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Pretreatment and desalination of flowback water from the hydraulic fracturing

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ABSTRACT

A process based on pre-treatment and membrane desalination was studied for the treatment of the flowback water from drilling for shale gas in Lubocino in Poland. The effectiveness of pre-treatment technology, which contained NaOH alkalization, $KMnO_4$ oxidation, filtration, sorption, and fine filtration, was studied. Also the usefulness of nanofiltration (NF) and reverse osmosis (RO) membranes for flowback desalination was tested. The study was carried out in the semi-pilot scale. The applied pre-treatment technology made possible to obtain a product that can be placed on the NF and RO elements (turbidity = 0.882 NTU, silt density index = 3.1). The 4040-SR100-N2 NF element was ineffective for flowback water purification, and the retention of contaminants was low (5.1% conductivity, 18.2% total hardness, 9.2% TOC). The AG4040FM RO element was characterized by higher retention (conductivity 93.9%, total hardness 98.3%, TOC 78.1%), but low volume concentration ratio (VCR) (VCR = 1.6) with more than 50% decrease in the permeate flux obtained. The AD-90 RO element was characterized by the highest retention (conductivity 99.3%, total hardness 99.8%, TOC 91.1%), and VCR was 4 by minimal decrease of permeate flux. Proposed pre-treatment technology combined with desalination on AD-90 RO element allows to obtain flowback water reusage. The return of flowback water to the environment requires the application of advanced oxidation to decrease the level of organic contamination.

Keywords: Flowback water; Pre-treatment; Nanofiltration; Reverse osmosis; Desalination

1. Introduction

Water is a strategic resource for shale gas extraction, as it is used for drilling and is the basis for the preparation of the fracturing fluid [1]. A typical fracturing fluid, the task of which is to prevent the fracture closing after reducing the pressure, consists of 96.0% water and 3.57% proppant (usually sand), and the rest are chemical additives designed to improve the fracturing process [2]. They include, among others,

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acids, potassium chloride, gelling agents, crosslinkers, surfactants, scale inhibitors, pH buffers, breakers, friction reducers, iron control agents, oxygen scavengers, corrosion inhibitors, biocides, and very small quantities of benzene, ethylene glycol, or naphthalene [2–4]. The composition of the fracturing fluids is generally similar, with slight differences due to the additives used, which are dependent on the composition of the geological formation and its physical and geomechanical properties. The list of additives, which are in hydraulic fracturing potentially used, is very large and contains substances with diverse physicochemical properties [5].

Within a few weeks after fracturing, the fluid flows out of the hole to the surface. It is characterized by variable and high content of suspended solids (TSS 10.8–3,220 mg/L, turbidity 2.3–1,540 NTU) and dissolved solids (TDS 680–345,000 mg/L, chlorides 1,670–181,000 mg/L) [6]. They distinguished the characteristic groups of flowback water pollutants as the following: (1) TSS and bacteria, (2) oil and grace, (3) hardness, and (4) TDS and salinity [7]. According to another division the following are distinguished as follows: (1) salts, (2) organic hydrocarbons, (3) organic and inorganic additives, and (4) naturally occurring radioactive material [8]. Among the ionic components, the dominant in the flowback water are sodium, calcium, and chlorides; the other are magnesium, potassium, iron, barium, carbonates, bicarbonates, sulfates, and bromides [6,8]. The composition of the flowback water is variable in time, and the observed increase of salinity at the final stage of discharge is the result of mixing of injection waters with highly concentrated *in situ* brines [9]. Its composition may also vary depending on the geologic basin and specific rock strata of formation [4].

The flowback water treatment technology can be divided into two stages: pre-treatment and desalination, which are carried out by various methodologies. In Kidder et al. [7], the authors proposed the treatment options for the pre-treatment to remove the suspended solids in the process of filtration on the filters with replaceable cartridges or bag filters. In the studies on ceramic membranes, it has been demonstrated that a serial operation using 1.4- and 0.2-mm MF membranes was effective for removing the suspended solids from flowback water characterized by low level of TSS [10]. MF and UF membranes efficiently removed only TSS, whereas the total organic carbon (TOC) and salinity were reduced not before the process of ion exchange. Other studies on the treatment of flowback water show that the hollow fiber UF membrane modification with polidopamine improved the flux of permeate and decreased transmembrane pressure (TMP), as well as improved the efficiency of membrane cleaning [11]. An effective way to treat the flowback water, allowing 99.6% reduction of suspended solids, is alkalization combined with $KMnO_4$ oxidation and fine filtration [12,13]. The method additionally allowed to reduce the iron concentration by 99.3% and manganese by 91.4%, but also did not decrease the content of organic carbon. Commercial experience with treatment of flowback water from the Marcellus formation shows the usefulness of sequential precipitation technology, where bivalent cations were precipitated in separate steps [14].

