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## APPLICATION OF REVERSE OSMOSIS IN TREATMENT OF WATER USED IN INDUSTRIAL COOLING CIRCUITS

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Cooling circuits are used in numerous industrial operations around the world. Water entering these systems must be constantly monitored and adjusted. Water treatment has two main objectives: to assign lowest amount of cooling water and to protect the cooling system from corrosion, biological and mineral deposits. The technology for water treatment has to develop together with industrial needs. Membrane separation processes represent appropriate processes for treatment of industrial cooling waters. The aims of this study was to determine the effectiveness of reverse osmosis (RO) membrane in removing compounds responsible for water hardness, and by using a computer program ROSA8 simulate 80% softening efficiency while continuously supplying plant with 880 m<sup>3</sup>h<sup>-1</sup> of cooling water.

**Key words:** cooling water, incrustations, reverse osmosis, modeling, ROSA8.

**Primjena reverzne osmoze u obradi vode za industrijske sustave hlađenja.** Rashladni sustavi se koriste u brojnim industrijskim operacijama diljem svijeta. Voda koja ulazi u te sustave mora biti stalno motrena i prilagođavana. Obrada vode ima dva glavna cilja: osigurati najmanju količinu vode za hlađenje i zaštititi rashladni sustav od korozije, bioloških i mineralnih naslaga. Tehnologija obrade vode mora se razvijati usporedno s industrijskim zahtjevima. Membranski separacijski procesi predstavljaju odgovarajuće procese za obradu industrijskih rashladnih voda. Ciljevi ovog istraživanja su utvrditi učinkovitost membrane za reverznu osmozu (RO) u uklanjanju spojeva odgovornih za tvrdoću vode, i pomoću računalnog programa ROSA8 simulirati učinkovitost omekšavanja od 80%, uz kontinuiran dotok u uređaj od 880 m<sup>3</sup> h<sup>-1</sup> vode za hlađenje.

**Ključne riječi:** modeliranje, naslage, reverzna osmoza, ROSA8, voda za hlađenje.

### INTRODUCTION

Probably every product in certain stages of production meets with water. Physical, chemical and biological properties of water depend on water structure and chemical composition. From the physical point of view substances in the water may be present as soluble ion (electrolytes), soluble nonionic (no electrolytes) or insoluble (floating). In water organic and inorganic substances are usually present. In industry water quality depends on the purpose of

water use. Water in industry is used for operations such as production, processing, washing, dissolving, cooling, transportation or it is directly used in the product. Industries often require large amounts of water with varying quality.

In general, most plants will require soft and clean water with neutral pH, with no iron and manganese, or only with their low content and without turbidity, color,

aggressive carbon dioxide, chloride and sulfate.

The aim of this study was to present removal of water hardness from water used for industrial cooling by membrane

