ANNALS OF FACULTY ENGINEERING HUNEDOARA
– International Journal of Engineering
Tome XI (Year 2013) – FASCICULE 4 (ISSN 1584 – 2673)

[1.] Martin SMORADA, [2.] Ružena KRÁLIKOVÁ, [3.] Hana SOKOLOVÁ, [4.] Ján POLÁK

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

[1-4.] TECHNICAL UNIVERSITY OF KOŠICE, FACULTY OF MINING, ECOLOGY, PROCESS CONTROL & GEOTECHNOLOGIES, INSTITUTE OF MONTANEOUS SCIENCES AND ENVIRONMENTAL PROTECTION, PARK KOMENSKÉHO 19, 043 84 KOŠICE, SLOVAKIA

ABSTRACT: 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^3 / h of cooling water.
KEYWORDS: cooling water, incrustations, reverse osmosis, modeling, ROSA8

INTRODUCTION

Probably every product in certain stages of production meets with water. 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. Water quality depends on the purpose of water use. 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 sulphate.

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 (nonelectrolytes) or insoluble (floating). In water organic and inorganic substances are usually present. 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. [12]

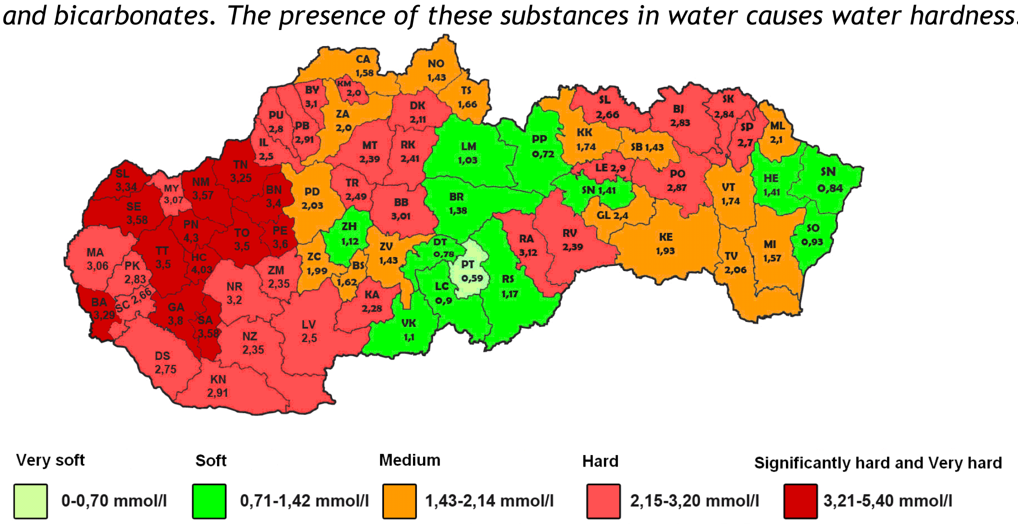

Figure 1. Water hardness in Slovakia [6]

To evaluate the water hardness, water hardness table is used. It represents ratio between calcium and magnesium cations expressed in mmol / l. According to this scale, water is: very soft when (0 to 0.7 mmol / L), soft when (0.71-1,42 mmol / L), medium when (1.43 to 2.14 mmol / l), hard when (2.15 to 3.2 mmol / L), significantly hard when (3.21 to 5.4 mmol / L) and very hard when (over 5.4 mmol / l). Major part of Slovakia (70%), has significantly hard or very hard water (see Figure 1) which has to be treated before used in industry. [15]

THEORETICAL PART

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 met criteria needed to prevent formation of corrosion, biological and mineral deposits. [10, 3, 11]

Raw water is usually hard and it contains a lot of dissolved mineral salts - mainly calcium bicarbonate Ca $(HCO_3)_2$ (see Figure 2).

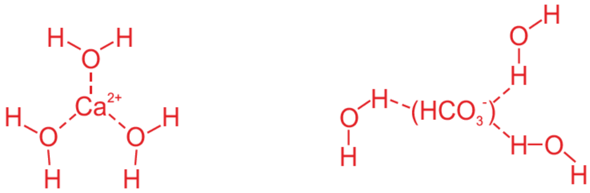

Figure 2. Calcium bicarbonate dissolved in water

When raw water is heated above 40°C decomposition reaction (equation 1), of $Ca(HCO_3)_2$ will take place producing calcium carbonate $CaCO_3$, which will precipitate from water as gray scum creating incrustations, which has a tendency to stick to walls of pipes, tanks, valves and segments of cooling towers (see Figure 3) [12,3,8,7].

