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**PRELIMINARY STUDIES FOR THE DESALINATION  
OF MODEL SOLUTION OF FLOWBACK WATER  
FROM SHALE GAS PRODUCTION  
IN THE NF/RO PILOT PLANT**

**Key words**

Nanofiltration (NF), reverse osmosis (RO), desalination, flowback water, shale gas.

**Abstract**

The impact of selected process parameters of an integrated NF/RO system on possibilities of the desalination of model solutions, containing salts in typical concentrations for flowback water from shale gas production, was analyzed in

this work. Based on the results of studies carried out in the pilot scale, it was found that the integrated NF/RO system allows for satisfactory reduction of the model solution of flowback water mineralization. It can be stated that the use of NF/RO system enables the re-use of the “real” flowback water during hydraulic fracturing.

## Introduction

In recent years the importance of shale gas in the political and technical capabilities grows and becomes a viable alternative to conventional gas. However, the shale gas extraction technology is more complicated because of the geology of rock in which it occurs. Shale is a rock with very low porosity and very low permeability [1]. Therefore, to enable gas extraction is necessary to use the hydraulic fracturing technology. This is technique in which rock is fractured by a pressurized liquid. The process involves the high-pressure injection of 'fracking fluid' into a well bore to create cracks in the deep-rock formations through which natural gas will flow more freely. When the hydraulic pressure is removed from the well, small grains of hydraulic fracturing proppants hold the fractures open [2]. Approx. 90% of the fracturing fluid is water, 9.5% are proppants (mainly sand), and 0.5% are chemical additives. The example composition of hydraulic fracturing fluid is shown in Table 1.

Hydraulic fracturing uses up to 20000 m<sup>3</sup> of water. There is not a relatively large volume but it can be a problem to provide a suitable amount of pure water in the field. After completion of drilling and fracturing part of the water used in an amount of 15–40% [3, 4] flows onto surface of the wellbore. Moreover, the process produces the flowback water. During preparation of the fracturing fluid a variety of different chemicals are added, and the fluid also washes out rock. Therefore the flowback water contain large amounts of dissolved salts (5000–261000 mg/dm<sup>3</sup>), suspensions (300–3500 mg/dm<sup>3</sup>), organic compounds (3.5–720 mg/dm<sup>3</sup>) and oil derivatives (5–31 mg/dm<sup>3</sup>). Furthermore, the flowback water contain a significant amount of harmful substances such as: sodium hydroxide, ethylene glycol, formaldehyde, methanol or hydrochloric acid [5, 6]. Therefore, it is proposed to purify the flowback water for its reuse in the hydraulic fracturing process.

Particular attention should be paid to the fact that the flowback water is up to nine times more saline than seawater. Re-use of the flowback water without adequate preparation (purification) is not possible because of the presence of large amounts of dissolved solids (mainly salts, including barium, magnesium, strontium or iron compounds) which can precipitate in the pipeline and, consequently, can lead to clogging and reduce efficiency of the process. Moreover, the chemical additives used in preparation of the fracturing fluid are incompatible at the high degree of salinity.

Table 1. Example composition of hydraulic fracturing fluid [1, 3, 4]

Component/ Additive type	Example Compound	Purpose	Percent Composition (by volume)
Water	-	Proppant carrier	90.000
Proppant	Quartz sand	Keep fractures open to allow gas flow out	9.510
Acid (15%)	Hydrochloric acid	Facilitates the dissolution of minerals	0.123
Antibacterial agent	Glutaraldehyde	Eliminate bacteria	0.001
Corrosion inhibitor	N,N-dimethyl formamide	Prevent pipe corrosion	0.002
Crosslinker	Borate salts	Maintain fluid viscosity as temperature increases	0.007
Friction reducer	Polyacrylamide, mineral oil	Minimize friction between fluid and the pipe	0.088
Gelling agent	Guar gum, hydroxyethyl cellulose	Thicken the fluid to suspend the proppant	0.056
Iron control	Citric acid	Prevent precipitation of metal oxides	0.004
Potassium chloride	-	Create a brain carrier fluid	0.060
Breaker	Ammonium persulfate	Allow delayed breakdown of the gel	0.010
pH adjusting agent	Sodium or potassium carbonate	Maintaining the effectiveness of other components	0.011
Scale inhibitor	Ethylene glycol	Prevent scale deposits in the pipe	0.043
Surfactant	Isopropanol	Increase the viscosity of the fluid	0.085

Currently, the main method used in desalination plants (e.g. water from the mine or sea) is reverse osmosis (RO) [4, 7, 8]. However, due to the properties of the nanofiltration membranes that allow for removal of multivalent ions and partial retention of monovalent ions, the nanofiltration (NF) process is increasingly proposed as an alternative or adjunct desalination of water and wastewater [7, 9–12].