The listed technological solutions can provide the treatment of flowback water to the state in which it can be introduced into the desalting installation or be reused for fracturing. In commercial desalination installations, reverse osmosis [15,16], as well as a multistage distillation in conjunction with crystallization [17,18], is used. Reverse osmosis (RO) is used when the TDS does not exceed the value of 40,000 mg/L, whereas at higher salinity, it is proposed to apply distillation [7]. The processes of evaporation and salt crystallization implemented in mobile evaporator units produce very good results, but this technology generates high investment and operating costs [19]. The results of computer software simulation demonstrated that dual-stage pressure-retarded osmosis/forward osmosis can be suitable for dilution of hypersaline flowback water before conventional RO desalination [20]. Installations for the flowback water treatment are manufactured as mobile units. Their mobility helps to minimize the fluid transportation to and from the treatment plant. On-site treatment is cost-effective and allows us to recover the water, thereby reducing water consumption for a new fracturing operation [1].

The objective of this study was to treat the flowback water from hydrofracturing using two-stage technology: pre-treatment and nanofiltration (NF)/RO membrane separation. Pre-treatment of the flowback water using MF and UF membranes is not particularly effective because they have a tendency to be blocked [10]. A more effective method of flowback clarification was to unite alkalization, oxidation of $KMnO_4$, and filtration [12,13], which was estimated in laboratory tests. Thus, there was a necessity to move the tests to a fractional–technical scale and confirm the usefulness of this technology for flowback clarification, which is shown in this study. The pre-treated flowback water requires removal of dissolute contaminants, especially salinity. The NF and RO processes are commonly used to desalinate water. However, observing a complex composition of the flowback their application can be difficult. The aim of this study was to investigate the suitability of an NF spiral-wound commercial element to soften the flowback, as well as low- and high-pressure RO spiral-wound commercial elements to desalinate the flowback rich in organic matrix. Flowback water was collected from a well in Lubocino in the northern part of Poland and is characterized by high content of organic compounds in comparison to flowback water taken from other hydrofracturing wells [21]. The overriding goal of the treatment technology discussed herein is to lower the level of impurities to the levels mandated by various regulations governing reuse or return of flowback water to the environment.

2. Experimental

2.1. Pre-treatment

The tested material was the flowback water after hydraulic fracturing of the well in Lubocino, in the northern part of the Poland. The experiment was conducted on a fractional–technical scale on the samples with a volume of 1 m^3. The flow diagram of the flowback water treatment system is shown in Fig. 1. Before the membrane separation processes, the flowback water was subjected to initial treatment that includedthe following: initial filtration, pH adjustment, oxidation, sedimentation, classic filtration, sorption, and fine filtration. For the initial filtration, the 10´´ (0.25 m) polypropylene string cartridge filter 100 μm was used. The pH adjustment was carried out on the flow to 7.5 with 4% solution of NaOH. For oxidation, 5% solution of $KMnO_4$ was used, which was metered by portions into the tank at a dose of 0.33 g/L. A mixture of flowback water and reagents was stirred for 20 min. This time allowed full reduction of the oxidizer [13]. Reduction of $KMnO_4$ was controlled by the presence of violet color in the sample of the mixture filtered through a filter paper. Next, 15-min sedimentation was applied. Supernatant fluid was delivered via pump onto the mechanical filter filled with quartz sand of grain size of 0.4–0.8 mm and a filtration layer height of 1.2 m. The filtration was carried out at speed of 14 m/h. The next element was an activated carbon filter (ACF—filtration rating 10 μm, length 10″ (0.25 m)). For the fine filtration, the polypropylene depth filter cartridge (PDFC—filtration rating 5 μm, length 10″ (0.25 m)) was used.

