Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2019.23910

157 (2019) 250–258
July

Pilot study of the impact of geothermal water RO concentrate volume minimization on the possibility of comprehensive further use

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Received 13 November 2018; Accepted 4 February 2019

ABSTRACT

Using membrane processes, especially reverse osmosis (RO), to concentrate geothermal waters can provide to obtain good quality new products, such as useful concentrates and permeates possible to use as drinking waters. Natural water, which possesses curative parameters, can be concentrated using membrane processes to produce curative solutions or crystalline salts used for healing baths or inhalations. Concentrates can also be a valuable resource for production metals, chemicals, and also magnesium, calcium, potassium and sodium salts or other products for cosmetology industry. The aim of this work was to present the results of the research oriented towards examine the influence of recovery value of geothermal water on the quality of concentrate obtained by means of RO process. The survey was carried out on the example of two geothermal waters extracted from wells located in Poland area, which exhibit elevated concentrations of major ions, silica and other components significant for therapeutic industry. RO processes conducted in laboratory scale have allowed for a detailed recognition of the influence of the concentrate volume minimization, in adopted process parameters of permeate recovery (50% and 75%), on theirs composition. The research indicate that minimization of concentrates volume caused significant elevation of content of the desired (in some cases also undesired) components, and consequently this concentrates can be a potential source of mineral solutions applied in different industries, among others balneology or cosmetics industry.

Keywords: Concentrate; Desalination; Reverse osmosis; Balneology; Mineral recovery

1. Introduction

Reverse osmosis (RO), as one of membrane processes, is well-known technology increasingly applied for providing fresh drinking water around the world and in tertiary wastewater treatment, due to high efficiency, low energy consumptions and other improvements in energy recovery systems made over past years [1–4]. Moreover, RO technology is becoming a useful method of desalination geothermal waters which often contain elevated concentrations of specific macro and microelements potentially valuable for reuse. Using membrane processes, especially RO, to concentrate geothermal waters can provide good quality new products, such as permeates having the possibility to be used as drinking waters and also valuable concentrates [5–9]. Optimal selection of process parameters and recovery values of permeates and concentrates will directly influence on their composition and possible comprehensive further reuse. The technology is struggling with a number of challenges consequent on the ever-increasing efficiency demand in parallel with environmental-friendly management of the produced concentrates, also called as retentates or brines [10–12]. RO concentrates are conventionally treated as waste and are disposed of by several means, to surface waters, sewers, via deep injection, disposal in evaporation ponds and land

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Presented at the EDS conference on Desalination for the Environment: Clean Water and Energy, 3–6 September 2018, Athens, Greece.

application of concentrate [12–14]. Concentrate management remains as one of main problems and limitations of this technology considering restricted or expensive available options of its disposal [15]. Untreated or improperly managed concentrate can result in negative environmental effects, due to high salinity, and in some cases also emerging contaminants contained in it [16–18]. However recently, RO retentates are also considered as a valuable resource for production mineral salts [15,19] or solutions, metals [20], precious chemicals [21] and other products for cosmetology, balneology and other industries [22]. Nearly all of the dissolved solids in the geothermal water (mainly NaCl) are retained in the concentrate. Retentate utilization and management is getting more and more attention in desalination process. In principle, concentrate utilization is redirected to recovering valuable components or further reuse [23]. NaCl is one of the most important material widely used in industry, among others in soda and chlor-alkali industry [24]. Consequently, despite of ecology and economy matter [25], reuse of salts retained in concentrates is a perspective to be resolved [24,26]. The suitable hydro-geochemical composition of recovery geothermal water concentrates will strictly determine applicable management and reuse. The use of antiscalants in the desalination processes will have a significant impact on the way the concentrates are managed and reused [23,27,28]. Additionally, curative properties of natural geothermal water can be concentrated by the use of membrane processes to produce curative solution or crystalline salt used for therapeutic treatments [29] and in cosmetic industry. The positive impact of the water on health aspects and well-being was observed centuries ago. The high content of dissolved elements and chemical compounds in geothermal waters positively affects the condition of the skin and alleviates the symptoms of dermatological diseases. Leading producers of cosmetics that are created on the basis of geothermal waters ensure that these products have soothing, softening and calming effect on the skin, strengthen the natural protective functions of the skin and help it fight the signs of aging. The most recognizable concerns producing cosmetics based on geothermal waters are Avene, La Roche Posay, Vichy and Blue Lagoon [30–32].

The work presents the results of the assay oriented towards the examination of the influence of recovery value of geothermal water on the quality of concentrate obtained by means of RO process. The survey was carried out on the example of geothermal waters extracted from wells located in Poland area. These waters exhibit elevated concentrations of magnesium, potassium, sodium, sulphates, silica and other components significant for therapeutic industry. RO processes conducted in laboratory scale have allowed for a detailed recognition of the influence of the concentrate volume minimization, in adopted process parameters of desalination, on their composition. The research was established for 50% and 75% permeate recovery.