In the study, the influence of selected process parameters (pressure and flow rates of the permeate and retentate) of an integrated NF/RO system on the possibility of desalination of the model solutions, with concentrations of salt typical for the flowback water after hydraulic fracturing of shale gas, was investigated.

## Experimental

The research was carried out in an NF/RO pilot plant shown in Fig. 1 using membranes which characteristics are reported in Table 2.

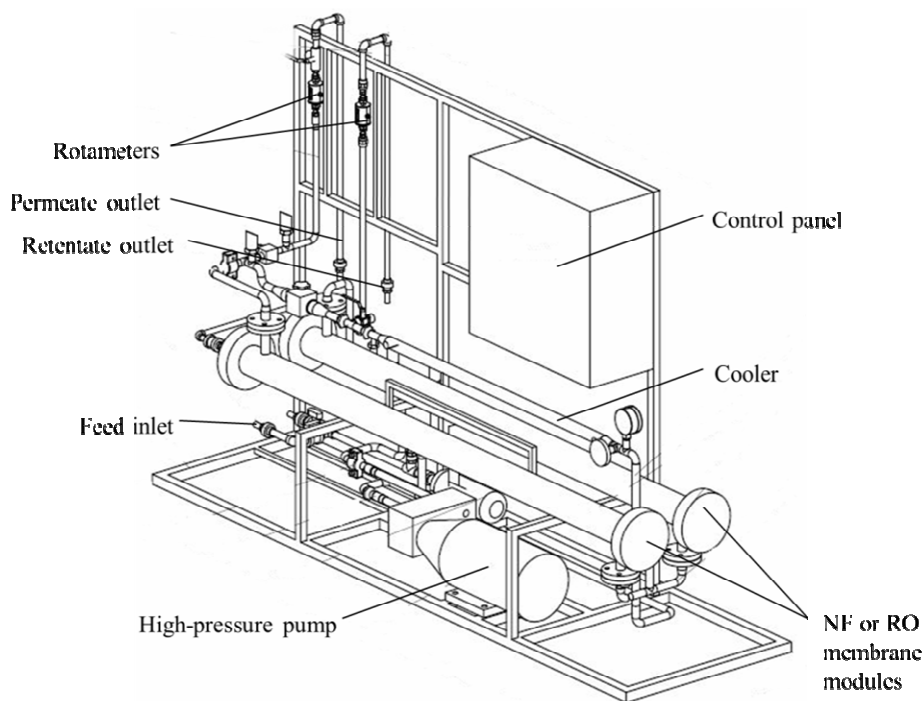


Fig. 1. Scheme of NF/RO installation

Table 2. Characteristics of NF and RO membranes used in the experiments

	NF	RO
Manufacturer	TRISEP	TORAY
Type	TS40	TM800V
Membrane active area, m <sup>2</sup>	8.2	8.0
Maximum Applied Pressure, bar	41	83
Maximum Operating Temperature, °C	45	45
pH operating range	3–10	2–11

The study was divided into two stages. In the first stage, the model solutions containing sodium chloride (NaCl, Chempur) and magnesium sulfate

(MgSO<sub>4</sub>, Chempur) were treated by nanofiltration. Two different solutions were applied:

- I – containing 23 200 mgCl/dm<sup>3</sup> and 1300 mg SO<sub>4</sub><sup>2-</sup>/dm<sup>3</sup>,
- II – containing 59 500 mgCl/dm<sup>3</sup> and 1300 mg SO<sub>4</sub><sup>2-</sup>/dm<sup>3</sup>.

The chloride and sulfate ions concentrations were selected on the basis of the average composition of flowback water. The volume of feed was equal to 200 dm<sup>3</sup>. During nanofiltration a constant ratio of flow rates of permeate and retentate on the level of 1:1 was kept.

In the second study stage, the permeates obtained after NF of solution I and II were treated by reverse osmosis. Each time, 180 dm<sup>3</sup> of NF permeate was applied as RO feed. The flow rates of RO permeate and retentate were kept at a ratio of 1:1. The concentration of chloride ions was determined by titration with silver nitrate in the presence of potassium chromate as indicator according to the standard ISO 9297: 1994. The concentration of sulfate ions was determined by the spectrophotometric method using the tests sulphates 1000 and 200 from NANOCOLOR Company.

## Results and discussion

In the first study stage, the influence of the permeate and retentate flow rate on chloride and sulfate ions retention during nanofiltration was analyzed. The investigation was conducted in the closed cycle. The experimental results conducted for process parameters given in Table 3 are illustrated in Fig. 2.