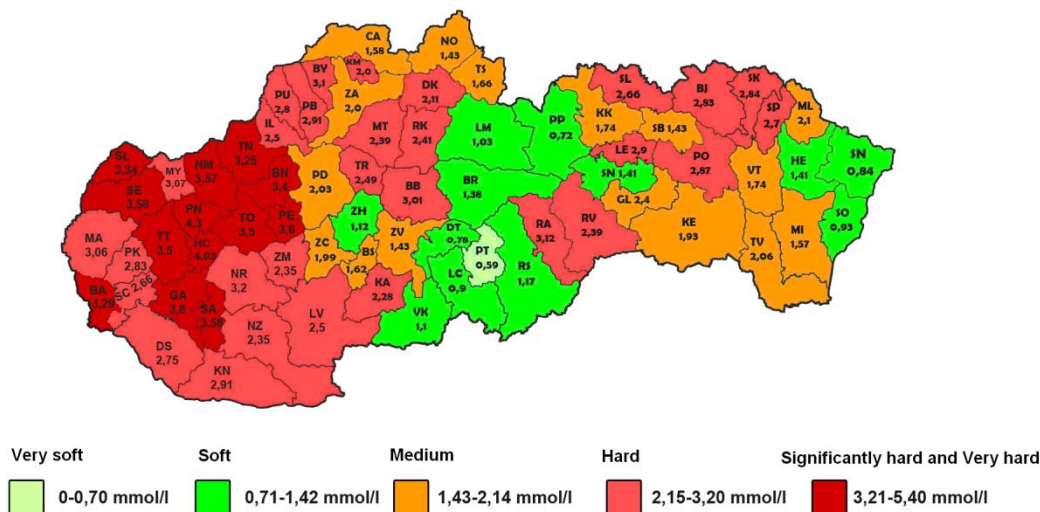
### Theoretical part

The main inorganic components in natural waters are usually calcium, magnesium and sodium cations. On the other hand mostly present anions are sulfates, chlorides and bicarbonates. The presence of these substances in water causes water hardness [1].

To evaluate the water hardness, water hardness table is used. It represents ratio between calcium and magnesium cations

separation process – reverse osmosis and by using computer program ROSA8, simulate treatment of  $880 \text{ m}^3\text{h}^{-1}$  water with 80% efficiency.

expressed in  $\text{mmol}^{-1}$ . According to this scale, water is: very soft when (0 to  $0.7 \text{ mmol}^{-1}$ ), soft when ( $0.71\text{-}1.42 \text{ mmol}^{-1}$ ), medium when ( $1.43$  to  $2.14 \text{ mmol}^{-1}$ ), hard when ( $2.15$  to  $3.2 \text{ mmol}^{-1}$ ), significantly hard when ( $3.21$  to  $5.4 \text{ mmol}^{-1}$ ) and very hard when (over  $5.4 \text{ mmol}^{-1}$ ). Major part of Slovakia (70%), has significantly hard or very hard water (Fig. 1) which has to be treated before used in industry [2].



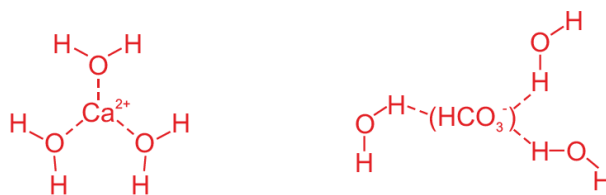
**Figure 1.** Water hardness in Slovakia [3]

**Slika 1.** Tvrdoća vode u Slovačkoj [3]

Major amount of water in industry is nowadays used for cooling. Cooling water is used to remove heat from objects or media such as heat exchangers, valves, hot gases and vapors. To use groundwater as cooling media chemical properties of water must meet criteria needed to prevent formation of

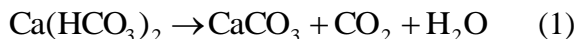
corrosion, biological and mineral deposits. [4, 5, 6]

Raw water is usually hard and it contains a lot of dissolved mineral salts - mainly calcium bicarbonate  $\text{Ca}(\text{HCO}_3)_2$  (Fig. 2).



