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Possibility of improvement of boiler water treatment process—ion exchange vs. reverse osmosis

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ABSTRACT

The boiler water in certain power plant is produced by chemical decarbonization, sand filtration, and ion exchange. Process ends with mixed bed ion exchange. The current boiler water treatment process is analyzed in terms of achieved water quality, quantity and quality of wastewater, and amount of chemicals needed. The main disadvantage of current process is consumption of large amount of chemicals. Ion exchange process could be replaced with the reverse osmosis, but pretreatment (decarbonization and filtration) should be retained. Since the permeate quality does not meet quality requirements, it would be advisable to use mixed bed ion exchange. If reverse osmosis is used, quantity of water that enters the treatment and wastewater would be for about 17.5 and 150% larger, respectively, but content of salt in wastewater would be about 20–30-fold less. Nevertheless, final decision on which technique to apply should be based on further economical considerations.

Keywords: Boiler water; Demineralization; Ion exchange; Reverse osmosis

1. Introduction

Power plants are large high-purity water consumers. The production of demineralized water for boiler feeding, as process water, has a particular attention. Since a substantial volume of process water is needed, water treatment should be simple, efficient, no chemical and energy demanding, and consequently cheap. Usually, the consideration related to quantity and quality of wastewaters generated during this water treatment processes is omitted. The aim of this work is comparison of production of demineralized water by ion exchange and reverse osmosis, primarily related to consumption of raw water and chemicals, and quantity and quality of generated wastewaters.

2. Present status of water treatment plant

The considerations are based on the example of one nearby power plant with average steam production of 900 t/h and steam pressure of 255 bars. Existing boiler feed water treatment process involves decarbonization by $Ca(OH)_2$ and $FeSO_4$, sand filtration, ion exchange with strong-acid cation exchanger, strong-base anion exchanger, and mixed bed. Block scheme of existing water treatment plant is presented in Fig. 1(a). There are two identical lines with ion exchangers. In Table 1, qualities of raw, decarbonized

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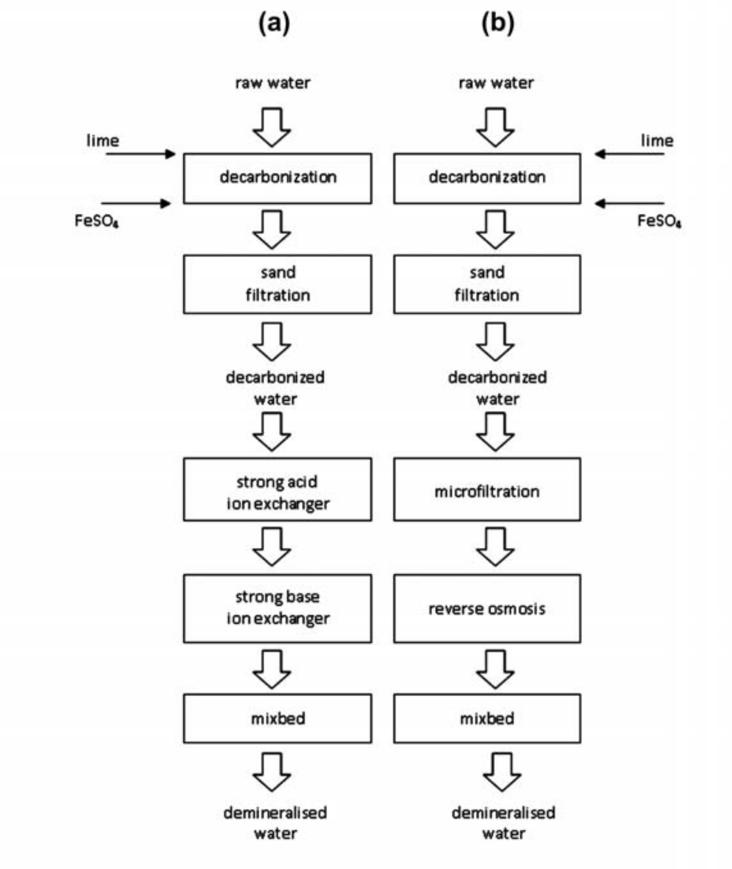

Fig. 1. Block schemes of (a) present water treatment plant and (b) water treatment plant with reverse osmosis.