2.2. Membrane treatment

Pre-treated flowback water formed the feed water introduced into desalination membranes whose characteristics are shown in Table 1. Data was taken from manufacturers information sheets. The membrane modules were operated in parallel. Each of the membranes was tested in the concentrating system, collecting permeate into a separate container and turning back the whole stream of retentate to the tank with feed water. The degree of the feed water concentration was determined by the volume concentration ratio (VCR) factor calculated from the formula:

$$\mathrm{VCR} = \frac{V_{\mathrm{fw}}}{V_{\mathrm{fw}} - V_p} \tag{1}$$

where V_{fw}—feed water volume (m^3), V_p—permeate volume (m^3).

Cross-flow and constant TMP, which amounted to 1,000 kPa for 4040-SR100-N2 membrane, 1,900 kPa for

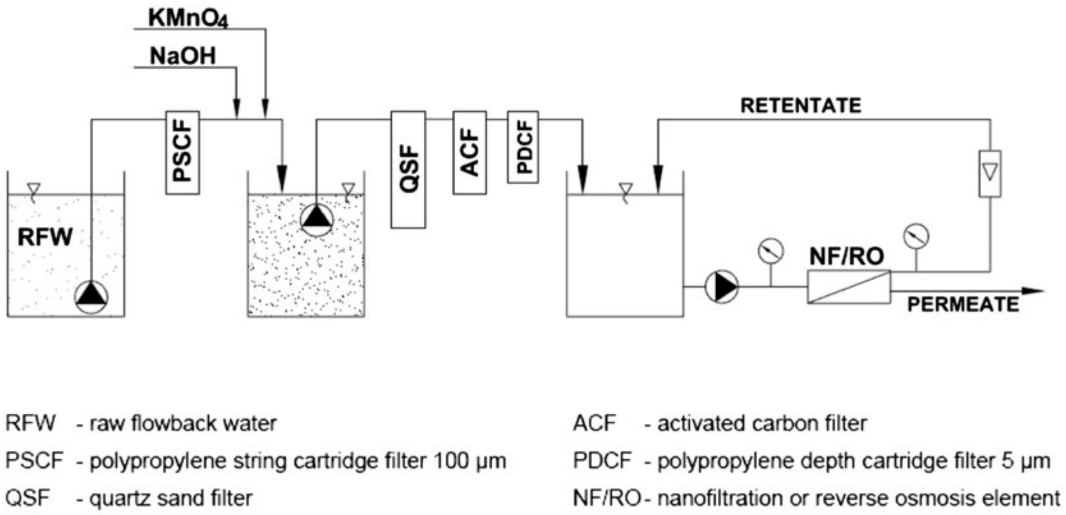

Fig. 1. Flow diagram of flowback water treatment system.

Table 1
Specification of tested membranes

Model	4040-SR100-N2	AG4040FM	AD-90
Manufacturer	Koch membrane systems	General electric company	General electric company
Process type	NF	Low-pressure RO	High-pressure RO
Architecture	Spiral-wound	Spiral-wound	Spiral-wound
Active area (m^2)	5.4	7.9	8.4
Average permeate flow (m^3/d)	3.3[a]	8.3[b]	5.7[c]
Rejection (%):			
Average	>99.0[a]	99.5[b]	99.75[c]
Minimum	–	99.0[b]	99.3[c]
Operating pressure (kPa):			
Average	1,380–4,140	1,379	5,516
Maximum	4,140	4,137	8,274
Feed water pH range for continuous operation	4–10	4–11	4–11
Maximum operating temperature (°C)	50	50	50
Feed water quality:			
Turbidity (NTU)	<1	<1	<1
SDI (−)	<5	<5	<5

[a] Testing conditions: 5 g $MgSO_4$/L solution at 655 kPa operating pressure, 25°C, pH 7.5, and 15% recovery.

[b] Testing conditions: 2 g NaCl/L solution at 1,551 kPa operating pressure, 25°C, pH 7.5, and 15% recovery.

[c] Testing conditions: 32 g NaCl/L and 0.005 g B/L solution at 5,516 kPa operating pressure, 25°C, pH 8.0, and 7% recovery.