**Figure 2.** Calcium bicarbonate dissolved in water  
**Slika 2.** Kalcijev hidrogenkarbonat otopljen u vodi

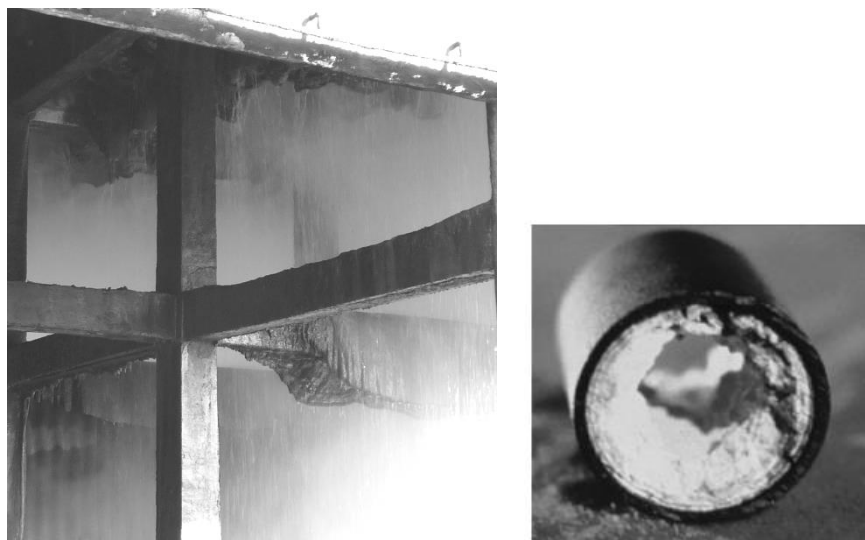
When raw water is heated above 40°C decomposition reaction (eq.1), of calcium bicarbonate  $\text{Ca}(\text{HCO}_3)_2$  will take place producing calcium carbonate  $\text{CaCO}_3$ , which will precipitate from water as gray



When water with flow rate of  $3.5 \text{ lmin}^{-1}$  and hardness of  $20^\circ\text{N}$  is heated to 40°C, 3.5 kg of calcium carbonate will precipitate from water. Because incrustations have a variety of negative impacts on technology in the process (insufficient heat transfer, reduction of the flow, weight of incrustations can damage the structure of the

scum creating incrustations, which has a tendency to stick to walls of pipes, tanks, valves and segments of cooling towers (Fig.3) [1, 5, 7, 8].

cooling towers) it is necessary to adjust water to prevent their occurrence by water softening. When applying softening, there is a need to comply with regulations. Very soft water is no desirable in technological processes either because it is aggressive and may cause corrosion [9].



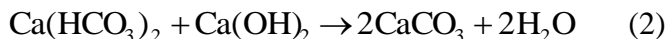
**Figure 3.** Incrustations in pipes and on cooling towers [5]  
**Slika 3.** Naslage u cijevima i rashladnim tornjevima [5]

Water hardness can be removed using two most common methods [1]:

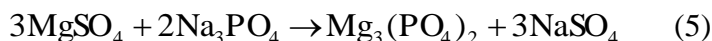
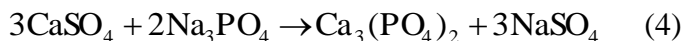
### Chemical methods

- *Using ion exchanger*
- *Using chemicals*

#### *Lime and soda*

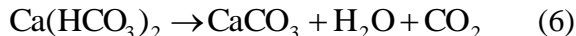


#### *Phosphates*



### Physical methods

- *Decarbonisation (heating)*



- *Membrane processes*

- nanofiltration
- reverse osmosis

### Membrane processes – Reverse osmosis

Reverse osmosis, also known as hyperfiltration, is a membrane process, which allows the transport of membrane solvent, while the soluble salts and low molecular weight components remain

trapped on the membrane whose pores have a size of only 0.0001 mm [10].

Flow rate across the reverse osmosis membrane  $J_w$  ( $\text{mols}^{-1}$ ) can be expressed as

$$J_w = A(\Delta P - \Delta \pi) \quad (8)$$

where A is a constant permeability of water,  $\Delta P$  (Pa) is the transmembrane

pressure difference and  $\Delta \pi$  (Pa) is the osmotic pressure difference of solution on

the side of membrane with low and high pressure [11].

In industries such as mining, electroplating, textile and paper industry,

chemical, electronics and pharmaceutical industries membrane processes are commonly used for removing unwanted pollutants from water [12].