2. Methodology and materials

2.1. Geothermal waters characteristic

Two geothermal waters (GT) obtained from wells located in the Poland area were used for tests and thus analyzed for selected physico-chemical parameters. The first geothermal water (GT-1) characterized with high total dissolved solids (TDS) (2.4 g L^{-1}), silica concentration (80 mg SiO_2 L^{-1}), and also elevated content of calcium (194 mg L^{-1}), magnesium (41 mg L^{-1}), sulphates (854 mg SO_4 L^{-1}), chlorides (488 mg Cl L^{-1}), sodium (489 mg Na L^{-1}) and other micro and macronutrients. GT-1 was established as SO_4–Cl–Na–Ca hydrogeochemical type, according to the Szczukariew-Priklonski classification. The second geothermal water (GT-2) had visibly higher concentration of TDS (6 g L^{-1}), however had lower content of silica (35 mg SiO_2 L^{-1}), calcium (125 mg L^{-1}), magnesium (21 mg L^{-1}), sulphates (83 mg SO_4 L^{-1}, almost 11 times lower than GT-1), chlorides (3.5 g Cl L^{-1}, almost 7 times higher than GT-1), sodium (2.2 g Na L^{-1}, almost 5 times higher than GT-1) and possessed Cl-Na hydro-geochemical type. In all conducted tests, the temperature of both GT-1 and GT-2 was 22°C. The electrical conductivity (EC), pH and temperature value of raw geothermal waters and concentrates were determined directly after RO processes in the laboratory using the electrometric method. The temperature was kept constant at a value of 22°C in order to carry out tests at a temperature similar to that geothermal water possesses after cascade use. The detailed physico-chemical characteristics of raw geothermal waters and concentrates were established, using inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES) and titration method (for chloride ions, in accordance with accredited testing procedures), in the accredited laboratory in accordance with international standards.

2.2. Apparatus

The tests were conducted in the laboratory scale with the use of one-step desalination RO system using the stirred cell device, in the high-pressure version operated in the dead-end mode utilizing a particular membrane and two geothermal waters (GT-1 and GT-2). The raw GT-1 and GT-2 were placed in the stirred cell under the established pressure. RO process divided the inflow from cell stream into two separate ones: (1) a permeate – a part of the feed water, which permeated through the membrane surface, flew out through permeate outlet and was collected in a vessel, and (2) a concentrate – a part of the feed water, which did not pass through the membrane, which retained in cell and contained rejected dissolved compounds. More detailed description of the apparatus and methodology can be found in the previous authors works [33,34].

Both processes, with GT-1 and GT-2, were conducted until 50% and 75% recovery of feed water (50% of permeate and 50% of concentrate and also 75% of permeate and 25% of concentrate in relation to raw water volume) was obtained. The RO process was carried out at the transmembrane pressure of 15 bar. Due to the specified further use of obtained permeates and concentrates, the tests proceeded without addition of any chemicals. During all tests, temperature of feed waters was maintained stable and amounted 22°C. The temperature was stabilized at a given level by applying a heat exchanger. The accuracy of temperature measurement was 0.5°C and oscillated in the scope of measurement error. RO processes were carried out to obtain specified value of recovery of permeate with measurement of the time required to gain each additional

5 mL of permeate. The accuracy of the volume measurement was 0.5 mL. A schematic diagram of the RO system applied in dead-end mode is presented in Fig. 1.

The DOW FILMTEC™ RO membrane, commercially marked as ROBW30HR-440i DOW FILMTEC™, was chosen for the tests. The membrane characteristic is shown in Table 1. The membrane was conditioned right before tests by filtration (RO process) of deionized water.

2.3. Analysis method

To analyze the quality of raw waters and concentrates obtained after RO processes, especially the difference between them, a detailed characteristics of the content of inorganic components were specified and retention coefficients R(%) were calculated based on the following formula:

$$R = \left(\frac{C_r}{C_n} - 1\right) \times 100\% \quad (1)$$

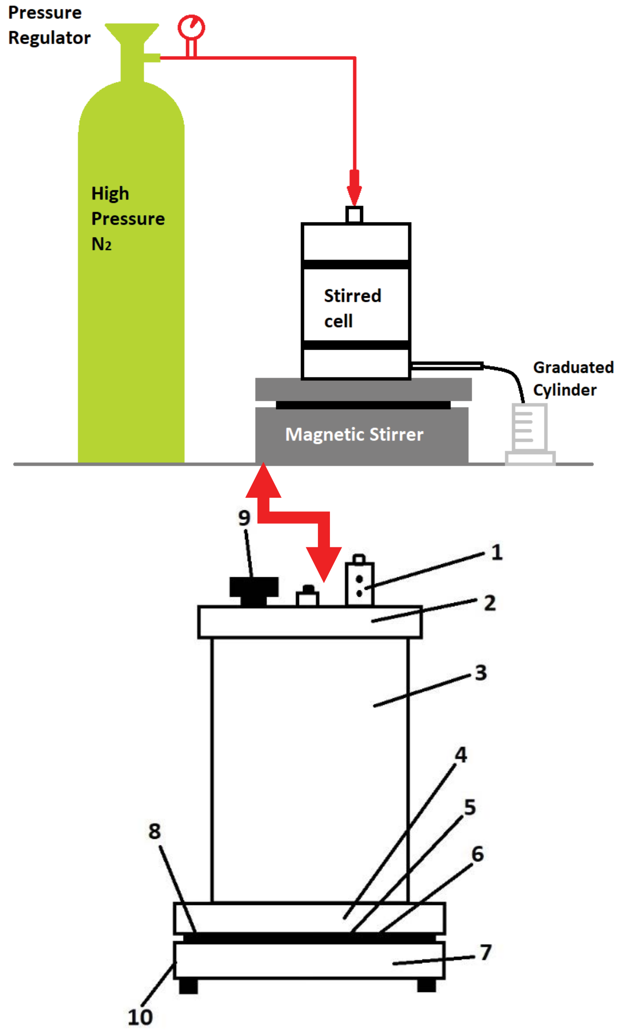

Fig. 1. Scheme of apparatus applied in both reverse osmosis processes (1, safety valve; 2, top cover; 3, pressure cylinder; 4, magnetic stirrer; 5, membrane; 6, perforated plate; 7, lower cover; 8, gasket; 9, gas supply and 10, permeate discharge).

where R – retention coefficient (%); C_r – concentration of particular parameter in concentrate (mg L^{-1}); C_n – concentration of particular parameter in raw water (mg L^{-1}).