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O \quad (1)$$

When water with flow rate of 3.5 l / min. and hardness of 20° N is heated to 40°C, 3.5 kg of $CaCO_3$ 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 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. [4]

Figure 3. Incrustations in pipes and cooling towers [3]

Water hardness can be removed using two most common methods [12]:

Chemical methods:

- *Using ion exchanger*
- *Using chemicals*
  - *Lime and soda*

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O \quad (2)$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2H_2O \quad (3)$$

- *Phosphates*

$$3CaSO_4 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 3NaSO_4 \quad (4)$$

$$3MgSO_4 + 2Na_3PO_4 = Mg_3(PO_4)_2 + 3NaSO_4 \quad (5)$$

Physical methods:

- *Decarbonisation (heating)*

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2 \quad (6)$$

$$Mg(HCO_3)_2 = MgCO_3 + H_2O + CO \quad (7)$$

- *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. [9]

Flow rate across the reverse osmosis membrane can be expressed as

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

where A is a constant permeability of water expressed as

$$A = \frac{D_w K_w C_{w0} v_w}{lRT} \quad (9)$$

which is a function of concentration on the side of membrane with high pressure. ΔP is the transmembrane pressure difference and Δπ is the osmotic pressure difference of solution on the side of membrane with low and high pressure. [5]

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. [2]

MATERIALS AND METHODS

Experimental part focused on two main goals:

- ***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 [14] 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

Analyzed constituent	Water quality before applying RO treatment (mg/l)
Ca^{2+}	82,6
Mg^{2+}	22,9
Na^{+}	3,2
K^{+}	2
NH_4^{+}	0,02
HCO_3^{-}	136
SO_4^{2-}	20,3
Cl^{-}	6,38
NO_3^{-}	15,7
NO_2^{-}	0,01

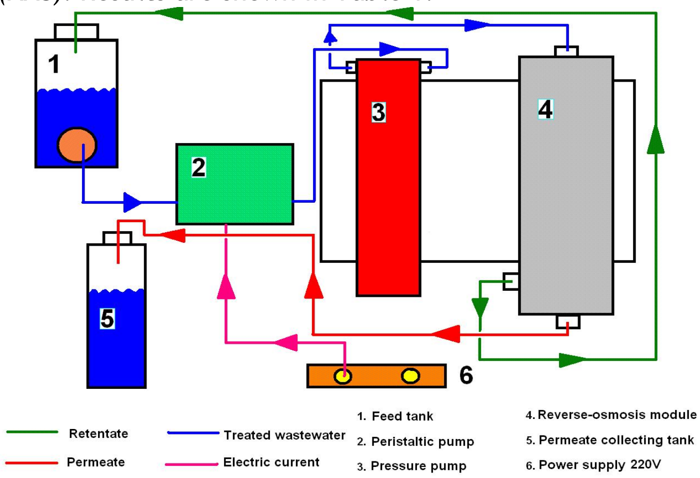

Figure 4. RO flow and connection schematic

After obtaining results, reverse osmosis module was set up according to the following scheme (see Figure 4).

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 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.

- ***Modeling of water softening process***

The aim of the second part was to use the computer program ROSA8 from DOW to simulate 80% softening efficiency while continuously supplying plant with 880 m^3 / h 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. [13]

When creating a design for water treatment plant two-input model was selected to secure maximum concentrated solution (see Figure 5). To supply large volumes of water design consisted of 240 membrane modules with a total active area of 38460.6 square meters fitted into 30 pressure pipes. To ensure 880 m^3 / h of cooling water 1100 m3/h of raw water is needed to be pumped under pressure 12.96 bar into RO for treatment.

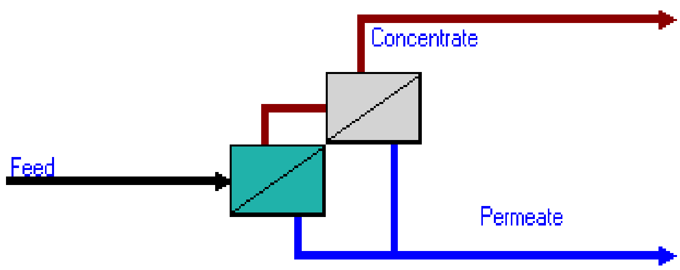

Figure 5. RO membrane design for obtaining maximum solution concentration [12]

After obtaining basic parameters of designed water treatment plan, feed parameters of treated raw water from Table 1 and desired quality of permeate were inserted into program. When done simulation was carried out. The obtained results (see Table 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 the permeate was analyzed and the results are entered into Table 2.