Table 1
Characteristics of raw water, decarbonized water, demineralized water, and required values for boiler feed water

Parameter	Raw water	Decarbonized water	DEMI water	Required values
Total hardness (°N)	13.34	4.37	0.00	0.00
Carbonate hardness (°N)	12.44	2.8	0.00	0.00
Noncarbonate hardness (°N)	0.90	1.57	0.00	0.00
Ca^{2+} (mg/L)	64.9	14.2		
Mg^{2+} (mg/L)	17.5	10.3		
Na^+ (mg/L)		6.9		
K^+ (mg/L)		1.9		
Fe total (mg/L)	0.056	0.2	<0.01	≤0.01
SiO_2 (mg/L)	4.54	1.7	<0.01	≤1
Cl^-, (mg/L)	7.86	3.5		
SO_4^{2-} (mg/L)	50.3	52.0		
HCO_3^- (mg/L)		31.0		
pH	7.79	10.4	6.5–7.3	9.1 ± 0.1
Conductivity (μS/cm)	448	237	0.05	≤0.1
Suspended solids (mg/L)	25.6	14.0		
$KMnO_4$ demand (mg/L)	11.28	5.53		

and water demineralized by ion exchangers, and required quality of boiler feed water, either as ASME or ABMA standards are presented [1].

2.1. Quantity of wastewaters from regeneration process

The output of one line between two regenerations, for existing treatment plant for water demineralization, is approximately 1,440 m^3. The time between two regenerations is 24 h. During the regeneration of ion exchangers the wastewaters are generated in quantities as shown in Table 2. The amount of chemical used for one regeneration is shown in Table 2, as well.

Total quantity of wastewater per one regeneration of one ion exchange line is 171.3 m^3 (53.6 + 117.7 m^3). Wastewater from regeneration of mixed bed is omitted in further considerations because regeneration of these ion exchangers takes place only 10 times per year.

2.2. Amount of chemicals needed for regeneration process

During the ion exchange and the regeneration of ion exchangers the reactions shown in Table 3 occur [2].

Based on results of activity of a thermal power plant collected over the years, it was adopted that the line I has 150 and line II 200 regenerations per year. That represents a total of 350 working cycles. Therefore, for regeneration of HCl and NaOH (on the base of data in Table 2) is spent:

$$310 \cdot 350 = 108,500 \text{ kg } 100\% \text{ HCl/year}$$

$$240 \cdot 350 = 84,000 \text{ kg } 100\% \text{ NaOH/year}$$

On the base of parameters for decarbonized water (Table 1), the exact minimal amounts of HCl and NaOH required for the exchange of ions bounded to

Table 2
Characteristics of ion exchange resins and quantities of wastewaters generated during ion exchange resins regeneration

	Strong-acid cation exchanger	Strong-base anion exchanger	Mixed bed
Kind of resin	Lewatit MonoPlus S 100	Lewatit MonoPlus M 500	Lewatit MonoPlus S 100 and M 500
Resin quantity (m^3)	4.0	6.7	1.1 + 1.1
Resin capacity (g CaO/L)	30	16	
Washing water (m^3) (*1*)	4.16	3.7	7.0
Solution for regeneration (m^3) (*2*)	4.44 (7% HCl)	6.0 (4% NaOH)	1.6 (7% HCl) 2.7 (4% NaOH)
Pure chemicals (100%)	310 kg HCl	240 kg NaOH	112 kg HCl 108 kg NaOH
Rinsing water (m^3) (*3*)	45.0	108.0	44.0
Total wastewater from regeneration (m^3) *1 + 2 + 3*	53.6	117.7	55.3