3. Results and discussion

3.1. Results of geothermal waters concentration

The detailed chemical and physical parameters of raw geothermal waters and concentrates after both RO processes with 50% and 75% recovery are shown in Table 2. In reference to the results of the research, it can be noticed that values of most of the selected parameters, including major cations (calcium, magnesium, potassium and sodium), major anions (bicarbonates, chlorides and sulphates) and other, inter alia silica which is one of the pharmaco-dynamic factors [36], have increased in varying amounts. The specific physico-chemical composition of feed geothermal water, applied treatment technology and process parameters determine the possible reuse of gained concentrates. Raw geothermal water, marked as GT-1, is characterized with elevated concentration of major anions, cations and silica – its value exceeded 70 mg H_2SiO_3 L^{-1} [36]. The TDS of raw GT-2 water was three times higher than for GT-1, similar tendency was observed in RO concentrates after the process with 50% of recovery, however after the process with 75% recovery this difference decreases to 2.5 times. Moreover, pH value of raw GT-1 was 6.80 and increase in the GT-1 RO concentrate up to 6.86 for the process with 50% recovery and up to 7.33 for 75% recovery. For GT-2,

Table 1
Characteristic of selected membrane [35]

Parameter	BW30HR-440i
Material	Polyamide thin-film composite
Maximum operating temperature (°C)	45
pH operating range	2–11 (continuous operation)
Maximum operating pressure (MPa)	4.1
Minimum salt rejection	99.40%
Stabilized salt rejection	99.70%
Stabilized NO^{-3} rejection	98.50%
Stabilized SiO_2 rejection	99.90%
Stabilized boron rejection	83.00%
Application	Designed to purify water with high-performance and productivity; high rejection brackish water RO element combining the highest active membrane area available in the industry today; membrane sheet sustains maximum rejection over the working time of the RO element of critical solutes, including silica, boron, ammonium and nitrate

Table 2
Physico-chemical parameters of raw waters and RO streams

Parameter	GT-1			GT-2		
	Raw water GT-1	GT-1 50%/50%[a] RO concentrate	GT-1 75%/25%[b] RO concentrate	Raw water GT-2	GT-2 50%/50%[*] RO concentrate	GT-2 75%/25%[**] RO concentrate
Mineralization (mg L^{-1})	2,587.70	4,285.40	6,423.00	6,251.20	10,819.10	15,498.10
TDS (mg L^{-1})	2,416.10	3,989.50	6,016.00	6,086.00	10,539.30	15,169.60
H-G type[c]	SO_4–Cl–Na–Ca	SO_4–Cl–Na–Ca	SO_4–Cl–Na–Ca	Cl–Na	Cl–Na	Cl–Na
EC[d] (mS cm^{-1})	3.35	5.33	7.38	10.74	22.4	22.5
pH	6.80	6.86	7.33	6.97	7.32	7.44
Na^+ (mg L^{-1})	488.68	831.38	1,248.28	2,132.31	3,702.02	5,627.00
K^+ (mg L^{-1})	47.64	81.05	125.11	19.88	37.37	47.44
Ca^{2+} (mg L^{-1})	194.10	347.93	479.60	125.61	209.63	286.50
Mg^{2+} (mg L^{-1})	41.58	72.41	102.20	22.60	39.02	47.85
Cl^- (mg L^{-1})	487.90	843.40	1,367.00	3,485.00	6,044.00	8,568.00
SO_4^{2-} (mg L^{-1})	854.71	1,319.94	2,009.01	83.12	143.42	165.68
HCO_3^- (mg L^{-1})	343.30	591.80	814.10	330.40	559.60	657.00
H_2SiO_3 (mg L^{-1})	79.43	132.62	188.94	37.49	48.81	59.74
I^- (mg L^{-1})	0.10	0.26	0.16	0.31	0.28	0.07
Li^{2+} (mg L^{-1})	1.14	2.01	3.08	0.18	0.29	0.37
Fe^{2+} (mg L^{-1})	0.23	0.03	0.24	1.64	1.97	0.64
Sr^{2+} (mg L^{-1})	6.24	10.87	15.12	5.04	8.59	11.43
Mn^{2+} (mg L^{-1})	0.005	0.008	0.007	0.042	0.071	0.082
Ba^{2+} (mg L^{-1})	0.044	0.084	0.093	0.099	0.146	0.163
As^{3+} (mg L^{-1})	0.002	0.020	0.011	0.014	0.019	0.011
Sb^{3+} (mg L^{-1})	0.0004	0.0011	0.0007	0.0002	0.0004	0.0002
Cr^{3+} (mg L^{-1})	0.019	0.029	0.019	0.039	0.053	0.041

[a]50% permeate and 50% concentrate.
[b]75% permeate and 25% concentrate.
[c]Hydro-geochemical (H-G) type according to the Szczukariew-Priklonski classification.
[d]Electrical conductivity.

this value increases from 6.97 to 7.32 and 7.44, respectively. The composition of gained concentrates determines possible reuse. To analyze the changes in selected physico-chemical parameters and consequently the quality of gained concentrates, detailed characteristics of the content of the inorganic components were identified and based on that the retention coefficients were calculated. Table 3 presents the calculated values of retention coefficients for both GT-1 and GT-2 RO concentrates.