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

Analyzed constituent	Water quality before applying RO treatment (mg/l)	Water quality after applying RO treatment (mg/l)									
		1	2	3	4	5	6	7	8	9	10
Ca^{2+}	82,6	8.62	8.84	4.46	3.94	4.56	5.96	8.40	2.93	6.75	8.21
Mg^{2+}	22,9	3.23	1.68	2.26	6.23	5.59	1.65	1.10	0.24	1.85	8.85
Na^{+}	3,2	0.14	0.88	1.15	1.47	0.81	0.10	1.79	0.71	0.77	0.25
K^{+}	2	0.22	1.52	1.95	1.20	1.38	1.23	1.72	0.03	1.81	0.07
NH_4^{+}	0,02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HCO_3^{-}	136	3.54	7.46	13.90	0.06	17.41	6.91	7.55	3.64	14.51	2.05
SO_4^{2-}	20,3	1.88	3.98	1.85	9.37	5.66	10.52	8.99	9.25	10.21	3.47
Cl^{-}	6,38	5.89	0.57	2.55	4.88	4.77	5.73	4.92	0.98	3.84	1.50
NO_3^{-}	15,7	5.44	0.72	4.40	1.72	0.18	2.05	0.45	5.79	5.67	4.27
NO_2^{-}	0,01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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 Ca^{2+}, Mg^{2+} and Na^{+} and anions HCO^{3-}, SO_4^{2-} and 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 NO3- where average removal was 80.45% and also on ions NH4 + and NO2- 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%.

From the results obtained and also shown in Figure 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. [16,1]

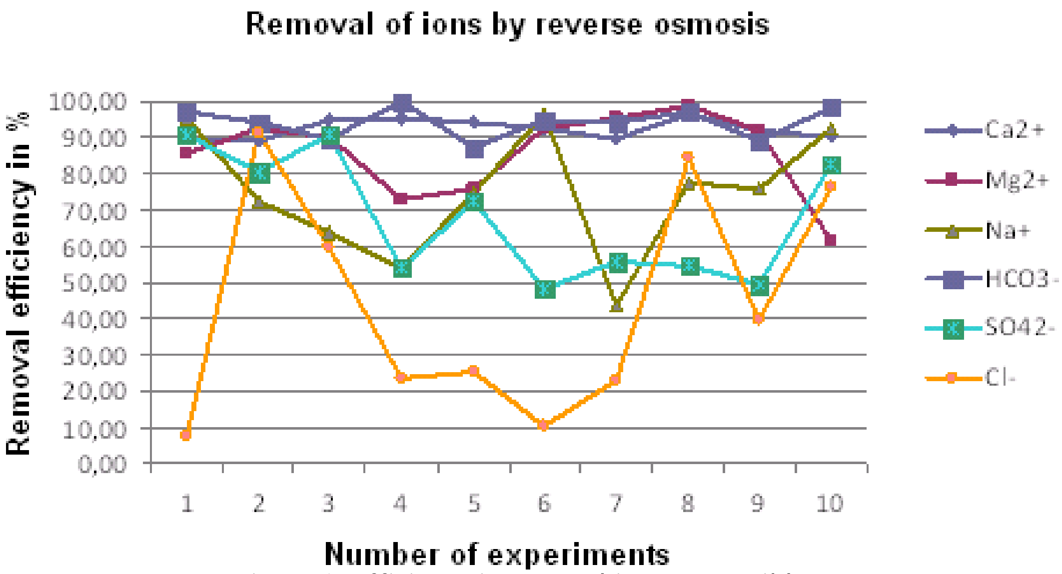

Figure 6. Efficiency in removal ions responsible for water hardness

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

From obtained results (see Table 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

Analyzed constituent	Water quality before applying RO treatment (mg/l)	Water quality after applying RO treatment (mg/l)				
		Concentrate		Permeate		Total
		1 stage	2 stage	1 stage	2 stage	Final treatment
Ca^{2+}	82,6	198,19	412,08	0,22	0,65	0,34
Mg^{2+}	22,9	54,36	113,03	0,06	0,18	0,09
Na^{+}	3,2	7,76	15,46	0,09	0,26	0,13
K^{+}	2	4,65	9,35	0,11	0,31	0,16
NH_4^{+}	0,02	0,05	0,1	0	0	0
HCO_3^{-}	136	323,14	664,34	0,64	1,24	0,79
SO_4^{2-}	20,3	48,72	101,42	0,01	0,04	0,02
Cl^{-}	6,38	277,39	576,85	0,28	0,83	0,43
NO_3^{-}	15,7	36,93	75,25	0,54	1,55	0,81
CO_3^{-}	0,41	2,39	8,69	0	0	0

