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TREATMENT OF WASTEWATER TO MEET THE REQUIREMENTS FOR COOLING WATER SYSTEMS IN JORDAN'S NUCLEAR PLANTS

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Scaling and corrosion associated with the use of natural hard water in cooling towers during recirculation pose great problems from both economical and technical points of view, such as decreased system efficiency and increased frequency of chemical cleaning. Treated municipal wastewater (MWW) is a promising alternative to freshwater as power plant cooling system makeup water, especially in arid regions. In this work, hybrid systems of salt precipitation (SP), nanofiltration (NF) and reverse osmosis (RO) were investigated, as potential pretreatment processes for wastewater reuse as cooling water in the planned Jordan nuclear power plants. The As-Samra wastewater was used to calculate the potential of carbonate and sulfate scale formation. The results were compared to scale potentials from Palo Verde wastewater. Four cases were investigated; SP, NF, SP-RO and NF-RO. The SP pretreatment cases showed the highest monovalent to divalent ratio because of a high removal of Ca and Mg and addition of Na from the chemicals of the SP step. The NF pretreatment cases, showed the lowest calcium sulfate scale potential and this potential decreases with the % pretreatment. The scale amount increases very slightly with concentration times when the SP and NF product is desalinated by RO step.

Keywords: cooling water, nuclear plants, wastewater treatment, scale deposition

1. INTRODUCTION

The primary purpose of cooling water systems is to cool process fluids so the plant can operate at maximum efficiency. Lack of attention to cooling systems can result in plant shut-downs due to scaling and the corrosion of critical heat exchangers, increased risk of *Legionellosis*, large quantities of water wastage, and increased water costs, wastewater costs and chemical treatment costs. The problems associated with the use of water for cooling purposes can be attributed to one or more of impurities such as hardness causing salts (i.e. Ca and Mg that deposit as scale on heat transfer surfaces), silica, iron, microbiological species, oils and dissolved gases. Scaling and corrosion associated with the use of natural hard water in cooling towers during recirculation pose great problems from both economical and technical points of view, such as decreased system efficiency and increased frequency of chemical cleaning (Kavitha et al., 2011). Consequently there are three components to a cooling water treatment program: scale and deposit control, corrosion control, and microbiological control.

The two major types of technologies that are used for the desalination of recirculating cooling water (RCW) can be broadly classified to (El-Zanati and El-Khatib, 2007; Fritzmann et al., 2007):

- Thermal process such as: Multi-Stage Flash Distillation (MSF), Multiple-Effect Distillation (MED), and Vapor Compression Distillation (VCD). These processes have rarely been used for desalination of RCW, because of the high costs involved.

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- Membrane technologies such as: Electrodialyis/Electrodialysis Reversal (ED/EDR), and Reverse Osmosis (RO).

In power plants, RO technology has gained significant popularity and its application for treatment of RCW is increasing. But RO membranes can be particularly susceptible to scaling and fouling and regular membrane cleaning is necessary. The key issue for successful RO plant operation is proper feed water pre-treatment. The pretreatment for RO typically consists of lime softening and filtration. However, membrane fouling has resulted frequently from poor softener/clarifier performance. At present, pretreatment such as coagulation, sedimentation, sand filtration, microfiltration (MF) and ultrafiltration (UF) are increasingly being used for the removal of suspended solids and biological matter from RCW before RO systems (El-Zanati and El-Khatib, 2007; Fritzmann et al., 2007).

Fouling in general can be described as the formation of unwanted deposits on a heat transfer surface. Mineral fouling or the formation of scales such as calcium carbonate is common in cooling-water applications, where pure water evaporates to remove heat gained from condenser (Cowan and Weintritt, 1976). Hence, circulating cooling water quickly becomes supersaturated even if make-up water is soft. As the supersaturated cooling water is heated inside condenser, the calcium ions precipitate due to the inverse solubility characteristics of $CaCO_3$ salt. The degree of scaling is dependent on the calcium hardness and bicarbonate alkalinity in the cooling water:

$$Ca^{2+} + HCO_3^{-} \leftrightarrow CaCO_3 + H^{+} \tag{1}$$

A number of methods exist to control scale formation. These are: (i) acid addition to reduce the pH, (ii) increasing the solubility of scale-forming substances, (iii) removing calcium hardness from the water, and (iv) precipitating the scale-forming substances. Calcium can be removed by lime soda softening, ion exchange or membrane filtration (nanofiltration or reverse osmosis).

A number of studies have been conducted to better understand mineral fouling process and its mitigation in cooling systems.

The performance of coagulation pretreatment and the effect of coagulation pretreatment on membrane distillation (MD) process for desalination of recirculating cooling water (RCW) were studied (Wang et al., 2008). RCW was desalinated by MD process after pretreatment by coagulation, precision filtration, acidification and degassing. Pre-coagulation of RCW with poly-aluminum chloride (PACl) coagulant improves the elimination of total organic carbon (TOC), and total phosphorus (TP) substances.

Treated municipal wastewater (MWW) is a promising alternative to freshwater as power plant cooling system makeup water, especially in arid regions (Li et al., 2011; Liu et al., 2012). A number of power plants already use MWW as makeup water in their recirculating cooling water systems. These power plants typically use MWW only as a fraction of the total makeup water needed or only after significant additional treatment to obtain better water quality. A prominent challenge for the successful use of MWW for cooling is potentially severe mineral deposition (scaling) on pipe surfaces. Li et al. (2011) conducted theoretical, laboratory, and field work to evaluate the mineral deposition potential of MWW and its deposition control strategies under conditions relevant to power plant cooling systems. Polymaleic acid (PMA) was found to effectively reduce scale formation when the makeup water was concentrated four times in a recirculating cooling system. To inhibit scale formation in cooling water systems, polyacrylic acid was synthesised and characterised by Kavitha et al. (2011). The ability of the synthesised polymer to mitigate the calcium carbonate and calcium sulphate scale formation was tested through chemical screening and electrochemical impedance techniques. It showed slightly better antiscaling properties, even at higher temperatures and *pH* for both $CaCO_3$ and $CaSO_4$ scales, compared to a commercial product.