Table 3
Ion exchange reaction in working cycle and during regeneration

Ion exchange in working cycle	Ion exchange during regeneration
Cation exchanger	
$Me^{*}–2H + Ca^{2+} \rightarrow Me–Ca + 2H^{+}$	$Me–Ca + 2HCl \rightarrow Me–2H + CaCl_2$
$Me–2H + Mg^{2+} \rightarrow Me–Mg + 2H^{+}$	$Me–Mg + 2HCl \rightarrow Me–2H + MgCl_2$
$Me–H + Na^{+} \rightarrow Me–Na + H^{+}$	$Me–Na + HCl \rightarrow Me–H + NaCl$
$Me–H + K^{+} \rightarrow Me–K + H^{+}$	$Me–K + HCl \rightarrow Me–H + KCl$
Anion exchanger	
$Me–OH + Cl^{-} \rightarrow Me–Cl + OH^{-}$	$Me–Cl + NaOH \rightarrow Me–OH + NaCl$
$Me–2OH + SO_4^{2-} \rightarrow Me–SO_4 + 2OH^{-}$	$Me–SO_4 + 2NaOH \rightarrow Me–2OH + Na_2SO_4$
$Me–OH + HSiO_3^{-} \rightarrow Me–HSiO_3 + OH^{-}$	$Me–HSiO_3 + NaOH \rightarrow Me–OH + NaHSiO_3$
$Me–OH + HCO_3^{-} \rightarrow Me–HCO_3 + OH^{-}$	$Me–HCO_3 + NaOH \rightarrow Me–OH + NaHCO_3$

Note: *Ion exchange resin matrix.

ion exchangers by H^+ and OH^- ions during the regeneration can be calculated:

$$G_{HCl} = 13 \cdot (Ca^{2+} + Mg^{2+} + Na^+ + K^+) \cdot 1,440 \cdot 0.001 = 118.5 \text{ kg } 100\% \text{ HCl/day}$$

$$G_{NaOH} = 14.3 \cdot (Cl^- + SO_4^{2-} + HSiO_3^- + HCO_3^-) \cdot 1,440 \cdot 0.001 = 136.2 \text{ kg } 100\% \text{ NaOH/day}$$

where 13 is a factor representing number of grams of 100% HCl corresponding to 1°N, 14.3 is a factor representing number of grams of 100% NaOH corresponding to 1°N, and 0.001 is a factor for calculating g to kg. All ion concentrations are in °N (1°N = 10 mg CaO/L).

It is necessary to use surplus of chemicals during the process of regeneration in order to achieve feedback exchange. The surplus of acid and base in wastewater after regeneration can be calculated as:

$$310 - 118.5 = 191.5 \text{ kg } 100\% \text{ HCl/day}$$

$$240 - 136.2 = 103.8 \text{ kg } 100\% \text{ NaOH/day}$$

and per year (350 working cycles):

$$191.5 \cdot 350 = 67,025 \text{ kg } 100\% \text{ HCl/year}$$

$$103.8 \cdot 350 = 36,330 \text{ kg } 100\% \text{ NaOH/year.}$$

2.3. Salt content in wastewater from the regeneration process

Salt content in wastewater from the regeneration of ion exchangers can be calculated based on the minimal amount of HCl and NaOH required for regeneration of the cationic and anionic exchanger and molar mass of HCl, NaOH, and salt. Salt content in the wastewater from regeneration of strongly acidic cationic exchanger is calculated on the basis of the reaction given in Table 3, as it was shown in the example of $CaCl_2$:

$$CaCl_2 = G_{HCl}(\text{only for } Ca^{2+}) \cdot \left(\frac{M_{CaCl_2}}{2M_{HCl}}\right) = 37.3 \cdot \left(\frac{110.9}{2 \cdot 36.45}\right) = 56.7 \text{ kg/day}$$

where is G_{HCl} (only for Ca^{2+}) = 13 · Ca^{2+} · 1,440 · 0.001 = 13 · 1.99°N · 1,440 · 0.001 = 37.3 kg 100% HCl/day.