Table 3. Nanofiltration process parameters

Transmembrane pressure, bar		Permeate or retentate flow, m <sup>3</sup> /h
NF of solution I	NF of solution II	
14	17	0.6
20	23	0.8
26	25	1.0

It was stated that nanofiltration allowed for the 99% retention of sulfate ions irrespectively of the applied permeate/retentate flow rate, the transmembrane pressure (TMP) and the initial chloride ions concentration. These results are in accordance with observations of other authors [4]. Moreover, it was observed that the NF enables the retention of chloride ions in the range of 19-31% (Fig. 2). Therefore, it is possible to partially retention of chloride at the NF stage depending on the applied pressure and permeate/retentate flow rate (Table 3). The highest retention of chloride ions (31%) for the solution I, was obtained at the TMP of 26 bar and the flow rate equal to 1 m<sup>3</sup>/h. In the case of the solution II, the maximum retention of chloride

ions was 16% (Fig. 2). As reported by the Religa et al. [10], it was due to more than double of the initial concentration of chloride ions in the feed.

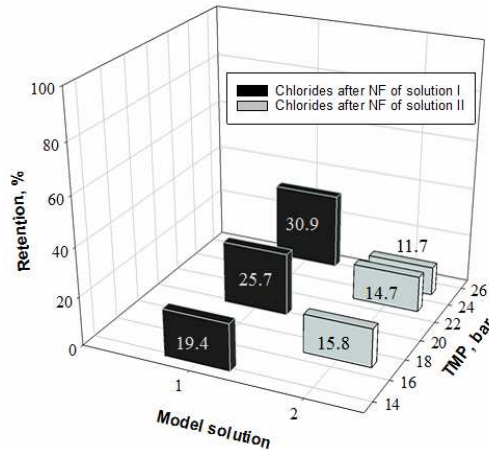


Fig. 2. Chlorides retention by NF membrane vs. transmembrane pressure in the closed cycles. Feed – model solutions containing: I – 22 400 mgCl/dm<sup>3</sup> and 1300 mg SO<sub>4</sub><sup>2-</sup>/dm<sup>3</sup>, II – 59 500 mgCl/dm<sup>3</sup> and 1300 mg SO<sub>4</sub><sup>2-</sup>/dm<sup>3</sup>

Subsequently, nanofiltration of model solution was performed in batch concentration mode, i.e. the permeate stream was collected in the permeate tank, while the retentate stream was recycled to the feed/retentate tank. The process was carried out maintaining a constant permeate (retentate) flow rate amount equal to 1 m<sup>3</sup>/h. The results of these studies were shown in Fig. 3.

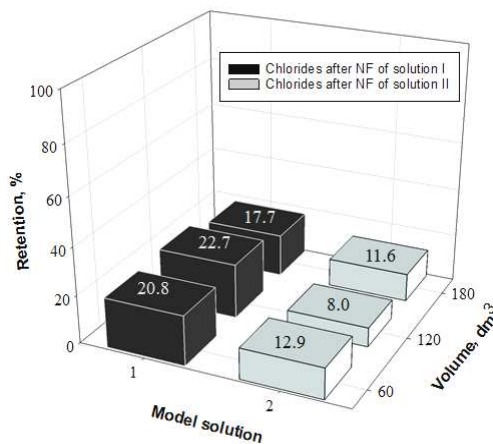


Fig. 3. Chlorides retention vs. the permeate volume for model solutions: I – 22 400 mgCl/dm<sup>3</sup> and 1300 mg SO<sub>4</sub><sup>2-</sup>/dm<sup>3</sup>, II – 59 500 mgCl/dm<sup>3</sup> and 1300 mg SO<sub>4</sub><sup>2-</sup>/dm<sup>3</sup> (NF I: TMP = 17 bar, NF II: TMP = 25 bar). Initial feed volume: 200 dm<sup>3</sup>

During nanofiltration of model solution I at TMP of 17 bar, after collection of 180 dm<sup>3</sup> of permeate, the retention of sulfate and chloride ions was 99.8% and 17.7% respectively (Fig. 3). During NF of model solution II the 12.0% retention of chloride ions and 98.4% retention of sulfate ions was obtained (Fig. 3). In addition, to maintain the permeate/retentate flow rate on the level of 1 m<sup>3</sup>/h each it was necessary to operate at the higher TMP of 25 bar. Under this conditions the process was carried out at a constant efficiency. The sulfate rejection remained stable whereas in the case of chlorides slight fluctuations were found (Fig. 3). Thus, as in the studies [12] which relate to water desalination, during NF almost complete removal of multivalent ions and partial retention of monovalent ions regardless of the chloride ions concentration in feed, can be achieved. The composition of permeate streams after NF of model solutions I and II is presented in Table 4.