Kim and Cho (2011) investigated the benefit of filtration in the physical water treatment used to mitigate mineral scale build-up in heat exchangers. Two types of filters were used: a 5-μm cartridge fabric filter and a sand filter with 20-μm pores, both of which were used at a side-stream loop in a laboratory cooling tower. Heat transfer fouling experiments were conducted using a double-pipe heat exchanger with cooling water at 5 and 8 cycles of concentration with a make-up water hardness of 200–240 ppm. The test results demonstrated that the filtration enhanced the performance of the physical water treatment (PWT) synergistically, resulting in a near initial peak heat transfer performance in the double-pipe heat exchanger. In order to prevent or mitigate the fouling problem, various PWT methods have been applied using one of the following means: magnetic fields, electric fields, alteration of surface charges, mechanical disturbance such as ultrasound, vortex flows, and sudden pressure changes. The effect of underwater pulsed spark discharge on the precipitation of dissolved calcium ions was investigated by Yang et al. (2010) Water samples with different calcium hardness were prepared by continuous evaporation of tap water using a laboratory cooling tower. It was shown that the concentration of calcium ions dropped by 20-26% after10 min plasma treatment, compared with no drop for untreated cases. It was hypothesised that the main mechanisms for the plasma-assisted calcium carbonate precipitation might include electrolysis, local heating in the vicinity of plasma channel and a high electric field at the tip of plasma streamers, inducing structural changes in the electric double layer of hydrated ions.

Membrane technologies are widely used for desalination. Pressure driven membranes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). These membranes are listed in order from lower to higher of removal capacity and energy requirements, with RO being the most energy intensive, but able to remove monovalent ions. In general, NF rejects multi-valent ions well. Altman et al. (2012) conducted a pilot study to determine whether membrane treatment on a side stream of recirculating cooling-tower water could reduce overall water usage and discharge. The treated permeate was returned to the cooling tower while the concentrate was discharged to the sanitary sewer. Flow rates, pressures and water chemistry were monitored.

Nanofiltration (NF) has been recognized as a potential pressure-driven membrane process, which is finding wide spread use in the treatment of water and wastewater, particularly for separating multivalent solutes from feed solutions containing univalent salts which could transport across the membrane. The separation characteristics of these membranes have been exploited in the treatment of hard water to produce soft water, which is used in many industrial applications. Negatively charged polyamide thin-film-composite nanofiltration membranes have been used to treat the sodium-enriched water, particularly cooling tower water, to separate hardness producing solute like $MgSO_4$ from univalent (Nanda et al., 2008). The flux declined with increasing ionic strength of the feed solution. The method was applied to the treatment of some tap waters, altering the ionic strength and pH, to show the validity of the findings.

Jordan is one of the driest countries in the world. In considering nuclear power plant design and citing, securing access to water and minimizing water usage are important factors. As Jordan continues to refine its feasibility study and national requirements, it is very helpful in this stage to investigate the possibility of using wastewater as a source to meet the requirements for the cooling system. In this work, hybrid systems of salt precipitation (SP), nanofiltration (NF) and reverse osmosis (RO) were investigated as potential pretreatment processes for wastewater reuse as cooling water in the planned Jordan nuclear power plants. Softening of wastewater treatment plant (WWTP) effluent is a necessity. Softening is performed to minimise scaling potential, minimise water use, and minimise quantity of water required. The As-Samra wastewater was used to calculate the potential of carbonate and sulfate scale formation. The results were compared to scale potentials from Palo Verde wastewater. Palo Verde is the only nuclear power plant (NPP) in the world that is located far from a large body of water; it uses treated wastewater to meet its cooling needs.

2. FOULING ON MEMBRANE AND HEAT TRANSFER SURFACES

Fouling, the accumulation of rejected constituents on the membrane surface, is a serious problem, resulting in permeate flux decline or increased transmembrane pressure. Inorganic fouling or scaling is the formation of hard mineral deposits on the membrane or heat transfer surfaces as the feed water becomes supersaturated by inorganic salts. The various operating conditions, influence scale formation, are: pH, temperature, operating pressure, permeation rate, flow velocity, and presence of other salts or metal ions. Importantly, concentration polarisation plays a vital role in scale formation in high pressure membrane systems, as it leads to elevated salt concentrations near the surface of the membrane where particles may deposit.

Al-Rawajfeh (2007, 2008) developed a model to simulate the simultaneous release of CO_2 with the deposition of $CaCO_3$ and investigated their mutual release-deposition relationship in MED (Al-Rawajfeh, 2007) and in the flash chambers in MSF distillers (Al-Rawajfeh, 2008). The influence of CO_2 injection on the carbonate chemistry and the scale formation were also studied (Al-Rawajfeh and Al-Amaireh, 2009). The model calculates the $CaCO_3$-$Mg(OH)_2$ (alkaline) scale in brine chambers, because part of the scale is deposited there and will be reduced from the total scale precipitate or reduce the ions available to precipitate $CaSO_4$ scale inside the tubes when it is recycled with the make-up. Details on the CO_2 release and alkaline scale modeling can be found in previous works (Al-Rawajfeh, 2007; Al-Rawajfeh, 2008; Al-Rawajfeh and Al-Amaireh, 2009; Al-Rawajfeh et al. 2008). The model was verified by comparing the calculated results of the model with experimental results from Hasson and Perl (1981) and model results of Chan and Ghassemi (1991a, 1991b). Hasson and Perl's model gives average values. Chan and Ghassemi's model fits very well the experimental values at low calcium ion concentrations, but it shows high deviation at higher concentrations.

High pressure membrane desalination processes; i.e. nanofiltration (NF) and reverse osmosis (RO), are the prevalent desalination operation for various feed types and accounts for 55% (RO – 51%; NF – 4%) of the total water produced by desalination (44.1 Mm^3/day) (Antony et al., 2011). The unique property of RO membranes to reject inorganic species, while passing relatively pure water has led to its widespread use in desalination. Achieving high product recovery with less fouling formation and minimizing process cost is a major challenge in RO operation. The water product recovery for membrane desalination has to be sufficiently high, i.e. ≥70–80% to be economically feasible.