Similarly, the content of other salts generated during regeneration of strong-acid cation exchanger can be calculated, so the total salt content in wastewater from regeneration is:

$$\Sigma(CaCl_2 + MgCl_2 + NaCl + KCl) = 56.7 + 58.2 + 50.4 + 10.8 = 176.2 \text{ kg/day}$$

Salt content in the wastewater from the regeneration of strong-base anion exchanger is calculated in the same manner, as shown in the example of NaCl:

$$NaCl = G_{NaOH}(\text{only for } Cl^-)\left(\frac{M_{NaCl}}{M_{NaOH}}\right) = 11.4 \cdot \left(\frac{58.45}{40}\right) = 16.6 \text{ kg/day}$$

The total salt content in the wastewater from the regeneration of anion exchanger is:

$$\Sigma(NaCl + Na_2SO_4 + NaHSiO_3 + NaHCO_3) = 16.6 + 113.3 + 144.3 + 6.93 = 281.2 \text{ kg/day}$$

The total content of all salts in the wastewater from the regeneration of the cationic and anionic exchangers is:

$$176.2 + 281.2 = 457.4 \text{ kg salts/day}$$

2.4. Neutralization of wastewaters from regeneration

There is a surplus of HCl and NaOH in wastewaters from regeneration of cationic and anionic exchangers. In order to neutralize them, acidic and basic wastewaters can be mixed. The neutralization of the surplus of NaOH in wastewater from regeneration of anion resin, in amount of 103.8 kg/day (as 100% NaOH), requires about 95 kg 100% HCl. Therefore, there will be a surplus of nonneutralized acid in amount of:

$$G_{HCl} = 191.5 - 95 = 96.5 \text{ kg } (100\% \text{ HCl})$$

During mixing of acidic and alkaline wastewaters certain amount of NaCl will be generated:

$$G_{NaCl} = G_{NaOH}\left(\frac{M_{NaCl}}{M_{NaOH}}\right) = 103.8 \cdot \left(\frac{58.45}{40}\right) = 151.8 \text{ kg NaCl/day}$$

Table 4
Comparative data for the production of demineralized water by ion exchange and reverse osmosis

	Ion exchange	Reverse osmosis
Produced demineralized water, m^3/year	444,045	444,045
Required decarbonized water, m^3/year	504,000	592,060
Produced wastewater, m^3/year	59,955	148,015
Quantity of 100% HCl, kg/year	108,500	4,480
Quantity of 100% NaOH, kg/year	121,065	4,320
Quantity of salts in wastewater, t/year	267.2	68.3

For further neutralization of the rest of nonneutralized HCl (96.5 kg), additional amount of NaOH is required:

$$G_{\mathrm{NaOH}}\ (\text{for neutralization}) = G_{\mathrm{HCl(rest)}} \cdot \left(\frac{M_{\mathrm{NaOH}}}{M_{\mathrm{HCl}}}\right) = 96.5 \cdot \left(\frac{40}{36.45}\right) = 105.9\ \text{kg}\ (100\%\ \text{NaOH})$$

The total amount of 100% NaOH spent in the water treatment plant is 240 + 105.9 = 345.9 kg/day or 121,065 kg per year.

The amount of NaCl that will be produced during the neutralization of the rest of nonneutralized HCl (96.5 kg) is calculated as:

$$G_{\mathrm{NaCl}} = G_{\mathrm{HCl}} \cdot \left(\frac{M_{\mathrm{NaCl}}}{M_{\mathrm{HCl}}}\right) = 96.5 \cdot \left(\frac{58.45}{36.45}\right) = 154.7\ \text{kg NaCl/day}$$

The calculated amounts of NaCl, generated during mixing of acidic and alkaline wastewaters, and during the further neutralization of remained HCl, are added to the total salt content in the wastewater from regeneration:

$$\begin{aligned}\text{Salt content (total)} &= 457.2 + 151.8 + 154.7\\ &= 764.1\ \text{kg salts/day}\\ &= 267.2\ t/year\end{aligned}$$