AG4040FM membrane, and 7,500 kPa for AD-90 membrane, were used. The effectiveness of treatment was determined on the basis of the percentage retention factor (R) for selected components of the flowback water, which was calculated from the formula:

$$R = \left(1 - \frac{C_p}{C_{fw}}\right)100\% \qquad (2)$$

where C_p—concentration of the component in permeate (mg/L) or (μs/cm), C_{fw}—concentration of the component in feed water (mg/L) or (μs/cm).

2.3. Analytical methods

The study of physicochemical parameters of the flowback water in the subsequent treatment steps was carried out using the following analytical methods: pH—electrometric method; turbidity—nephelometric method [22]; conductivity—conductometric method [22]; chlorides—argentometric titration method [22]; total alkalinity—potentiometric titration method [22]; total hardness—complexometric titration method [22]; ammonium ion—Nessler's reagent colorimetric method [23]; total nitrogen—colorimetric method, TNT persulfate digestion colorimetric procedure Hach No. 10071 [24]; total phosphorus—colorimetric method, TNT Phos Ver 3 acid persulfate digestion procedure Hach No. 8190 [24]; chemical oxygen demand (COD)—colorimetric method, reactor digestion procedure Hach No. 8000 [24]; iron and manganese—air/acetylene flame atomic absorption spectrophotometry method [22]; barium, strontium, and bromine—total reflection X-ray fluorescence method [25]; and TOC—non-purgeable organic carbon method [22]. The 15-min silt density index (SDI_{15}) in feed water (the product of pre-treatment) was tested according to the method described in [26].

3. Results and discussion

3.1. Pre-treatment

The physicochemical parameters of the flowback water at various stages of treatment are presented in Table 2. The results are shown for averaged samples. The process of flowback water pre-treatment allowed for the removal of 99.3 % of suspended impurities that caused turbidity. Oxidation allowed removal of iron and manganese from the flowback water with the effectiveness of 99.5 and 84.1%, respectively. Removal of iron partly translated into the observed decrease in total hardness. During the pH adjustment, the precipitation of green-colored salts of iron(II) was observed. Iron oxide is the main component of the submicron

Table 2
Characteristics of the flowback water at subsequent treatment stages

Parameters	Unit	Raw flowback water	Pre-treatment product (feed water)	4040-SR100-N2 membrane permeate	AG4040FM membrane permeate	AD-90 membrane permeate
pH	–	4.7	7.4	6.9	6.8	6.3
Turbidity	NTU	127	0.882	0.211	0.195	0.204
Conductivity	ms/cm	26.6	27.2	25.8	1.67	0.181
Chlorides	mg/L	11,190	11,180	10,540	548	80
Total alkalinity	mg $CaCO_3$/L	1,150	1,305	1,260	39	10.5
Total hardness	mg $CaCO_3$/L	4,625	4,170	3,411	69.5	6.5
Ammonium ion	mg/L	37.5	35.5	30.5	4.16	2.8
Total nitrogen	mg N/L	57	53	49	12	8.7
Total phosphorus	mg P/L	0.21	0.13	0.12	0.08	0.02
Iron	mg/L	55.7	0.26	0.12	0.03	<0.03
Manganese	mg/L	1.07	0.17	0.15	0.03	<0.01
Barium	mg/L	28.0	0.86	0.79	0.30	0.06
Strontium	mg/L	123.2	125.9	146.9	1.6	0.25
Bromine	mg/L	139.9	160.3	146.2	8.6	0.81
TOC	mg/L	1,610	1,514	1,374	332	135
COD	mg O_2/L	5,270	4,531	4,059	1,038	451

Notes: The presented values were measured in averaged samples of flowback water.
A limitation in the analysis of metal contents in the fracturing fluid is a matrix in the form of high salinity and lack of appropriate methodology [5]. Results of analyzes of the contents of Ba, Sr, and Br for the test, in which they appear as macro-constituents, are characterized by low statistical accuracy of the estimation, so the result should be treated as an approximation.