The total fouling load and scale type percentage were calculated using ROIFA-4 software which has been developed specifically for the RO inorganic fouling assessment. It has been subjected to many laboratory tests and field investigations and found to be satisfactory (El-Manharawy and Hafez, 2011). El-Manharawy and Hafez (2000) presented a comprehensive study covering water chemical analyses, and XRF analysis of scale samples from different RO-plant cases. The obtained results indicated a strong relationship between the feed water chemical characteristics and the generated scale potential and type. The “Dehydration Model” (El-Manharawy and Hafez, 2002) provides a reasonable explanation of the inorganic fouling mechanism occurring during RO membrane dewatering. This study revealed that the solubility of carbonate and sulfate minerals increases, in different ways, with the increase of chloride concentration. The mathematical correlation between the theoretical and experimental fouling results proved that the proposed model is accurate and considered as a valuable tool for predicting inorganic fouling load.

3. RESULTS AND DISCUSSION

3.1. Pretreatment processes and wastewater chemistry

Pre-treatment of the cooling water involves reduction of salinity and hardness and hence reducing or in some cases eliminating scale forming species to a certain level. This will increase the efficiency of the process, reduce the pumping power (in reverse osmosis (RO) systems), reduce or eliminate the scale and consequently reduce the cost. The cooling water should be sampled daily to monitor the individual scale-forming ions and major constituents. Normally, blowdown (BD) is based on chloride or total dissolved solids (TDS) and solubility of scale-forming compounds. The BD rate is adjusted to control the concentrations of these chemicals. In this work, hybrid pretreatment processes including salt precipitation (Al-Rawajfeh and Al Zarooni, 2008) and nanofiltration (SP-NF) (Hussain and Al-Rawajfeh, 2009; Hussain, 2007) will be investigated. Nanofiltration (NF) has been recognised as a potential pressure-driven membrane process, which is finding wide spread use in the treatment of water and wastewater, particularly for separating the multivalent solutes from the feed solutions containing univalent salts which could transport across the membrane. The separation characteristics of these membranes have been exploited in the treatment of hard water to produce soft water, which is used in many industrial applications. Precipitation process deals with supersaturating the saline solution by addition of chemical reagents which results in the precipitation of some of the salts in the wastewater. The purpose of co-precipitation process is to reduce the concentration of dissolved salts (solutes) in the feed water (solution), such as seawater, brackish water or industrial brine solutions so that it can be more effectively desalinated and higher percentage of fresh water can be recovered from it. Alkalisation to $pH > 10$ by NaOH is a potential choice for treatment of high sulfate feeds by efficient removal of Ca^{2+} and Mg^{2+} ions. It can economically remove the scale forming ions and can strongly disinfect the treated feed.

Figure 1 illustrates the SP-NF pre-treatment processes. They were divided into four cases:

- Case A (Figure 1A): % SP, where % feed is treated by SP and the product mixed with the rest (100-%SP) feed from the wastewater and the product passed to a desalination unit.
- Case B (Figure 1B): % NF, where % feed is treated by NF and mixed with the rest (100-%NF) from the wastewater and the product passed to a desalination unit.
- Case C (Figure 1C): % (SP-RO), where % feed is treated by SP followed by RO and mixed with the rest (100-%) from the wastewater.
- Case D (Figure 1D): % (NF-RO), where % feed is treated by NF followed by RO and mixed with the rest (100-%) from the wastewater.

Table 1. The maximum concentrations of the different species in the pretreated feed

Case	Wastewater	Pre-treatment [%]	Ca^{2+}	Mg^{2+}	Na^{+}	HCO_3^-	SO_4^{2-}
A (SP)	As-Samra	0	95	60	230	520	26
		100	1.9	0.6	634.8	10.4	11.44
	Palo Verde	0	68	30	200	201	183.7
		100	1.36	0.3	552	4.02	80.828
B (NF)	As-Samra	100	28.025	10.56	163.3	195	3.198
	Palo Verde	100	20.06	5.28	142	75.375	22.595
C (SP-RO)	As-Samra	100	0.019	0.006	38.088	0.312	0.1144
	Palo Verde	100	0.0136	0.003	33.12	0.1206	0.8083
D (NF-RO)	As-Samra	100	0.2803	0.1056	9.798	5.85	0.032
	Palo Verde	100	0.2006	0.0528	8.52	2.2613	0.226