## MATERIALS AND METHODS

Experimental part focused on two main goals:

### 1. Determine the effectiveness of water softening by chosen RO membrane

The aim of the first part was to determine the effectiveness of spiral wound

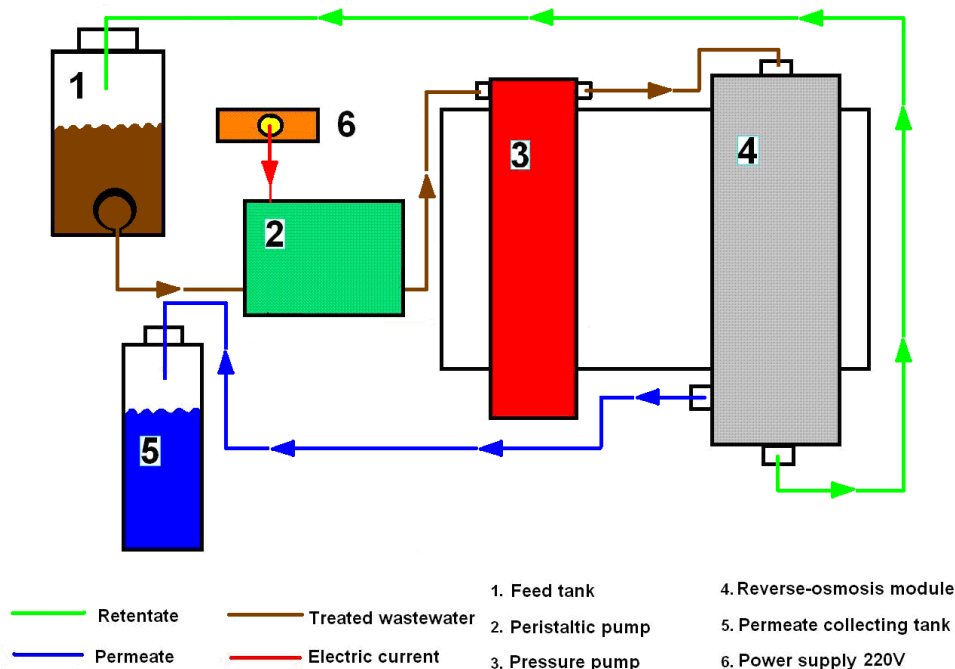
RO membrane composition type TW30-1812-50 [13] in reducing water hardness of water assigned for cooling valves in industrial operations. Before application of membrane process the chemical composition of water was analyzed by atomic absorption spectrometry (AAS). Results are shown in Table 1.

**Table 1.** Chemical composition of treated water  
**Tablica 1.** Kemijski sastav vode prijne obrade

Analyzed constituent	Water quality before applying RO treatment (mg l <sup>-1</sup> )
Ca <sup>2+</sup>	82.6
Mg <sup>2+</sup>	22.9
Na <sup>+</sup>	3.2
K <sup>+</sup>	2
NH <sub>4</sub> <sup>+</sup>	0.02
HCO <sub>3</sub> <sup>-</sup>	136
SO <sub>4</sub> <sup>2-</sup>	20.3
Cl <sup>-</sup>	6.38
NO <sub>3</sub> <sup>-</sup>	15.7
NO <sub>2</sub> <sup>-</sup>	0.01

After obtaining results, reverse osmosis module was set up according to the

following scheme (Fig. 4):



**Figure 4.** RO flow and connection schematic  
**Slika 4.** Shema toka RO

After building the module, a sample of ten liters of ground water was poured into the feed container. The container was connected with rubber tubing to peristaltic pump type *Heidolph pumpdrive 5106*. After peristaltic pump was put into operation, also pressure pump placed before the reverse-osmosis module started to operate. Water sample was due to applied pressure 5 bar pumped into the reverse-osmosis module where particular treatment took effect. The obtained permeate was discharged from the bottom of the reverse-osmosis module