particles in flowback water, which would be responsible for the fouling effect [27]. Alkalization of flowback water was not sufficient to achieve an appropriate degree of purification and was assisted by $KMnO_4$ oxidation, as shown in previous studies [12]. The $KMnO_4$ oxidant caused a very effective destabilization of the colloidal suspension in flowback water. The stability of the colloidal particles in flowback water may be caused by the presence of scaling inhibitors and friction reducers. However, the addition of oxidant (H_2O_2) led to a destabilization of submicron particles by oxidizing the organic compounds as well as a reduction of turbidity in flowback water [27]. The advantage of use of $KMnO_4$ was the ease of control of its residues in the case of incomplete reduction of the oxidant. As a result of dispensing the reagents, sludge was formed in the reactor which sedimented very well after 15 min. Some sludge which had not sedimented and remained in the depths was separated on a sand filter. The filtration efficiency was high, and the filtrate turbidity values fluctuated around 1–2 NTU. Further removal of the suspended fraction was carried out on 10-μm carbon filter and especially on 5-μm depth filter. The depth filter has turned out to be very effective, and the product was received with a turbidity <1 NTU. In addition, the SDI test was performed for the final product of the pre-treatment system. The test was performed at the beginning and end of the treatment of 1 m^3 of the flowback water. The SDI values were 3.1 and 3.0, respectively, and testify for a sufficient removal of suspended solids from the flowback water. This value is accepted. The pre-treatment allowed for lowering the barium concentration with 96.9% efficiency. Most likely, the effect was caused by the precipitation of the barium compounds with very low solubility ($Ba(OH)_2$, $BaCO_3$) as a result of dosing NaOH. Some slight decrease in the content of nitrogen compounds, with no technological importance was observed in the product of pre-treatment. Ammonium ion was not susceptible to oxidation under the conditions of the experiment. Similarly, the total nitrogen content did not undergo significant reduction. The pH of the final filtrate was 7.4. This value is consistent with the requirements of the manufacturers of the tested membranes for the feed water reaction (Table 1).

The organic compounds measured as TOC were removed in the pre-treatment process with the small efficiency of 6%, which indicates that they were mainly in the dissolved phase. The reduction of the concentration of TOC was already noted in the filtrate from the quartz bed, but the concentration of organic carbon remained unchanged after filtration through activated carbon. Probably organic compounds introduced as additives for fracturing are not susceptible to the sorption on activated carbon, or the type of carbon was mismatched. The efficiency of treatment measured by COD parameter was 14%, and the higher value was due to the fact that COD allows the measurement of organic compounds susceptible to chemical oxidation but also some of the reduced inorganic compounds such as salts of iron(II). In order to achieve more effective treatment, the organic pollution load should be removed before the membrane separation. Oxidation with $KMnO_4$ has not given the expected results; therefore, further study must consider the Fenton oxidation reaction. It is facilitated by the low pH of the fracturing fluid. High concentration of iron(II) in the flowback water may reduce the need for its additional introduction for catalyzing the reaction of formation of hydroxyl free radicals. Another solution to maintain the oxidation step is using $KMnO_4$, which brings very good results in the reduction of turbidity and the content of iron, manganese, barium, and application of subsequent advanced oxidation H_2O_2/UV carried out on clear liquid. Another potential solution at a pre-treatment stage is the reduction of organic compound concentration by applying sorption by powder activated carbon combined with separation on the MF/UF membranes. However, in field conditions, this method cannot be applied due to the necessity of transportation of the sorbent and its utilization after the use.

The applied technology of flowback water pre-treatment after hydraulic fracturing made it possible to obtain a product that can be placed on the NF and RO membranes. This is evidenced by the parameters: turbidity and SDI, whose values are in line with the recommendations of the manufacturers of membranes (Table 1). In addition, a very large load of iron and manganese was removed, which concentration has been lowered to a level of about 0.2 mg/L, which counteracted their excessive precipitation in the form of deposits blocking the NF/RO membrane surface. This amount of residual iron and manganese forces, however, the need for periodic chemical cleaning of the membranes. The applied technology is just as effective for TSS removal from flowback as the serial MF/UF membrane treatment [10] and similarly does not allow for the elimination of organic impurities (TOC), but its advantage is a flux many times larger than ceramic membranes. Extremely high total hardness of flowback water that generates the scale on the membrane surface can be alarming. The applied pre-treatment technology did not include the processes clearly aimed at softening, although the use of NaOH could lead to partial decarbonisation, which resulted in the observed reduction in hardness. The precipitation and thermal methods were abandoned in the study because of the total hardness to total alkalinity ratio, which suggests a presence of mainly non-carbonate hardness. Another potential solution was softening by ion exchange. Unfortunately, this process generates large quantities of post-regeneration fluids, which are not advantageous in the operation of the mobile treatment plant. For these reasons, it was decided to remove the hardness at the stage of desalination in the membrane separation process.