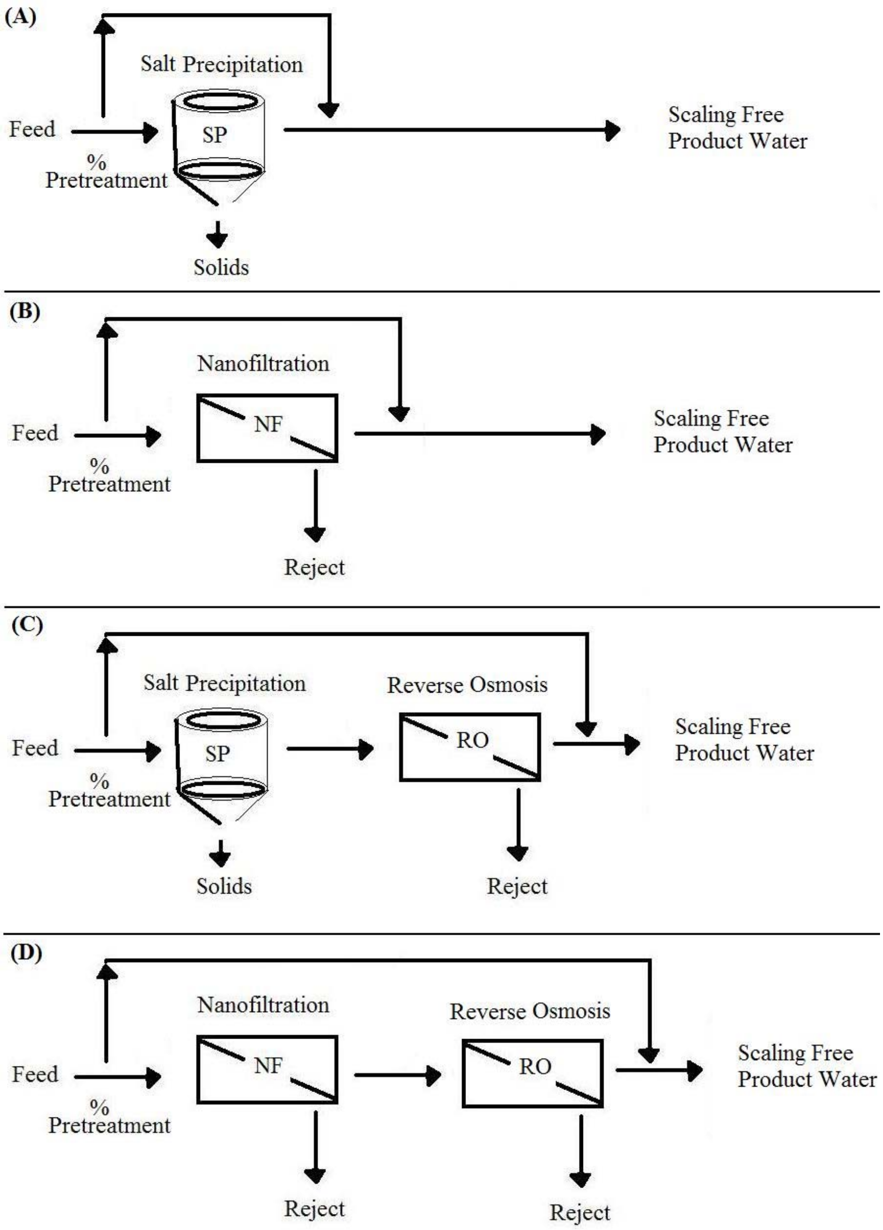

Fig. 1. The different cases of SP-NF-RO pre-treatment

Table 1 shows the chemical composition of the feed wastewater. The original concentration is the concentration of the wastewater from the As-Samra wastewater plant, Jordan. The chemical composition of Palo Verde (USA) wastewater is shown for comparison. The As-Samra concentrations of calcium, magnesium, sulfate, and bicarbonate are 95, 60, 26, and 520 ppm, and for Palo Verde wastewater are 68, 30, 183.7, and 201 ppm, respectively. The salt precipitation pretreatment significantly decreases the concentration of these species but adds monovalent (Na^+) ions. Nanofiltration significantly decreases the divalent ions, but has less influence on monovalent ions. Alkalinity predominates the low-chloride water types while sulfate excessively occupies the higher chloride types. The sodium ion is mostly proportional with chloride at the higher salinity water types, but with lower chloride it seems that the calcium ion can be accepted better than sodium and magnesium. Also, magnesium is favored over calcium in the high salinity water types (El-Manharawy and Hafez, 2011).

The chemistry of the original feed (As Samra wastewater) and the SP-NF-RO treated feed, sulfate ratio to alkalinity (SO4/Alk) and the sodic/calcic ratio of monovalent to divalent ions (Na+K/Ca+Mg) are shown in Figure 2 (Hydranautics NITTO DENKO ESNA1-LF2 nanofiltration and DOW Chemical RO-

4040-FF reverse osmosis spiral wound membranes). Case A, of SP pretreatment, shows the highest monovalent to divalent ratio because of the high removal of Ca and Mg and addition of Na from the chemicals of the SP step. Case B, of NF pretreatment, shows the lowest sulfate scale potential and this potential decreases with the % treatment. El-Manharawy and Hafez (2000; 2002) indicated a strong relationship between the feed water chemical characteristics and the generated scale type, as well as its potential in RO plants. It was clear that the molar ratio (SO4/HCO3) is gradually and positively correlated with the chloride molar concentration for most of the natural waters. The variation in most of natural waters is so tight that SO4/HCO3 ratio ranges between 0 to ~20. For example, River Nile water is ~0.12, brackish ground waters 1-5, salty waters 5-10, oceanic water ~12, and Red Sea water ~13. Some anomalous sulfate-enriched groundwater brines could be higher than 30.

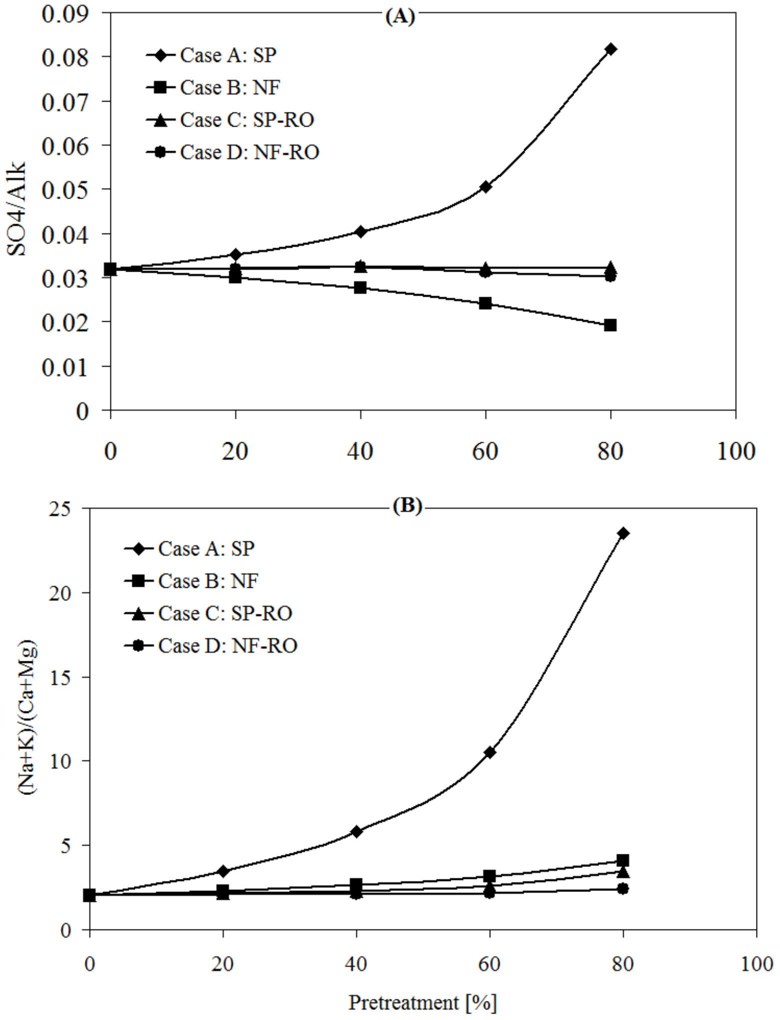

Fig. 2. The chemistry of the original and the treated wastewater, (SO4/Alk) and (Na+K/Ca+Mg)