The amount of water entering the treatment plant for demineralization, i.e. annual water consumption of the facility is:

$$1,440 \cdot 350 = 504,000\ \mathrm{m^3/year}$$

Amount of demineralized water spent for rinsing and washing of resins after regeneration, and amount of water spent for preparation of regenerates, should be subtracted from amount of 1,440 m^3 water/day. So, the actual amount of water delivered to the boiler plant is 1,440–171.3 = 1,269 m^3/day. Consequently, the quantity of demineralized water that is delivered to the boiler per year is $1,269 \cdot 350 = 444,045\ \mathrm{m^3/year}$, and total annual quantity of wastewaters from the exchanger regeneration is $171.3 \cdot 350 = 59,955\ \mathrm{m^3/year}$.

Annual data for the amount of delivered and consumed water, generated wastewaters, the amount of spent chemicals (HCl and NaOH) and the total salt content in wastewater, for the existing water treatment plant are shown in Table 4.

3. Reverse osmosis instead ion exchangers

In existing water treatment scheme is planned replacement of only strong-acid cation and strong-base anion exchangers by reverse osmosis. The liming coagulation, clarification, and sand filtration will be retained, because of raw water composition and also the fact that they still represent usual preliminary water treatment process in most large cogeneration plants [3]. Pretreatment of raw water minimizes the fouling and scaling problems, especially in large plants [2]. Because of high value of pH and suspended solids in decarbonized water it is necessary to correct pH and use microfiltration before reverse osmosis. Also, mixed bed is necessary to be retained as a polishing step. The predicted water treatment scheme with reverse osmosis is presented at Fig. 1(b).

Based on characteristics of reverse osmosis membranes of, for example, Dow Chemical Co. (http://www.dowwaterandprocess.com), which are commonly used for water treatment in power engineering [3], it was adopted that the membrane capacity is 100 m^3/h (two elements per 50 m^3/h), and the percentage of permeate is 75%. Therefore, it is required 592,060 m^3/year of decarbonized water for the production of 444,045 m^3 demineralized water per year. Quantity of retentate, in fact wastewater, is 592,060–444,045 = 148,015 m^3/year.

It is assumed that 95% of dissolved salts will remain in retentate. According to the salt content in decarbonized water and the salt content in water that enters the membrane, the content of, for example Ca, in retentate is:

$$\begin{aligned}Ca^{2+} &= 0.0142\ \text{kg/m}^3 \cdot 592{,}060\ \text{m}^3\text{/year} \cdot 0.95\\ &= 7{,}986.9\ \text{kg/year}\end{aligned}$$

In the same way the content of other cations and anions in retentate can be calculated. Based on these calculations, total content of salts released with the retentate per year can be calculated:

$$\begin{aligned}&Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}\\ &\quad = 7{,}986.9 + 5{,}793.3 + 3{,}880.9 + 1{,}068.7\\ &\quad = 18{,}730\ \text{kg/year}\end{aligned}$$

$$\begin{aligned}&Cl^{-} + SO_4^{2-} + HSiO_3^{-} + HCO_3^{-}\\ &\quad = 1{,}968.6 + 956.2 + 29{,}247.7 + 17{,}436.1\\ &\quad = 49{,}608.6\ \text{kg/year}\end{aligned}$$

$$\begin{aligned}&\text{Quantity of salts in wastewater} = 18.7 + 49.6\\ &\quad = 68.3\ \text{t/year}\end{aligned}$$