## 2. Modeling of water softening process

The aim of the second part was to use the computer program ROSA8 from

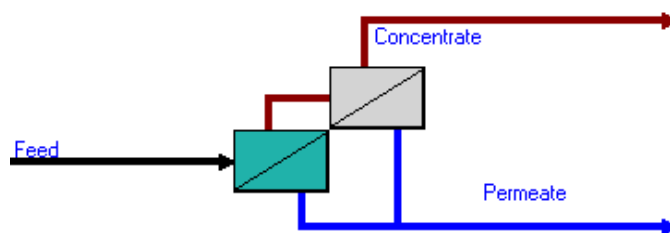
through secured rubber tubing into the collecting 0.5 l beaker. Retentate was discharged from the side of the module through secured rubber tubing back into feed container. After obtaining sufficient amount of permeate, the equipment was turned off and collected permeate was sent for analysis. This procedure has been repeated for 10 more times and values have been noted in a table. After the experiment the RO module was turned off, rinsed with distilled water and disassembled.

company DOW to simulate 80% softening efficiency while continuously supplying plant with  $880 \text{ m}^3\text{h}^{-1}$  of cooling water. Due to the need of supplying large volumes of purified water RO membrane SW30ULE

1725 has been chosen for this purpose. This type of membrane is designed for treatment of water with a high content of soluble substances, and has an extremely low energy consumption (ULE - ultra low energy), which is the big advantage when used for industrial purposes [14].

When creating a design for water treatment plant two-input model was

selected to secure maximum concentrated solution (Fig. 5). To supply large volumes of water design consisted of 240 membrane modules with a total active area of 38,460.6 square meters fitted into 30 pressure pipes. To ensure  $880 \text{ m}^3\text{h}^{-1}$  of cooling water  $1,100 \text{ m}^3\text{h}^{-1}$  of raw water is needed to be pumped under pressure 12.96 bar into RO for treatment.



**Figure 5.** RO membrane design for obtaining maximum solution concentration [1]

**Slika 5.** Dizajn RO membrane za postizanje maksimalne koncentracije otopine [1]

After obtaining basic parameters of designed water treatment plan, feed parameters of treated raw water from Tab. 1 and desired quality of permeate were inserted into program. When done simula-

tion was carried out. The obtained results (Tab. 3) from program ROSA8 were lower compared to results obtained from the first part of the experiment.

## RESULTS AND DISCUSSION

The first part 10 experiments focused on removing of water hardness by RO membrane type TW30-1812-50 were carried out. After obtaining sufficient volume, permeate was analyzed and the results are entered into Table 2.

According to the results obtained after application of RO significant improvements in water quality were achieved. Reduction in concentration of cations and anions responsible for water quality was determined by AAS. Attention

was focused on cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  and anions  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  where efficiency of cation removal from raw water was 92.41%, 85.73% and 74.75% respectively and for chosen anions 94.34%, 67.89% and 44.16% respectively. Excellent removal was noted for  $\text{NO}_3^-$  where average removal was 80.45% and also on ions  $\text{NH}_4^+$  and  $\text{NO}_2^-$  which were removed completely from raw water. On the other hand poor removal was noted for potassium cations, which removal efficiency was only 44.39%.