The results of the experiments indicated that after the tests with 50% permeate recovery for both waters was observed quite high retention of major ions, metasilicic acid and lithium. The average value of the retention coefficients for mentioned ions oscillates around 70% for both waters. The exceptions were identified for sulphates, iron, antimony, chromium and iodide ions, for which low values of retention coefficients were calculated, even negative ones. In the case of iron, the decrease of its content was caused by that iron colloids precipitated from the retentate and settle on the membrane surface, so it is necessary to implement iron removal before applying the membrane process. Regarding iodides, it should be noted that the content in the raw water was very low, and as a result of concentration cannot be excluded that some of the iodides vanished, what caused the identified decrease. Moreover, due to the low content of iodides (close to the limit of quantification) and the high concentration of dissolved solids (over 1,000 mg L^{-1}) the uncertainty of measurements increases and the precision of determination of these element decreases [37]. For GT-1, the water concentrate retention coefficients of iodide and barium ions were amounted about 165% and 92%, respectively. For GT-2 concentrate, for more than half of selected parameters the retention rates were slightly lower than for GT-1 and varies up to 88%, only few of them exceeded 70%. To elevate concentrations of desired ions in retentates, for further tests higher value of permeate recovery (75%) was applied. It was provided to increase process efficiency, potential reuse of permeates as drinking or industrial water, and also to expand possible concentrates reuse in different industries, among others balneology or cosmetology. The results presented in Tables 2 and 3 indicated that, for 75% permeate recovery, concentration of most parameters in both concentrates significantly increased compared with the processes with 50% permeate recovery. The most visible changes were observed for major mono- and divalent ions. Monovalent major cations retention coefficients in GT-1 concentrate increased more than two times (up to about 160%), whereas this values raised in GT-2 retentate more than two times only for K^+.

Table 3
Retention coefficients established for GT-1 and GT-2 concentrates

Parameter	GT-1		GT-2	
	Retention coefficient for GT-1 concentrate (permeate recovery 50%) *R*(%)	Retention coefficient for GT-1 concentrate (permeate recovery 75%) *R*(%)	Retention coefficient for GT-2 concentrate (permeate recovery 50%) *R*(%)	Retention coefficient for GT-2 concentrate (permeate recovery 75%) *R*(%)
Mineralization	66	148	73	148
Na^+	70	155	74	164
K^+	70	163	88	139
Ca^{2+}	79	147	67	128
Mg^{2+}	74	146	73	112
Cl^-	73	180	73	146
SO_4^{2-}	54	135	73	99
HCO_3^-	72	137	69	99
H_2SiO_3	67	138	69	107
I^-	165	61	–8	–78
Li^{2+}	76	171	64	109
Fe^{2+}	–85	5	20	–61
Sr^{2+}	74	142	70	126
Mn^{2+}	64	33	70	96
Ba^{2+}	92	114	48	65
As^{3+}	727	348	35	–21
Sb^{3+}	146	52	76	–5
Cr^{3+}	55	5	35	6

For divalent cations, among others Mg^{2+} and Ca^{2+}, retention coefficients were amounted around 145% for GT-1 and 118% for GT-2. Elevation of concentrate compaction caused significant increase of SO_4^{2-} in GT-1 concentrate (from 54% to 135%); however, in GT-2 this value changed only from 73% to 99%. Rising the permeate recovery value caused in lower retention of I^- (more than 2 times up to 61%), Mn^{2+} (about 2 times up to 33%) in GT-1 concentrate and visible decrease of I^- (almost 10 times), Fe^{2+} (about 4 times) in GT-2 retentate. The results indicated that for higher permeate recovery retention coefficients of most selected parameters in concentrates significantly increased, even doubled its value or more, especially this tendency was observed for major ions. The results of the experiments indicated that for GT-1 the maximum rejection of salts (97%), boron (72%) and SiO_2 (97%) were established for the process with 75% permeate recovery (which corresponds with retention coefficients in concentrates) and these values are close to maximum rejection values presented by manufacturer for given membrane (Table 1). Similar tendency was observed for GT-2 water (except boron), for which maximum rejection values of salts, boron and SiO_2 amounted 94%, 36% and 95%, respectively.