Since it was adopted that reverse osmosis removes 95% of salts from decarbonized water, in permeate will remain, for example, 0.71 mg/L of calcium, 0.52 mg/L of magnesium, etc. Therefore, mixed bed ion exchangers need to be regenerated more frequently, so the amount of wastewater, the amount of HCl and NaOH for mixed bed regeneration, and the amount of salts in wastewater from its regeneration will be higher than in case of ion exchange demineralization plant. If the mixed bed regeneration was performed 20 times in one treatment line per year required amounts of HCl and NaOH for this process (based on data from Table 2) in both lines of water treatment will be:

$$\begin{aligned}&112\ \text{kg HCL per regeneration} \cdot 20\ \text{regeneration} \cdot 2\ \text{lines}\\ &\quad = 4{,}480\ \text{kg (100\% HCl)/year}\end{aligned}$$

$$\begin{aligned}&108\ \text{kg NaOH per regeneration} \cdot 20\ \text{regeneration}\\ &\quad \cdot 2\ \text{lines}\\ &\quad = 4{,}320\ \text{kg (100\% NaOH)/year}\end{aligned}$$

In addition, the actual amounts of HCl and NaOH will be higher than required, because these chemicals are used also for washing of membranes for reverse osmosis and microfiltration.

Annual data for the amounts of delivered and consumed water, generated wastewaters, the amount of spent chemicals (HCl and NaOH), and the total salt content in wastewater, for the water treatment plant with reverse osmosis are shown in Table 4.

The usage of reverse osmosis showed occurrence of significantly less amount of salts in wastewater compared to wastewater from ion exchange, as it was expected. The amount of chemicals required is significantly less as well. However, required amount of decarbonized water that enters membrane is higher for 17.5% compared to ion exchange process, which means that required amounts of chemicals for decarbonization and production of higher amounts of wastewaters from decarbonization are increased by the same amount.

Table 5
Factors to be considered for selecting resin ion exchange or reverse osmosis for feed water demineralisation

Factor	Ion exchange	Reverse osmosis (with mixed bed)
Reliability	Reliable	Reliable
Feed water pretreatment	Necessary	Necessary
Quality of treated water	High	Medium (without mixed bed) high (with mixed bed)
Flexibility	More flexible	Less flexible
Fouling by organics	Much more easily cleaned	Main problem
Plant capital costs	Lower	Higher
Plant operating costs	70–80% of total costs (mainly for chemicals)	70–80% of total costs (mainly for energy)
Membrane and resins replacement costs	Lower	Higher
Plant maintenance	Lower	Higher
Manpower	Similar	Similar
Costs of feed water and wastewater treatment	Lower	Greater

Purolite guidelines [4] are specified factors that need to be considered for selecting ion exchange or reverse osmosis for feed water demineralization (Table 5), which indicated that it is very difficult to choose right option even though results presented in Table 4 undoubtedly favors reverse osmosis. Variation in power and chemicals costs from region to region can significantly influence the operating costs of both the reverse osmosis and the ion exchange plants and should be carefully considered when selecting a water treatment system. Eventually, instead of reverse osmosis, electrodialysis unit or instead mixbed electrodeionization can be installed. The different demineralization methods have different requirements as well as different operational costs, which also differ depending on water treatment plant capacity [5]. Although it seems that the usage of reverse osmosis is better than ion exchangers, during its implementation, larger problems in comparison with robust ion exchange system may appear. In the application of reverse osmosis, it is necessary to pay attention to the following recommendations: minimizing energy usage by enhanced system design, high efficiency pumping, energy recovery, introduction of innovative technologies, and, what is a very important, use of advanced material membranes to reduce the problems that makes fouling [6].

4. Conclusion

The reverse osmosis, a new technique for high-purified water production was rising in recent years. It has certain advantages and disadvantages compared to the, up to now, most frequently used technique—ion exchange. On the base of consideration of water treatment in one nearby power plant, it can be concluded that the application of reverse osmosis can significantly reduce quantity of required chemicals, but also increase raw water demand and especially quantity of discharged wastewater, compared to the ion exchange. Because of high energy consumption of reverse osmosis plants and risk of membrane fouling and scaling, one should be very careful in making the decision to replace the ion exchange by reverse osmosis, as well as in designing of new water treatment plant.

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