3.2. Carbonate and sulfate scale deposition

Since heat removal from condenser tubes requires the evaporation of feed water, the concentration of mineral ions such as calcium and magnesium in the circulating cooling water increases with time. Even though the makeup water is relatively soft, the continuous circulation eventually increases the hardness of the water due to pure water evaporation. These mineral ions can cause various problems, including the loss of heat transfer efficiencies in condensers and pipe clogging due to scale formation.

The total fouling load (*TFL*) is the sum of the individual fouling flux of the investigated salts. The individual fouling load (*FL*) obtained from multiplying the compound analytical molar concentration (in mM/kg) by the estimated fouling fraction ($F_f = 0\text{-}1$) at a given Cl^- concentration:

$$FL_{Scale} = [Scale] \cdot F_f \tag{2}$$

where F_f can be calculated from a formula similar to

$$F_f = a[Cl^-] + b \tag{3}$$

where a and b are constants depending on the scale type and the chloride ion concentration level. They can be found elsewhere (El-Manharawy and Hafez, 2011).

The fouling flux (F_x) of individual foulant could be predicted from its concentration in brine that flows in a 1 mm thickness layer spreading over 1 cm^2 of membrane surface per time, which is normally around 1 s:

$$F_x = F_L \cdot F_f \cdot A_C \times 10^{-3} \tag{4}$$

where (F_x): number of hardness atoms found in 0.1 cm^3 per unit time (second), (F_L) is the fouling load, in mM/0.1 cm^3, (F_f) is the fouling fraction, and (A_C) is the Avogadro's number.

Figure 3 shows the total fouling load for the four SP-NF-RO pretreatment cases. The values were calculated using ROIFA-4A software (El-Manharawy and Hafez, 2011). Figure 4 shows the percentage of the scale type; sulfate or carbonate in the four investigated cases. Cases A and C show the lowest total fouling load (TFL). The percentage scale type is constant in cases B and D; it is > 97% carbonate scale, while in cases A and C, the change in scale type percentage is very small, carbonate scale decreases slightly with the percentage pretreatment and sulfate scale increases.

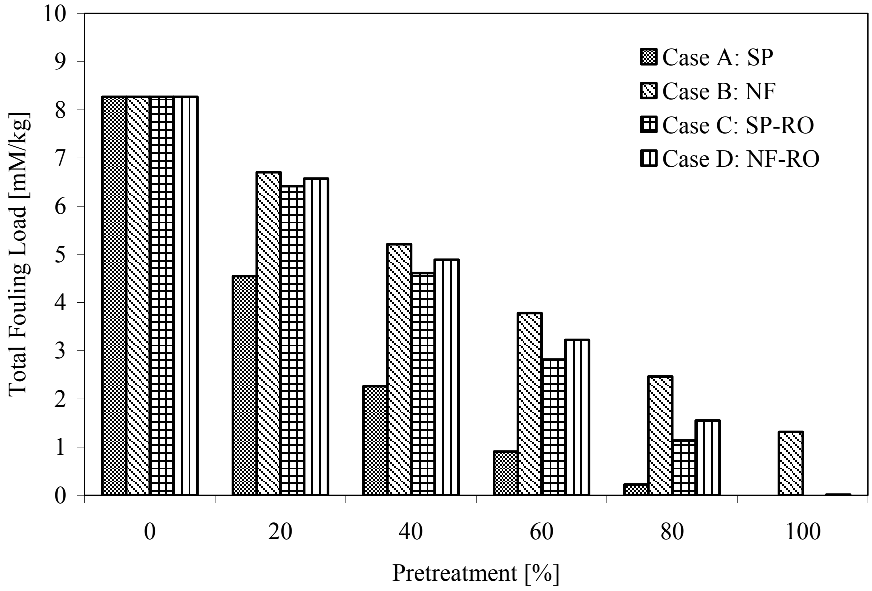

Fig. 3. The total fouling load (TFL) for the four pretreatment cases

Accompanying the drop of the calcium ion concentration, the *pH* of the treated water is normally decreasing, possibly because of the liberation of H^+ ions according to Equation 1 (Snoeyink and Jenkins, 1982). In a saturated condition, the forward reaction of the precipitation of $CaCO_3$ does not take place as both calcium and bicarbonate ions are hydrated. When water is supersaturated and sufficient energy is supplied, the water molecules are disturbed or become freed from the ions, resulting in the precipitation of $CaCO_3$. The backward reaction of Equation 1 shows the dissolution of solid calcium carbonate by acid, a process that takes place during acid cleaning of scaled heat exchangers. In reality, precipitation and dissociation reactions are much more complicated. There combination and crystallization rates of calcium and carbonate ions are controlled by three reactions. Reaction 1 (Equation 5) relates the dissociation of bicarbonate ions into the hydroxyl ions OH$^-$ and carbon dioxide (ΔG = 43.60 kJ/mol)

$$\mathrm{HCO_3}^- \leftrightarrow \mathrm{OH}^- + \mathrm{CO_2} \tag{5}$$

The forward reaction indicates the dissociation of the bicarbonate ions, which is the most critical step from the precipitation process. Bicarbonate ions do not cause any harm in terms of scaling as long as they remain bicarbonate ions. Reaction 1 (Equation 5) shows the first step in the conversion of bicarbonate to carbonate ions. The presence of hydroxide ions is best indicated by a local increase in pH, and carbon dioxide typically evolves from the water as gas over time. In Reaction 2 (Equation 6) hydroxyl ions produced from reaction 1 further react with existing bicarbonate ions, producing carbonate ions and water (ΔG = -20.9 kJ/mol)

$$HCO_3{}^- + OH^- \leftrightarrow H_2O + CO_3{}^{2-} \tag{6}$$

Reaction 3 (Equation 7) is the reaction between calcium and carbonate ions, resulting in the precipitation and crystallisation of calcium carbonate particles (ΔG = -47.7 kJ/mol)

$$\mathrm{Ca}^{2+} + \mathrm{CO_3}^{2-} \leftrightarrow \mathrm{CaCO_3} \tag{7}$$

