number of concentration cycles from 2.4 until 5, and the use of more simple chemistry. In that case the payback time is in the order of magnitude of a year when CIEX/AIEX softening is chosen.

For a system with already a high amount of cycles and low operational costs, no benefits regarding costs and water use could be obtained by the alternative treatment methods.

The model calculations as such are inconclusive with regard to the effects of partial softening on corrosiveness and microbiological growth in the cooling tower system (as part of the cooling water treatment triangle), but for both phenomena the specific conditions created by partial softening of make-up water in the circulating cooling water itself (high pH, low TOC, low phosphate, low ammonia) should be considered as advantageous as they tend to suppress corrosiveness and microbiological growth in a natural way. Although on a low level, but disadvantageous is the fact that, due to softening, the natural zinc background-level of the makeup water will not reach the cooling tower water anymore. This results in the absence of the cathodic corrosion inhibition it normally implies.

7.3 Recommendations

When developing and designing future cooling systems the option of partial or preferably full softening of the make-up water should be part of the considerations as it might be a cheaper, more environmental friendly option and it will make the owner independent of complicated water conditioning regimes currently delivered by specialized water treatment companies.

The effects of partial and especially full softening of make-up water on corrosion and microbiological growth may look promising but they have to be confirmed under practical conditions. To study both phenomena at the same time performing a cooling water pilot test according to NEN-ISO 16784-2 would be strongly recommended. This specific standard describes a method for preliminary evaluation of the performance of treatment programmes for open recirculating cooling systems. It is based primarily on laboratory testing but the heat exchanger testing facility can also be used for on-site evaluation.

After confirmation of the positive effects of (partial) softening of make-up water on all three phenomena that form the virtual triangle of cooling water conditioning, the awareness of industries and water companies to change towards a more environmental friendly type of cooling water conditioning should be stirred up by redefining the BREF (dating from 2001) for cooling water conditioning.

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GE Water Factsheet GE 2020 EDR Systems

Appendix I Case data

Detailed information on both case studies is considered as classified and therefore not published in this public report.