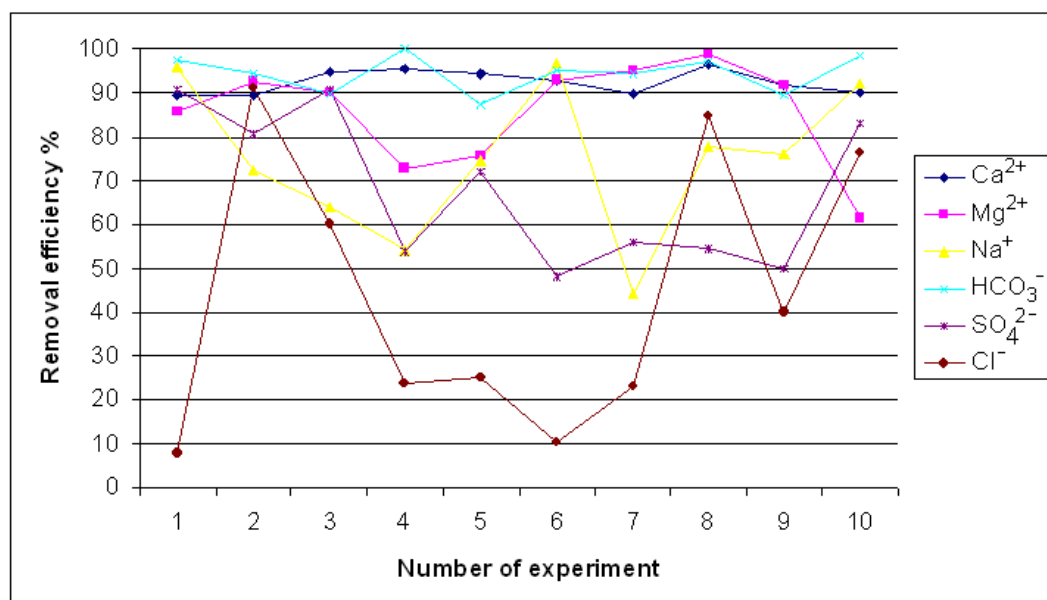
**Table 2.** Concentration of analyzed constituents after application of RO - TW30-1812-50

**Tablica 2.** Koncentracija sastojaka određenih nakon primjene RO - TW30-1812-50

Analyzed constituent	Water quality before applying RO treatment (mg <sup>l</sup> <sup>-1</sup> )	Water quality after applying RO treatment (mg <sup>l</sup> <sup>-1</sup> )									
		1	2	3	4	5	6	7	8	9	10
Ca <sup>2+</sup>	82.6	8.62	8.84	4.46	3.94	4.56	5.96	8.40	2.93	6.75	8.21
Mg <sup>2+</sup>	22.9	3.23	1.68	2.26	6.23	5.59	1.65	1.10	0.24	1.85	8.85
Na <sup>+</sup>	3.2	0.14	0.88	1.15	1.47	0.81	0.10	1.79	0.71	0.77	0.25
K <sup>+</sup>	2	0.22	1.52	1.95	1.20	1.38	1.23	1.72	0.03	1.81	0.07
NH <sub>4</sub> <sup>+</sup>	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HCO <sub>3</sub> <sup>-</sup>	136	3.54	7.46	13.90	0.06	17.41	6.91	7.55	3.64	14.51	2.05
SO <sub>4</sub> <sup>2-</sup>	20.3	1.88	3.98	1.85	9.37	5.66	10.52	8.99	9.25	10.21	3.47
Cl <sup>-</sup>	6.38	5.89	0.57	2.55	4.88	4.77	5.73	4.92	0.98	3.84	1.50
NO <sub>3</sub> <sup>-</sup>	15.7	5.44	0.72	4.40	1.72	0.18	2.05	0.45	5.79	5.67	4.27
NO <sub>2</sub> <sup>-</sup>	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

From the results obtained and also shown in Fig. 6 it can be concluded that reverse osmosis is suitable membrane process, which can find application in reducing the hardness from water planned to

use for cooling equipment in industrial plants. This result is also supported by other scientific works in this particular field [15, 16].


**Figure 6.** Efficiency in removal ions responsible for water hardness

**Slika 6.** Učinkovitost uklanjanja iona odgovornih za tvrdoću vode



In the second part we simulated conditions for RO membrane SW30ULE-1725 needed to reach 80% softening efficiency while continuously supplying plant with  $880 \text{ m}^3\text{h}^{-1}$  of cooling water.

From obtained results (Tab. 3) it can be seen that the application of reverse osmosis had a significant impact on

concentration of cations and anions responsible for water hardness 98-99% decrease of ions. RO membrane SW30ULE-1725 is therefore appropriate to use for reduction of water hardness from raw water assign for cooling equipment in industrial plants.