As heat is removed via the evaporation of pure water at cooling tower, the need for make-up water is about 28 m^3/min, to compensate the water loss through evaporation, wind drift and blowdown (El-Wakil, 1984). Assuming that the make-up water has a $CaCO_3$ hardness of 75 mg/L, the total amount of $CaCO_3$ it brings into the cooling tower is 2100 g/min:

$$28\,\frac{\mathrm{m}^3}{\mathrm{min}} \times 75\,\frac{\mathrm{mg}}{\mathrm{L}} \times (10^3\ \mathrm{L/m}^3 \times 10^{-3}\ \mathrm{g/mg}) = 2100\,\frac{\mathrm{g}}{\mathrm{min}} \tag{8}$$

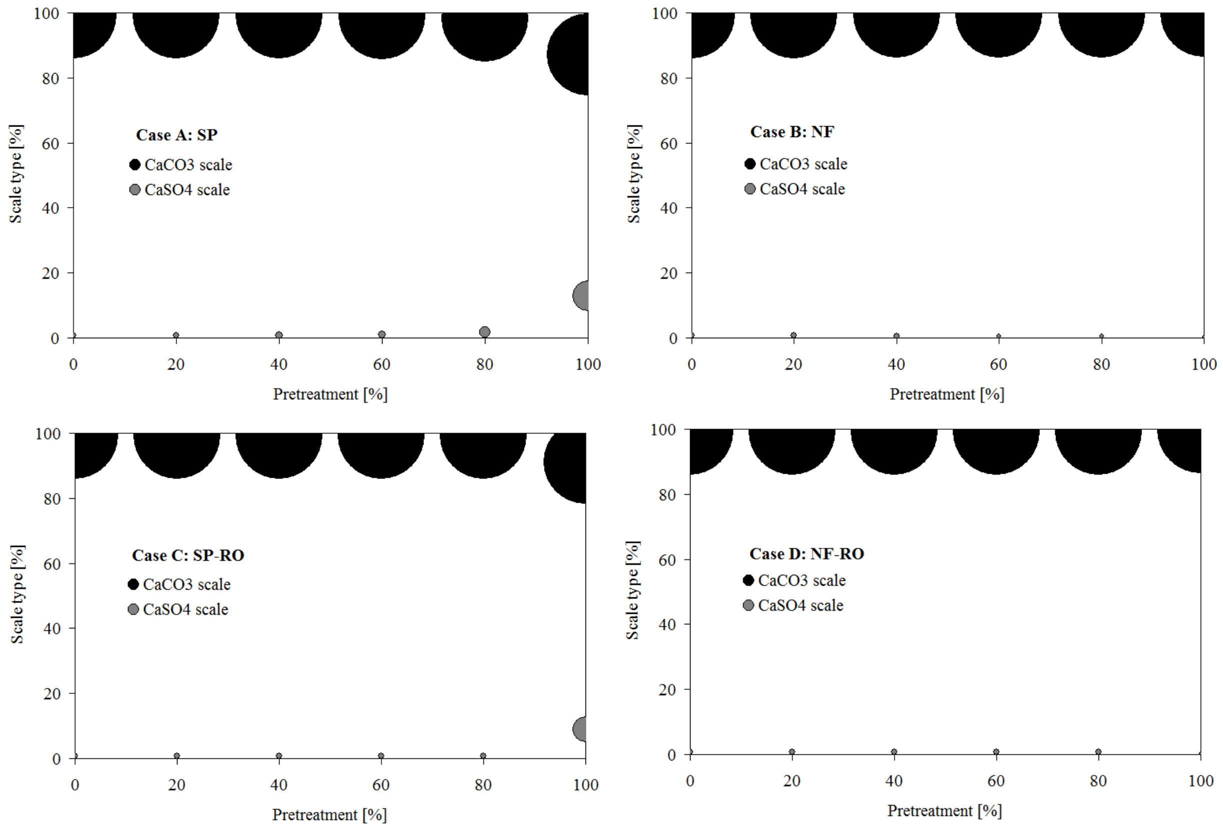

Fig. 4. The percentage of the scale type in the four investigated cases

Table 2 shows a comparison between the wastewater chemistry, total fouling load, and scale type percentage of As Samra and Palo Verde wastewaters. Palo Verde shows lower total fouling load but higher sulfate scale potential because of the high original sulfate concentration. As Samra wastewater shows higher total fouling load because of high carbonate scale potential.

Table 2. The wastewater chemistry, total fouling load, and scale type percentage of As-Samra and Palo Verde wastewaters

Case	Wastewater	Pre-treatment [%]	(SO4 / Alk)	Na+K / Ca+Mg	Total Fouling Load [mM/kg]	Carbonates [%]	Sulfates [%]
A (SP)	As-Samra	0	0.0318	2.0675	8.265756	99.3287	0.6713
		100	0.6962	383.12	0.001502	87.0963	12.9037
	Palo Verde	0	0.5805	2.9681	2.752396	89.0055	10.9945
		100	12.862	518.85	0.001389	26.7597	73.2403
B (NF)	As-Samra	0	0.0318	2.0675	8.265756	99.3287	0.6713
		100	0.0104	6.1701	1.315778	99.7787	0.2213
	Palo Verde	0	0.5805	2.9681	2.752396	89.0055	10.9945
		100	0.1904	8.5836	0.394869	96.1066	3.8934
C (SP-RO)	As-Samra	0	0.0318	2.0675	8.265756	99.3287	0.6713
		100	0.2329	2292.72	0.000009	91.0928	8.9072
	Palo Verde	0	0.5805	2.9681	2.752396	89.0055	10.9945
		100	4.2661	3113.08	0.000007	36.6508	63.3492
D (NF-RO)	As-Samra	0	0.0318	2.0675	8.265756	99.3287	0.6713
		100	0.0035	31.3475	0.012801	99.8295	0.1705
	Palo Verde	0	0.5805	2.9681	2.752396	89.0055	10.9945
		100	0.0624	51.6325	0.003081	97.1341	2.8659