In order to assess possible concentrates reuse for therapeutic treatments, ca. the concentration of metasilicic acid was evaluated. The high retention of this compound was identified in GT-1 and GT-2 concentrates, for 50% of recovery, respectively, 67% and 69%. For higher concentrate compaction, the permeate recovery level has been elevated from 50% to 75% which consequently resulted in an increase in the value of the coefficient up to 138% for GT-1 and to 107% for GT-2. Moreover, based on Table 2 can be noticed that concentration of metasilicic acid for GT-1 increased from 79.43 to 132.62 and 188.94 mg L^{-1} for, respectively, 50% and 75% permeate recovery. Whereas, for GT-2 retentate concentration of this ion also slightly increased from 37.49 to 48.81 and 59.74 mg L^{-1}. The elevation of permeate recovery rate allowed for greater recovery of desired ions from raw geothermal waters. Specific ions, inter alia, metasilicic acid can determine the medicinal property of brine, including usefulness in therapeutic treatment. No additional chemicals were applied, water was only concentrated and the composition has not been changed through chemical processes, so RO concentrates can be considered as natural water and potentially classified as therapeutic water. According to classification of therapeutic groundwaters (created based on their pharmaco-dynamic factors) [36] both raw GT-1 water and GT-1 concentrates can be potentially classified as therapeutic waters because the content of metasilicic acid significantly exceeded 70 mg L^{-1} (threshold value for therapeutic waters), however for GT-2 water and its concentrates concentration of this parameter did not exceeded 70 mg L^{-1} (even after substantial minimization of concentrate volume). The concentrate volume minimization allowed for greater recovery of major ions, metasilicic acid, lithium, strontium and manganese from desalinated water. Moreover, based on the results presented in Tables 2 and 3 it can be concluded that both raw waters and RO concentrates (especially GT-2 concentrates) can be regarded as a valuable resource for production of mineral solution, because of high content of sodium ions and chlorides. Gained RO retentates can also potentially be a source of other products for industry, especially cosmetology and balneology. After application of RO process with 75% permeate recovery, almost all of the dissolved solids from the feed water remained in the gained concentrates. Moreover, for the GT-2 water, visibly higher mineralization and content of major ions are observed in generated concentrates. The issues regarding the possibility of comprehensive further reuse, obtaining mineral substances, ions, salt, metals and managing of concentrates, including RO streams, are the subject of many studies. Rioyo et al. [15] showed that the integration of an intermediate 'high-pH precipitation treatment' between subsequent RO stages can increase the salt recovery and minimize the volume of concentrate. It is accomplished by treated RO concentrate with different alkaline reagents, resulting in significant removal of scale-forming precursors (e.g., magnesium, calcium, strontium and barium), by softening RO concentrate with lime and soda ash, by pH re-adjustment, and by antiscalant addition. As a consequence, permeate recovery can be increased up to 97% [15]. Joo and Tansel [16] indicate that RO concentrates usually are problematic to utilization. Using hybrid processes or integrated different membrane processes can be an effective method to enhancing overall recovery rate, even moving towards near-zero discharge [16]. Jeppesen et al. [20] also emphasize that removal of some elements can have beneficial effect on the environment (e.g., phosphorus), whereas extraction of sodium chloride or rubidium can be economically viable and can increase profitability of process. Also indicate that adoption of zero-liquid discharge desalination systems can reduce environmental effects associated with RO concentrate management and allow extraction of mineral by-products from concentrate [20]. Tang et al. [21] proposed a hybrid process (three-step NF-NF-DiaNF) to selectively separating divalent ions from raw water in cost-effective fashion for further reuse of gained products and for concentrate volume minimization [21]. Kim [26] has reviewed different techniques for salt recovery for concentrate and indicated that suitable technique selection for salt recovery requires taking into account several parameters, such as geological, hydrogeological, climatic and economic [26]. Naidu et al. [38] investigated wastewater RO concentrate treatment methods for potential water reuse. They tested membrane distillation as a treatment option for wastewater RO concentrates for water production, selective ion precipitation and as consequence promising zero-liquid discharge technique. They gained similar results for ion rejection and permeate flux decline.

Apart from the larger recovery of the particular components gained by increasing the value of permeate recovery rate (up to 75%), an important factor affecting the efficiency of the desalination process (e.g., RO) is the flow rate of the permeate in time. The processes desalinating GT-1 water proceeded with slightly decrease in the permeate flux in time (Fig. 2). For the process with 50% of permeate recovery this value decreases from 82% to 73% in the final phase of the test, whereas for 75% permeate recovery this value changes from 59% to 43%. The process with the use of GT-2 water and with 50% recovery of feed water proceeded with a significantly lower efficiency of permeate flux than for the GT-1 water (Fig. 3). Similar tendency was observed for the process with 75% of permeate recovery, where permeate flux decreased

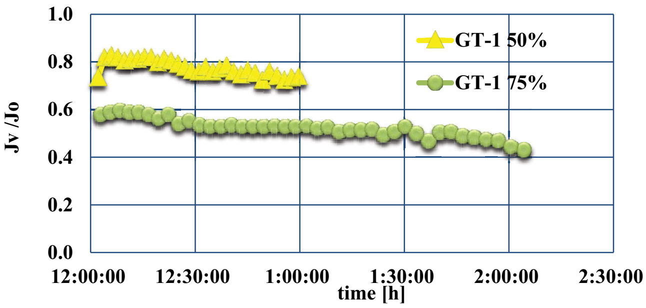

Fig. 2. Changes of permeate flux during RO processes of first geothermal water (GT-1) with 50% and 75% permeate recovery.

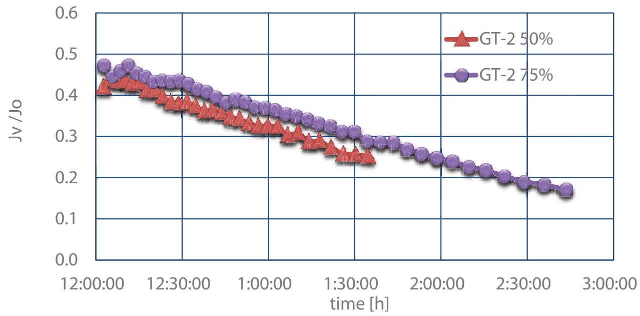

Fig. 3. Changes of permeate flux during RO processes of first geothermal water (GT-2) with 50% and 75% permeate recovery.

from 48% to 18% in the final phase. Despite such a significant increase in retention coefficients for most of considered ions in concentrates obtained from the processes with 75% permeate recovery, the efficiency of the process will strictly depend on the occurring decrease in permeate flux efficiency over time caused by scaling phenomenon. Figs. 2 and 3 show the change in relative permeate flux J/J_0 (J – volumetric flux of permeate, J_0 – volumetric flux of deionized water) with time during processes.