**Table 3.** Concentration of analyzed constituents after application of RO - SW30ULE-1725  
**Tablica 3.** Koncentracija sastojaka određenih nakon primjene RO - SW30ULE-1725

Analyzed constituent	Water quality before applying RO treatment ( $\text{mg l}^{-1}$ )	Water quality after applying RO treatment ( $\text{mg l}^{-1}$ )				
		Concentrate		Permeate		Total
		1 stage	2 stage	1 stage	2 stage	Final treatment
$\text{Ca}^{2+}$	<b>82.6</b>	198.19	412.08	0.22	0.65	<b>0.34</b>
$\text{Mg}^{2+}$	<b>22.9</b>	54.36	113.03	0.06	0.18	<b>0.09</b>
$\text{Na}^+$	<b>3.2</b>	7.76	15.46	0.09	0.26	<b>0.13</b>
$\text{K}^+$	<b>2</b>	4.65	9.35	0.11	0.31	<b>0.16</b>
$\text{NH}_4^+$	<b>0.02</b>	0.05	0.1	0	0	<b>0</b>
$\text{HCO}_3^-$	<b>136</b>	323.14	664.34	0.64	1.24	<b>0.79</b>
$\text{SO}_4^{2-}$	<b>20.3</b>	48.72	101.42	0.01	0.04	<b>0.02</b>
$\text{Cl}^-$	<b>6.38</b>	277.39	576.85	0.28	0.83	<b>0.43</b>
$\text{NO}_3^-$	<b>15.7</b>	36.93	75.25	0.54	1.55	<b>0.81</b>
$\text{CO}_3^-$	<b>0.41</b>	2.39	8.69	0	0	<b>0</b>

## CONCLUSION

Cooling circuits are part of industrial plants and they play important role in transferring heat away from warmed up media or equipment used in technological processes. To ensure faultless operation demanded amount of water with certain quality criteria has to be delivered. The aim of the work was to assess the possibility of effective removal of ions responsible for water hardness and formation of scale deposits by membrane processes, namely RO.

In conducted laboratory experiments RO membrane TW30-1812-50 was used. After performed experiments significant reduction in the concentration of cations and anions responsible for water hardness was observed. The average efficiency in removal of monitored ions was as follow: For cations:  $\text{Ca}^{2+}$  92.41%,  $\text{Mg}^{2+}$  85.73% and  $\text{Na}^+$  74.75%. For anions:  $\text{HCO}_3^-$  94.34%,  $\text{SO}_4^{2-}$  67.89% and  $\text{Cl}^-$  44.16%. Excellent removal was noted for  $\text{NO}_3^-$  where average removal was 80.45% and also on ions  $\text{NH}_4^+$  and  $\text{NO}_2^-$ .

which were removed completely from raw water. On the other hand poor removal was noted for potassium cations, which removal efficiency was only 44.39%.

In the second part simulation on RO membrane SW30ULE-1725 was conducted. The aim of this simulation was to simulate 80% softening efficiency of chosen RO membrane while continuously supplying 880 m<sup>3</sup>h<sup>-1</sup> of cleaned water which would be later used as cooling water in plant. For simulation computer program ROSA8 from DOW was used.

Program calculated that for supplying plant with m<sup>3</sup>h<sup>-1</sup> of cleaned water, volume of

1,100 m<sup>3</sup>h<sup>-1</sup> of raw water needs to be pumped into SW30ULE-1725 RO membrane under pressure 12.96 bar. For given amount of raw water 240 membrane modules with a total active area of 38,460.6 m<sup>2</sup> fitted into 30 pressure pipes would be needed. When simulation was done significant concentration reduction of cations and anions (average of 98-99%) responsible for water hardness was observed. This again confirmed the effectiveness and suitability of the RO process for treatment of raw water for industrial cooling purposes.

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