Calcium sulfate scale potential (*CSSP*) (Al-Rawajfeh, 2011; Al-Rawajfeh et al. 2012; Skillman et al., 1969) estimates the likelihood of calcium sulfate scaling. When calcium is the limiting reactant, the amount of calcium sulfate, in mg/kg, formed in the solution is proportional to the difference between actual and equilibrium concentration:

$$CSSP\alpha\ ([\mathrm{Ca}]_{\mathrm{x}} - [\mathrm{Ca}]_{\mathrm{eq}}) \tag{9}$$

$$[\mathrm{Ca}]_{\mathrm{eq}} = 1000 \cdot \left(\sqrt{q^2 + 4s^2} - q\right). \tag{10}$$

where q is the absolute value of the excess common-ion concentration of calcium and sulfate ions:

$$q = \left|2.5\,[\mathrm{Ca}^{2+}] - 1.04\,[\mathrm{SO}_4^{2-}]\right| \cdot 10^{-5} \tag{11}$$

The solubility (s), in g/L, can be determined as a function of temperature (T), in $^{\mathrm{o}}$C:

$$s = 2.091 + 0.003173\,T - 8.193 \cdot 10^{-5}\,T^2 \tag{12}$$

The more positive (less negative) value the highest the scale potential the case. Similar to previous studies (Al-Rawajfeh, 2011; Al-Rawajfeh et al. 2012), the sulfate scale potential, expressed by Skillman index, for seawater from 0 to 100% NF-treated make-up in BR-MSF reference plant was investigated. The scale potential increases with increasing temperature and decreases with increasing the percentage of NF-treated feed.

Figure 5 show the calcium sulfate scale potential (*CSSP*) of the product of the four SP-NF-RO cases. The *CSSP* of the As-Samra wastewater increases, exponentially, with the temperature. Cases including SP pretreatment (Cases A and C) are the best for carbonate scale prevention, while the cases include NF pretreatment (Cases B and D) are the best for sulfate scale prevention. For similar scale potential, there is 10 °C advantageous temperature of As-Samra over Palo Verde case. In a previous studies on pretreatment of seawater (Al-Rawajfeh, 2010; Al-Rawajfeh, 2011; Al-Rawajfeh et al. 2012; Al-Rawajfeh, 2012), the effect of calcium ion concentration in the feed for different feed water composition in different intakes from the Arabian Gulf for once-through (OT) and brine recycle (BR) MSF distillers, on sulfate scale, was investigated. The $CaSO_4$ scale potential increases with increasing the calcium ion content in the feed water. The effect of sulfate ion concentration in the make-up showed a similar trend but calcium is the limiting species. The $CaSO_4$ scale potential increased with seawater salinity. This can be attributed to the fact that the solubility of sulfate scale decreases with salinity. As a rule of thumb, each 1% pretreatment portion increases the reference Top Brine Temperature (*TBT*) of 115°C by 0.6°C. For example, if the 30% of the feed is treated by SP-NF pretreatment, the *TBT* may reach 133°C, with less possibility of sulfate scale formation.

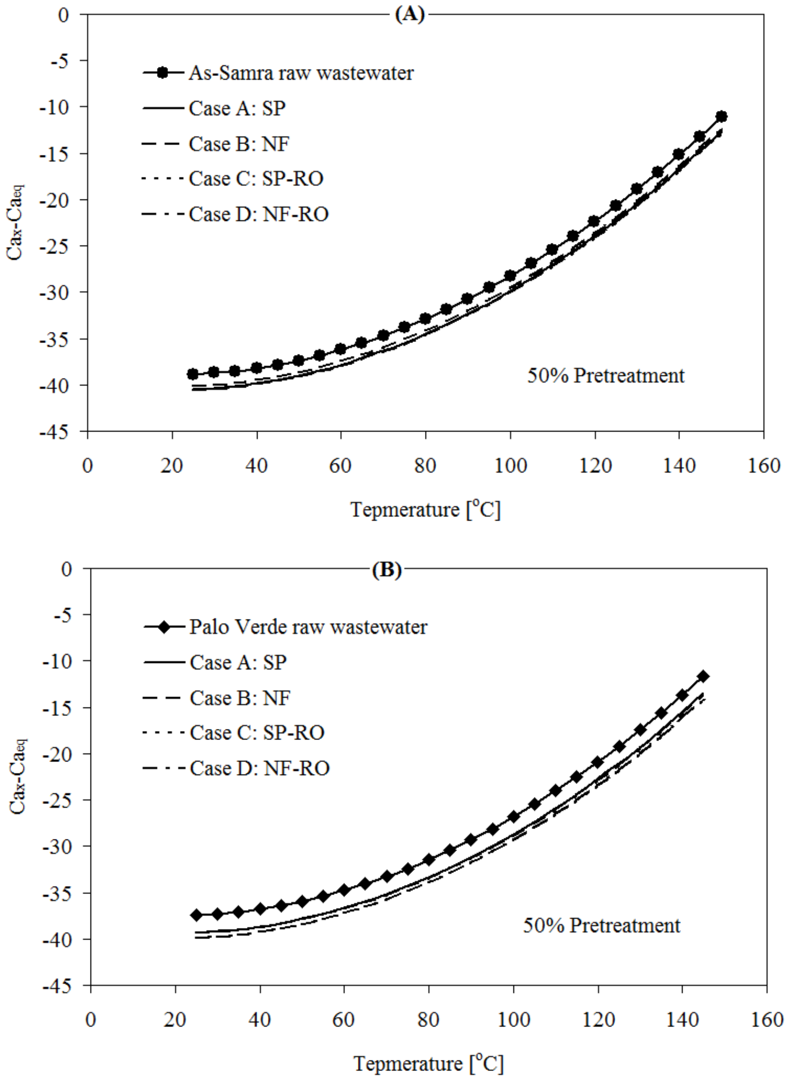

Fig. 5. Variations in calcium sulfate scale potential with changing the temperature of 50% pretreatment