Additionally, the quantity of undesirable and toxic components, among other heavy metals such as chromium and lead, in desalination concentrates may exceed highest acceptable concentrations or discharge limits and thus it can restrain possible management or reuse of retentates, because of its disadvantageous influence on the environment and non-compliance with legal requirements.

3.2. Concentrates as useful products in therapeutic treatments

The assessment of the possibility of reuse of the gained concentrates, which is based on experimental data can potentially be regarded as useful products in therapeutic treatments (e.g., in health baths), in the case of Poland area requires the assessment in order to meet the requirements of the Regulation of the Minister of Health [39]. The highest acceptable amounts of undesirable and toxic components in therapeutic waters, in reference to their concentrations in tested raw waters, GT-1 and GT-2 concentrates are shown in Table 4. Based on gained experimental data, a particularized comparison of the admissible concentration of undesired components in relation to the therapeutic waters, used for example as drinking water, inhalation and external use

Table 4
Concentration of undesirable constituents in obtained concentrates, according to regulation of Minister of Health (MH) [39]

Parameter	Highest acceptable concentrations of undesirable components according to regulation of Minister of Health			GT-1			GT-2		
	Drinking treatments ($mg\ L^{-1}$)	Inhalations ($mg\ L^{-1}$)	External use ($mg\ L^{-1}$)	GT-1 raw water ($mg\ L^{-1}$)	GT-1 RO concentrate (permeate recovery 50%) ($mg\ L^{-1}$)	GT-1 RO concentrate (permeate recovery 75%) ($mg\ L^{-1}$)	GT-2 raw water ($mg\ L^{-1}$)	GT-2 RO concentrate (permeate recovery 50%) ($mg\ L^{-1}$)	GT-2 RO Concentrate (permeate recovery 75%) ($mg\ L^{-1}$)
Ni	0.03	0.03	–	0.001	0.005	0.003	0.002	0.003	0.004
Pb	0.01	0.01	–	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Hg	0.001	0.001	–	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Cd	0.003	0.003	–	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
Al	0.1	0.1	–	0.008	0.009	0.008	0.005	0.005	0.005
Cr	0.01	0.01	–	0.019	0.029	0.019	0.039	0.053	0.041
B	5.00	30.00	–	9.76	12.14	16.74	0.35	0.58	1.39
As	0.05	0.1	–	0.002	0.020	0.011	0.014	0.019	0.011
Sb	0.01	0.01	–	0.0004	0.0011	0.0007	0.0002	0.0004	0.0002
Ba	1.0	10.0	–	0.044	0.084	0.093	0.099	0.146	0.163

water showed that, in GT-1 raw waters and both concentrates, content of boron exceeded permissible value to use them for drinking water therapy and inhalations. Moreover, in both GT-1 and GT-2, raw waters and their concentrates content of chromium also exceeded permissible content and they could not be used in drinking water therapy and inhalations. The permissible concentration of chromium indicator is 0.01 mg L^{-1}, while content of chromium in GT-1 RO concentrate after the process with 50% permeate recovery exceeded permissible value about three times, while after the process with 75% recovery only two times (as in the case of raw GT-1 water). For boron, similar tendency was observed, its value exceeded acceptable amount two times in raw water and in GT-1 concentrate (50% permeate recovery), whereas for second GT-1 concentrate exceeded more than three times. The results of the tests conducted with GT-2 revealed that because of chromium content in raw GT-2 water and its concentrates, which exceeded four times established standard in GT-2 raw water and concentrate (after the process with 75% recovery) and five times in second concentrate, cannot be used in drinking water treatments and inhalations. The results indicated that all concentrates could potentially be used in external treatment therapy or they could be a source of a number of valuable substances, among others therapeutic salts and also as a source product for cosmetics production and balneology industry. Minimizing the volume of the obtained concentrates did not limit the possibility of their use, both for GT-1 and GT-2 water, in accordance with the regulations of the Minister of Health.

4. Summary and conclusions

The aim of this work was to present the results of the assay oriented towards the examination of the influence of minimization of the geothermal water concentrate, obtained by means of RO process, on their quality and possibilities of further multi-variant reuse. The tests were conducted based on two geothermal waters extracted from wells located in Poland area. Naturally they exhibit elevated concentrations of main ions and other components, which can be valuable for therapeutic industry. RO processes conducted in laboratory scale have allowed for a detailed recognition of the influence of the concentrate volume minimization, in adopted process parameters of desalination, on theirs composition. The presented results indicated that minimization of concentrate volume can be a promising solution for treatment of cooled, previously used for heating geothermal waters in order to gain products useful for different branch of industry. The study results revealed that concentrates gained from RO tests with 75% recovery of permeate are characterized with significantly higher value of TDS than for the tests with 50% permeate recovery. Generally, the assay has shown that growth in permeate recovery from 50% to 75% influences on the value of retention coefficients of specific physico-chemical parameters. The process with 75% permeate recovery allowed to gain additionally higher concentrated product, for most of the parameters, values of retention coefficients have been at least doubled.