3.2. Membrane treatment

Desalination using the NF membrane 4040-SR100-N2 was carried out at a constant permeate flux, amounting to 0.111 m^3/m^2 h. The process was characterized by low desalination efficiency of 5.1 and 5.7%, calculated as the average retention of conductivity and chlorides concentration. The softening efficiency was higher (18.2% retention of total hardness). This effect is unsatisfactory as compared to the NF membranes used in other applications where the rejection of water/wastewater constituents was achieved more than 83, 84, or 90% [28] or 90% [29]. The observed phenomenon can follow from the chemical composition of the flowback water in which non-carbonate hardness dominates and the majority of calcium and magnesium cations are connected with chloride anions which appear in a very high concentration (typical for the brines). It is likely that high concentration of the chlorides increased the transmission of calcium and magnesium cations trough the membrane. Work [30] shows that in the case of separation of the $MgCl_2$ solution using the NF membrane, monovalent chloride anions diffused faster through the membrane causing development of the electrostatic field. In the membrane on the permeate side, the negative charge dominated, which abnormally accelerated magnesium cations diffusion in the material of the NF membrane. High retention of the 4040-SR100-N2 membrane was determined by the manufacturer for the solution of salt with bivalent cation and anion ($MgSO_4$). This did not apply in the case of the flowback water with a very high concentration of $MgCl_2$ or $CaCl_2$, and that is why the effect of softening was very low. Similarly, the separation of organic compounds of the flowback water was very low (9.2% retention of TOC and 10.4% retention of COD). The quality parameters of the feed water delivered on the membrane 4040-SR100-N2, such as turbidity, SDI rate, and pH, were consistent with the manufacturer’s requirements. It can be concluded that this is not the right type of the membrane for the treatment of the flowback water after hydraulic fracturing by the NF method.

The changes in permeate flux during desalination of flowback water on the membranes of low- and high-pressure RO are illustrated in Fig. 2. The low-pressure membrane AG4040FM was tested at a much lower flux (0.009 m^3/m^2 h), because high salinity of the solution, and the osmotic pressure connected with it. This excluded the obtaining higher flux value at a given, typical for this membrane pressure. During the separation on the membrane AG4040FM, an intense decrease in the permeate flux was observed as a result of the growing concentration of the feed water and increase in the osmotic pressure. The low VCR factor, amounting to 1.6 with more than 50% decrease in the permeate flux was obtained. The membrane AD-90 operating at a higher TMP allowed to obtain a higher concentration ratio (VCR = 4) with a slight decrease in the permeate flux. The use of the high-pressure membrane was much more advantageous, since it allowed obtaining 75% volume of cleaned flowback water and 25% concentrated concentrate. The use of RO membranes led to a significant increase in the efficiency of desalination of the flowback water. The low-pressure membrane AG4040FM was characterized by retention: conductivity 93.9%, chlorides 95.1%, bromides 94.6%, ammonium ion 88.3%, total alkalinity 96.9%, total hardness 98.3%, and strontium 98.7%. The retention of components on the membrane AD-90 was higher and amounted as follows: conductivity 99.3%, chlorides 99.3%, bromides 99.5%, ammonium ion 92.1%, total alkalinity 99.2%, total hardness 99.8%, and strontium 99.8%. The retention of chlorides was comparable to that obtained on the high-pressure RO membrane (SWC3 + Hydranautics) and its analog modified by polydopamine (98.2 and 99.6%, respectively) [11]. In the case of organic compounds of flowback water, their retention on the tested membranes was lower and amounted as follows: TOC 78.1% and COD 77.1% for AG4040FM; TOC 91.1% and COD 90.0% for AD-90. They are the retentions calculated for the averaged sample of feed water at the beginning of the process and the averaged sample of permeate after membrane filtration (data from Table 2). The sample was averaged by mixing the total tank volume. During the membrane separation, the growth of concentration of the feed water components took place, resulting from the recirculation of the retentate stream. A changing concentration of components in permeate was also observed. Taking this into account the partial retention of conductivity, chlorides and TOC were calculated in successive stages of separation defined by subsequent values of the VCR factor, assuming the instantaneous concentration of the components in the feed water and permeate. The results are shown in Fig. 3. The separation on the membrane AG4040FM was characterized by the decrease in a partial retention in the function of feed water concentration and increase of osmotic pressure. The partial retention of TOC on the membrane AD-90 were similar. Partial retention of chlorides and conductivity on the membrane AD-90 was constant and at high level of 99.6–99.8%, which confirms its suitability for desalination of flowback water after hydraulic fracturing. A changing concentration of components in the permeate, connected with the concentration of feed water, was observed. A very intense increase in the conductivity in the permeate of the membrane AG4040FM already at a concentration level (VCR) of about 1.5 practically disqualifies the membrane to desalinate the flowback water. The increase