Figure 6 shows the influence of the pretreatment on the calcium sulfate scale potential for the different four SP-NF-RO pretreatment cases at 50% pretreatment and 25°C. The As-Samra wastewater shows lower potential of sulfate scale because of the lower values of sulfate ions in the original feed. The study of Liu et al. (2012) revealed that the use of tertiary-treated municipal wastewater (nitrification and sand filtration) in a recirculating cooling system has not lead to significant inorganic scale formation. This study also demonstrated that it is possible to manage scaling problems associated with the use of municipal wastewater either through *pH* control or tertiary treatment commonly used in municipal wastewater treatment practice.

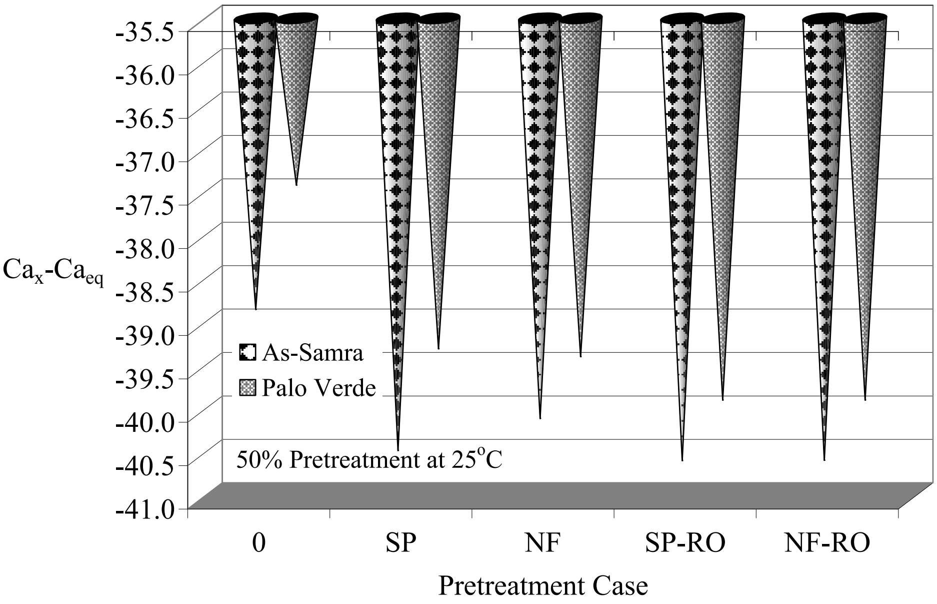

Fig. 6. The influence of pretreatment on the calcium sulfate scale potential for the different four SP-NF-RO cases at 50% pretreatment and 25°C

Cycles of concentration (*CoC*) measure the number of times the water circulates within the cooling system before it is lost to blowdown. It is the ratio of an ion in the cooling water C_{cw} to that of the make-up water C_{mu}

$$CoC = \frac{C_{cw}}{C_{mu}} \tag{13}$$

Typically the ions considered are magnesium or silica. For convenience, total dissolved solids (*TDS*), conductivity or chlorides (when the chlorides contribution from chlorination is insignificant) are also used. The objective is to maximise *CoC* so that water loss through blowdown is minimised. The maximum *CoC* that can be maintained in a cooling water system is subject to the salinity of make-up water quality and other considerations such as system metallurgy.

Table 3. The Ca$_x$-Ca$_{eq}$ values of the four cases at different cycles of concentration (*CoC*), using As- Samra wastewaters, at 100% pretreatment and 50°C

Case	Cycle of Concentration (*CoC*)			
	10	15	20	25
A (SP)	-38.6179	-37.4876	-36.3631	-35.2445
B (NF)	-31.8542	-28.0649	-24.7146	-21.7562
C (SP-RO)	-40.8736	-40.8621	-40.8507	-40.8392
D (NF-RO)	-40.7960	-40.7458	-40.6957	-40.6456

Table 3 shows the influence of concentration factor of the 100% SP-NF-RO pretreated As-Samra wastewater at 50^{o}C. The Palo Verde cooling towers reduce hot water temperature from 48.9 to 26.7^{o}C. The sulfate scale potential increases with increasing the concentration times in the SP and NF pretreatment processes. The scale amount increases very slightly with concentration times when the SP and NF product are desalinated by RO step. The NF pretreatment case leads to the worst sulfate scaling, with concentrating the feed, among the four cases. This may be attributed to the high concentration of calcium ion stay in the feed after NF treatment. Better calcium ion rejection NF membranes should be used if the process is planned to be exploited for wastewater pretreatment for the cooling purposes.

4. CONCLUSIONS

This study investigated carbonate and sulfate scaling behavior and its control when using tertiary-treated municipal wastewater as an alternative cooling system make-up water to replace freshwater. Two types of tertiary-treated municipal wastewater that were compared included As-Samra (Jordan) and Palo Verde (USA) wastewaters as it is the only nuclear power plant (NPP) in the world that is located far from a large body of water; it uses treated wastewater to meet its cooling needs. Four different tertiary treatment hybrid configurations including salt precipitation, nanofiltration, reverse osmosis and combinations of them were suggested and investigated by changing the percentage of pretreatment from 0 to 100%. The scale potential decreases with increasing the percentage of SP and/or NF-treated feed. The SP including cases showed the best values for sulfate scale prevention and the highest values of increasing the monovalent ions relative to the divalent scale forming ions. Sulfate scale is significant in SP process while carbonate scale is significant in NF. Salt precipitation was suggested because it is less costly than nanofiltration, but nanofiltration has been kept in use here because it is efficient in the removal of sulfate ions.

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