The processes of desalinating GT-1 and GT-2 geothermal waters with 75% permeate recovery proceeded with slightly significant decrease in permeate flux with time compared with processes with 50% of permeate recovery. For GT-1 numbers varies from 82% to 73% for 50% recovery and from 59% to 43% for 75% permeate recovery, whereas for GT-2 smaller differences were observed. The permeate flux changes between 45% and 25% for the process with 50% recovery and from 48% to 18% for 75% permeate recovery.

Additionally, the assessment of the possibility of using the concentrates as therapeutic products in Poland area was made on the basis of applicable legal regulations. The results of the research showed that in GT-1 and GT-2 concentrates, regardless of the level of permeate recovery, content of chromium and boron (only for GT-1 concentrates) exceeded permissible level for drinking therapeutic treatment and inhalations. Generally, the research showed that all concentrates can be used for external treatments, for example, balneological treatments, sanitary bath and recreational pools. However, due to the visibly higher value of retention coefficients of selected parameters, concentrates after process with 75% are potentially more valuable source of different minerals, because of significantly higher content of major ions, silica and other dissolved solids. Elevated concentration of metasilicic acid (more than 70 mg L^{-1}) in GT-1 concentrates creates opportunities to use them also in the balneology and cosmetology industry. The research indicates that minimization of concentrates volume caused significant elevation of content of the desired (in some cases also undesired) components, and consequently these concentrates can be a potential source of mineral solutions applied in different industries.

Acknowledgements

The presented work was financed by the Polish National Centre for Research and Development, Project No. 245079 (2014–2017) and partly from AGH University of Science and Technology, grant No. 15.11.140.002 and 11.11.140.031.

References

[1] V.G. Gude, Geothermal source potential for water desalination – current status and future perspective, Renew. Sustain. Energy Rev., 57 (2016) 1038–1065.
[2] J. Bundschuh, B. Tomaszewska, Eds., Geothermal Water Management Series, Sustainable Water Developments Resources, Management, Treatment, Efficiency and Reuse, CRC Press, Balkema, 2018.
[3] W.F. da Silva, I.F.S. dos Santos, M.C.C. de Oliveira Botan, A.P.M. Silva, R.M. Barros, Reverse osmosis desalination plants in Brazil: a cost analysis using three different energy sources, Sustain. Cities Soc., 43 (2018) 134–143.
[4] M. Shah, A. Sircar, R. Varsada, S. Vaishnani, U. Savaliya, M. Faldu, D. Vaidya, P. Bhattacharya, Assessment of geothermal water quality for industrial and irrigation purposes in the Unai geothermal field, Gujarat, India, Groundwater Sustain. Dev., 8 (2019) 59–68.
[5] I.G. Wenten, Khoiruddin, Reverse osmosis applications: prospect and challenges, Desalination, 391 (2016) 112–125.
[6] B. Tomaszewska, M. Tyszer, Assessment of the influence of temperature and pressure on the prediction of the precipitation of minerals during desalination process, Desalination, 424 (2017) 102–109.
[7] B. Tomaszewska, E. Kmiecik, K. Wątor, M. Tyszer, Use of numerical modelling in the prediction of membrane scaling. Reaction between antiscalants and feedwater, Desalination, 427 (2018) 27–34.
[8] Meer A.M. Khan, S. Rehman, Fahad A. Al-Sulaiman, A hybrid renewable energy system as a potential energy source for water desalination using reverse osmosis: a review, Renew. Sustain. Energy Rev., 97 (2018) 456–477.
[9] B. Tomaszewska, L. Pająk, J. Bundschuh, W. Bujakowski, Low-enthalpy geothermal energy as a source of energy and integrated freshwater production in inland areas: technological and economic feasibility, Desalination, 435 (2018) 35–44.
[10] N. Kabay, P. Koseoglu, E. Yavuz, U. Yuksel, M. Yuksel, An innovative integrated system for boron removal from geothermal water using RO process and ion exchange-ultrafiltration hybrid method, Desalination, 316 (2013) 1–7.
[11] A. Subramani, Joseph G. Jacangelo, Treatment technologies for reverse osmosis concentrate volume minimization: a review, Sep. Purif. Technol., 122 (2014) 472–489.
[12] B. Tomaszewska, M. Tyszer, M. Bodzek, M. Rajca, The concept of multivariant use of geothermal water concentrates, Desal. Wat. Treat., 128 (2018) 179–186.
[13] B. Bozicek, S. Lojen, M. Dolenec, G. Vizintin, Impacts of deep groundwater monitoring wells on the management of deep geothermal Pre-Neogene aquifers in the Mura-Zala Basin, Northeastern, Groundwater Sustain. Dev., 5 (2017) 193–205.
[14] B. Tomaszewska, A. Szczepański, Possibilities for the efficient utilization of spent geothermal waters, Environ. Sci. Pollut. Res., 21 (2014) 11409–11417.
[15] J. Rioyo, V. Aravinthan, J. Bundschuh, M. Lynch, Research on 'high-pH precipitation treatment' for RO concentrate minimization and salt recovery in a municipal groundwater desalination facility, Desalination, 239 (2018) 168–178.
[16] S.H. Joo, B. Tansel, Novel technologies for reverse osmosis concentrate treatment: a review, J. Environ. Manage., 150 (2015) 322–335.
[17] S. Shanmuganathan, M.A.H. Johir, A. Listowski, S. Vigneswaran, J. Kandasamy, Sustainable processes for treatment of waste water reverse osmosis concentrate to achieve zero waste discharge: a detailed study in water reclamation plant, Procedia Environ. Sci., 35 (2016) 930–937.
[18] H.R. Tomasini, M.C. Hacifazlioglu, N. Kabay, L. Bertin, T.O. Pek, M. Yuksel, Concentrate management for integrated MBR-RO process for wastewater reclamation and reuse-preliminary tests, J. Water Process Eng., 2019, https://doi.org/10.1016/j.jwpe.2017.07.020.
[19] F. Mohammadesmaeili, M.K. Badr, M. Abbaszadegan, P. Fox, Mineral recovery from inland reverse osmosis concentrate using isothermal evaporation, Water Res., 44 (2010) 6021–6030.
[20] T. Jeppesen, L. Shu, G. Keir, V Jegathessan, Metal recovery from reverse osmosis concentrate, J. Clean. Prod., 17 (2009) 703–707.
[21] S.C.N. Tang, L. Birnhack, P. Nativ, O. Lahav, Highly-selective separation of divalent ions from sweater and sweater RO retentate, Sep. Purif. Technol., 175 (2017) 460–468.
[22] B. Kim, H. Kwon, S. Hee Ko, G. Lim, J. Han, Partial desalination of hypersaline brine by lab-scale ion concentration polarization device, Desalination, 412 (2017) 20–31.
[23] T. Istriokhatun, M.N. Dewi, H.I. Ilma, H. Susanto, Separation of antiscalants from reverse osmosis concentrates using nanofiltration, Desalination, 429 (2018) 105–110.
[24] J. Liu, J. Yuan, Z. Ji, B. Wang, Y. Hao, X. Guo, Concentrating brine from sweater desalination process by nanofiltration-electrodialysis integrated membrane technology, Desalination, 390 (2016) 53–61.
[25] Thomas M. Missimer, Robert G. Maliva, Environmental issues in sweater reverse osmosis desalination: intakes and outfalls, Desalination, 434 (2018) 198–215.
[26] D.H. Kim, A review of desalting process techniques and economic analysis of the recovery of salts from retentates, Desalination, 270 (2011) 1–8.
[27] L.F. Greenlee, F. Testa, D.F. Lawler, B.D. Freeman, P. Moulin, The effect of antiscalant addition on calcium carbonate precipitation for a simplified synthetic brackish water reverse osmosis concentrate, Water Res., 44 (2010) 2957–2969.
[28] Y. Chen, J.C. Baygents, J. Farrell, Removing phosphate antiscalants from membrane concentrate solutions using granular ferric hydroxide, J. Water Process Eng., 19 (2017) 18–25.
[29] J.W. Lund, Balneological use of thermal and mineral waters in the U.S.A., Geothermics, 25 (1996) 103–147.