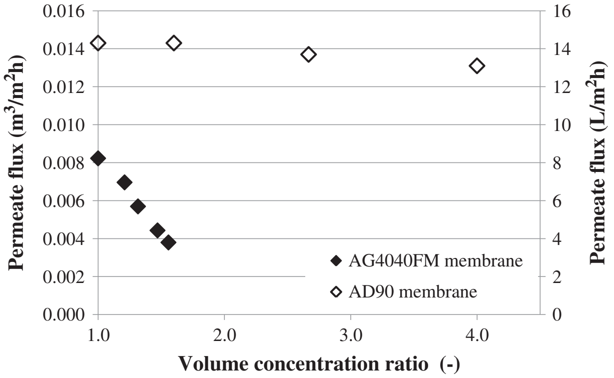

Fig. 2. Changes in permeate flux in the function of feed water VCR for RO elements (AG4040FM and AD90).

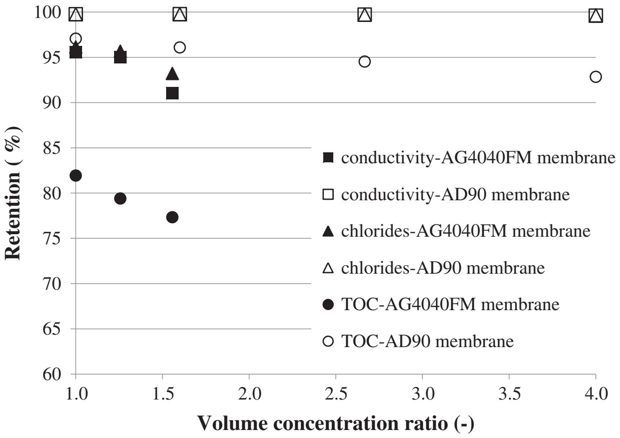

Fig. 3. Changes in retention of conductivity, chlorides, and TOC in the function of feed water VCR for RO elements (AG4040FM and AD90).

of conductivity in the permeate from the membrane AD-90 was less intense in spite of achieving a higher coefficient of VCR. The intensity of the increase in the TOC concentration in the permeate indicates insufficient efficiency of the process, particularly for the AG4040FM membrane.

The flowback water after hydraulic fracturing can be considered hazardous waste to the environment, which needs to be cleaned before reentering the environment. The proposed treatment technology may allow discharging the flowback water into the environment after increasing the efficiency of the oxidation of organic compounds because the concentration of COD and TOC in accordance with the Polish law valid for industrial effluents discharged into water and soil, which is 125 mg O_2/L and 30 mg C/L, respectively, was not achieved. The reduction of suspended solids, nutrients N and P, and substances that cause salinity to required level has been achieved. The performed analysis does not include the full spectrum of substances required by law, but only the selected indicators of impurities allowing estimating the effectiveness of treatment.