CONCLUSIONS

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: Ca^{2+} 92.41%, 85.73% Mg^{2+} and Na^{+} 74.75%. For anions: HCO^{3-} 94.34%, SO_4^{2-} 67.89% and Cl^{-} 44.16%. Excellent removal was noted for NO^{3-} where average removal was 80.45% and also on ions NH_4^{+} and 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^3/h 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 880 m^3/h of cleaned water, volume of 1100 m^3/h 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 38460.6 m^2 fitted into 30 pressure pipes would be needed. When simulation was done significant reduction in the concentration of cations and anions responsible for water hardness - an average of 98-99% were observed. This again confirmed the effectiveness and suitability of the RO process for treatment of raw water for industrial cooling purposes.

Acknowledgments

This article was created as a part of the project KEGA 032TUKE-4/2012.

REFERENCES

[1] Altmana, J.S., Jensenb, P.R., et. all: Membrane treatment of side-stream cooling tower water for reduction of water usage. Desalination, 285 (2012) 177–183

[2] Chai, X., Chen, G., Yue, P., Mi, Y.,: Pilot scale membrane separation of electroplating waste water by reverse osmosis. Journal of Membrane Science. 123 (1997) 235-242

[3] Demadis, D.K., Mavredaki, E., Stathoulopoulou, A., Neofotistou, E., Mantzaridis, Ch.,: Industrial water systems: problems, challenges and solutions for the process industries. Desalination, 213 (2007) 38-46

[4] Ghizellaoui, S., Euvrard, M.,: Assessing the effect of zinc on the crystallization of calcium carbonate. Desalination, 220 (2008) 394-402

[5] Greenlee, F.L., Lawler, F.D., Freeman, D.B., Marrot, B., Moulin, P.,: Reverse osmosis desalination: Water sources, technology, and today's challenges. Water Research, 43 (2009) 2317-2348

[6] How hard is our water: CONETIX.SK [online]. 2013. Aktualizované 20-3-2013 [cit 2013-03-14]. Dostupné na internete: < http://bocianiehniezdo.conetix.sk/content/ pranie-v-tvrdej-vode-alebo-aka-tvrda-je-moja-voda/>.

[7] Huff, F.G.,: Aquifer composition and the tendency toward scale-deposit formation during reverse osmosis desalination — examples from saline ground water in New Mexico, USA. Desalination, 190 (2006) 235–242

[8] *Jefferies, M., Comstock, D.,: Predicting calculating scaling tendency in membrane plants. Desalination, 139 (2001) 341-344*

[9] *JELÍNEK, L., et. all.,: Desalinační a separační metody v úpravě vody. Praha: VŠCHT, 2008. 171s. ISBN 978-80-7080-705-7*

[10] *Ross, F.F., Whitehouse, W.J.,: Cooling towers and water quality. Water Research , Volume 7, Issue 4, (1973), 623–631*

[11] *Ružena Králiková: Čistejšia výroba - nové kritérium posudzovania projektov 1999. In: Envirautom. - Košice : TU-SjF, 1999 Roč. 4, č. 1 (1999), s. 231-235.*

[12] *SINCERO, P.A., SINCERO,A.G.,: Physical-chemical Treatment of Water and Wastewater. IWA Publishing, 2002. 784s. ISBN 1-58716-124-9*

[13] *SW30ULE-1725 DOW Reverse osmosis membrane: NSF.COM [online]. 2013. Aktualizované 20-3-2013 [cit 2013-03-14]. Dostupné na internete: < http://www.nsf.com/Certified/consumer/ >.*

[14] *TW30-1812-50 DOW Reverse osmosis membrane: LENNTECH.COM [online]. 2013. Aktualizované 20-3-2013 [cit 2013-03-14]. Dostupné na internete: < http://www.lenntech.com/Data-sheets/Dow-Filmtec-TW30-1812-50.pdf >.*

[15] *Water hardness: MOJAVODA.SK [online]. 2013. Aktualizované 20-3-2013 [cit 2013-03-14]. Dostupné na internete: < http://www.mojavoda.sk/voda-clanky/tvrdost-vody >.*

[16] *Xianguo, H., Yanga, H.L.,: Experimental evaluation on concentrating cooling tower blowdown water by direct contact membrane distillation. Desalination. (2013)*

ANNALS of Faculty Engineering Hunedoara

– International Journal of Engineering