[30] A. Huang, S. Seite, T. Adar, The use of balneotherapy in dermatology, Clin. Dermatol., 36 (2018) 363–368.
[31] J.W. Lund, Balneological Use of Thermal Waters, Geo-Heat Center, Klamath Falla, OR, USA. Available at: https://www.oit.edu/docs/default-source/geoheat-center-documents/publications/balneology/tp109.pdf?sfvrsn=2.
[32] I. Bacle, S. Meges, Ch. Lauze, P. Macleod, P. Dupuy, Sensory analysis of four medical spa spring waters containing various mineral concentrations, Int. J. Dermatol., 38 (1999) 784–786.
[33] B. Tomaszewska, M. Bodzek, M. Rajca, M. Tyszer, Geothermal water treatment. Membrane selection for the RO process, Desal. Wat. Treat., 64 (2017) 292–297.
[34] B. Tomaszewska, M. Rajca, E. Kmiecik, M. Bodzek, W. Bujakowski, M. Tyszer, K. Wątor, Process of geothermal water treatment by reverse osmosis. The research with antiscalants, Desal. Wat. Treat., 74 (2017) 1–10.
[35] DOW FILMTEC ROBW30HR-440i Nanofiltration Element for Commercial System – Product Information (Form No. 609-02171-0609). Available at: https://www.lenntech.com/Data-sheets/Dow-Filmtec-BW30HR-440i.pdf.
[36] W. Ciężkowski, J. Chowaniec, W. Górecki, A. Krawiec, L. Rajchel, A. Zuber, Mineral and thermal waters of Poland, Przegląd Geologiczny, 58 (2010) 762–774.
[37] M. Dwornik, E. Kmiecik, M. Bebek, Influence of analyses method on uncertainty associated with halogens determination in Upper Odra River Basin surface water and colamine water inducted to it, Przegląd Geologiczny, 68 no. 10/1 (2015) 705–709.
[38] G. Naidu, S. Jeong, Y. Choi, S. Vigneswaran, Membrane distillation for wastewater reverse osmosis concentrate treatment with water reuse potential, J. Membr. Sci., 524 (2017) 565–575.
[39] Regulation of the Minister of Health of 13 April 2006 on the Scope of the Studies Required to Determine the Medicinal Properties of Natural Medicinal Resources and Medicinal Properties of Climate, the Criteria for Their Evaluation and a Specimen Certificate Confirming These Properties (consolidated text: Journal of Laws 2018 item 605).