Treatment of the flowback water allows for recovery of water that can be used as raw material for subsequent fracturing. Many operators, for practical reasons, use only a minimal amount of treatment of the flowback water before reuse [31]. The liquid should be cleared of suspended solids, ions causing scaling (Ca, Mg, Sr, Ba, Fe, Mn), excess of organic substances, and microorganisms [32]. It is assumed that a partial pre-treating of the flowback water to remove the above constituents and desalting allows its reuse for the preparation of the fracturing fluid by blending with the make-up freshwater to TDS level of 50,000 mg/L [31]. It is believed that the increased salinity of the fracturing fluid may have advantages in that by reducing the water absorption through the clay, it facilitates the mining and drilling work, while the high content of Ca and Mg is undesirable because it adversely affects the operation of the constituents of the fracturing fluid, such as surfactants, breakers, or friction reducers [33]. It was determined the feed water quality guidelines to mitigate the compatibility concerns of water-based crosslinked fluid: pH 6–8, iron <25 mg/L, total hardness <15,000 mg $CaCO_3$/L, oxidizing and reducing agents 0, carbonate <600 mg $CaCO_3$/L, bicarbonate <600 mg $CaCO_3$/L, silica <35 mg/L, bacteria 0 CFU/ml, TDS 50,000 mg/L, and TSS 50 mg/L [3]. Presented pre-treatment technology including alkalizing, $KMnO_4$ oxidation, and filtration allows for effective removal of suspended solids from flowback water and reduction of the level of iron many times below 25 mg/L. In this way, the components causing blockages in the fracturing system are effectively removed. The flowback water after pre-treatment stage meets the criteria for reuse for the preparation of the fracturing fluid with the exception of the content of the bicarbonate (alkalinity), the level of which is likely to be reduced to the desired one after mixing with freshwater. Microbiological contamination was not studied. Alarming may be a high level of dissolved organic compounds, since they are nutrient substrate for microorganisms, but their maximum level is not mentioned [3]. Application of desalinating system in this case is not justified, because the tested sample of the flowback water was characterized by a salinity of 11,190 mg Cl^-/L. It is a low value against the salinity present in the flowback water 1,670—181,000 mg Cl^-/L [6]. In the case of salinity higher than permitted one, the solution will be additional desalination on the RO membrane AD-90, which can provide a suitable retention of ionic compounds of flowback water after hydraulic fracturing.

4. Conclusions

Based on the studies carried out on a fractional-technical scale, it is possible to confirm the usefulness of alkalization, $KMnO_4$ oxidation, and filtration for pre-treatment of flowback water, because they lead to the destabilization of the colloidal particles and their separation from the liquid phase. This technology allows very effective clarification of the flowback and reaching the turbidity < 1 NTU and SDI < 5. The level of purification allows introduction of the pre-treated flowback water to the NF and RO spiral-wound elements. The applied technology of pre-treatment hardly ever removed the organic compounds which appeared in the flowback water in the diluted fraction. The low usefulness of the nanofiltration membrane 4040-SR100-N2 was shown as for desalination and removal of the organic compounds from the pre-treated flowback water. Low efficiency of softening was also observed. This was caused by the appearance of non-carbonate hardness which in turn was caused by a high concentration of chlorides which supported transmission of bivalent cations through the membrane. Further work should be devoted to research on flowback water softening on other NF membranes characterized by different properties. The efficiency of desalination and removal of the organic compounds on the low- and high-pressure RO membranes (AG4040FM and AD-90) were compared. Higher retention coefficients were obtained for the high-pressure membrane, as well as a constant value of the permeate stream in the function of concentration of the feed water which is determined by the VCR coefficient. The usefulness of the high-pressure

RO process for desalination of flowback water from hydraulic fracturing was demonstrated. The biggest problems were encountered in the removal of organic compounds, which were present in very high concentrations. This parameter caused the most difficulties in adjusting the quality of the flowback water to its reuse or its discharge to the environment. The rest of the analyzed parameters of the flowback water treated using the technology of pre-treatment and high-pressure RO desalination did not exceed the levels mandated by various regulations governing reuse or discharge of flowback water to the environment.

List of symbols

VCR — volume concentration ratio (−)
V_{fw} — feed water volume (m^3)
V_p — permeate volume (m^3)
R — percentage retention factor (%)
C_{fw} — concentration of the component in feed water (mg/L) or (μs/cm)
C_p — concentration of the component in permeate (mg/L) or (μs/cm)

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