Table 4. Composition of permeate streams after nanofiltration of solution I (NF permeate I) and solution II (NF permeate II). Process parameters: TMP during NF of solution I: 17 bar, TMP during NF of solution II: 25 bar; permeate and retentate flow = 1 m<sup>3</sup>/h)

Solutions	NF permeate I	NF permeate II
Volume, dm <sup>3</sup>	180	180
Conductivity, mS/cm	22.4	145.3
pH	7.2	7.2
Concentration of Cl <sup>-</sup> , mg/dm <sup>3</sup>	22400	53700
Concentration of SO <sub>4</sub> <sup>2-</sup> , mg/dm <sup>3</sup>	10	20

In the next stage of the study, the permeate obtained during NF of the model solutions (Table 3) were treated by RO. For readers convenience the permeate obtained during NF of solution I will be denoted later as NF permeate I, while the permeate obtained during NF of solution II will be denoted as NF permeate II. The results obtained during RO of NF permeate I (permeate after NF I in Table 4) operated in closed cycle (the process parameters are presented in Table 6) showed that the RO process enables over 99% retention of chloride ions irrespectively of the permeate and retentate rates. It should be noted that for permeate (retentate) flow rate of 0.9 m<sup>3</sup>/h it was necessary to apply TMP of 75 bar, but the maximum operating pressure of the pump was equal to 80 bar.

Table 5. Reverse osmosis process parameters

Transmembrane pressure, bar	Permeate or retentate flow, m <sup>3</sup> /h
66	0.5
69	0.7
75	0.9

Subsequently, the reverse osmosis of NF permeate I (Table 4) with the collection of permeate in separate tank allowed for the retention of chloride ions on the level of 99.2% (Table 6). Furthermore, the conductivity of the solution was reduced from 67.800 mS/cm to 1.116 mS/cm. However, for the so high initial concentration of chloride ions, the reverse osmosis process could be carried out only within a narrow range of process parameters. This is related to high osmotic pressure and thus the technical limitations of available high-pressure pumps [7]. The collection of 120 dm<sup>3</sup> of permeate at permeate (retentate) flow rate equal to 0.2 m<sup>3</sup>/h caused a pressure increase from 60 to 77 bar.

Table 6. Composition of permeate and retentate streams after reverse osmosis of NF permeate I. proces parameters: TMP = 77 bar, permeate (retentate) flow rate: 0.2 m<sup>3</sup>/h

	Permeate	Retentate
Volume, dm <sup>3</sup>	120	60
Conductivity, mS/cm	1.116	112.3
pH	6.2	7.6
Concentration of Cl <sup>-</sup> , mg/dm <sup>3</sup>	280	35100

During reverse osmosis of 180 dm<sup>3</sup> of NF permeate II (Table 4) the only permeate (retentate) flow rate was possible to be obtained in the applied RO installation was equal to 0.05 m<sup>3</sup>/h at the TMP of 76 bar. Due to the limited power of the pump it was impossible to carry out the RO process with collection of permeate in separate tank. In the closed cycle, the retention of chloride ions was 97.8% and the conductivity was reduced from 127.50 mS/cm to 3.94 mS/cm. It means that in the case of flowback water containing chlorides at a concentration in exceeding of 54 000 mg/dm<sup>3</sup> is necessary to reduce the content of this ions (approx. to 25 000 mg/dm<sup>3</sup>) before the RO treatment. As reported by Dong Zhou et al. [12] the solution to this problem could be the use of two- or more steps of NF system. However, the author emphasize the fact that the two- steps desalination process may increases the complexity and cost of desalination plant.

## Conclusions

Based on the results of the study, it was found that integrated NF/RO system can be applied for the desalination of the flowback water from the hydraulic fracturing of natural gas from shale formations. However, in the case of flowback water with a mineralization above 54 000 mg/dm<sup>3</sup> it is necessary to reduce ions concentration before implementation of the RO process. However, the experiments carried out in the pilot scale confirmed that an integrated



NF/RO system reduces the concentration of chloride and sulfate ions in model solution of flowback water to a level that enables the re-use of the “real” flowback water in hydraulic fracturing. However, it is necessary to perform further tests on “real” flowback water.

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### **Badania nad możliwością odsalania modelowego roztworu płynu powrotnego ze szczelinowania hydraulicznego złóż gazu łupkowego w pilotowej instalacji NF/RO**

#### **Słowa kluczowe**

Nanofiltracja (NF), odwrócona osmoza (RO), odsalanie, płyn powrotny, gaz łupkowy.

#### **Streszczenie**

W pracy zbadano wpływ wybranych parametrów procesowych zintegrowanego systemu NF/RO na możliwość odsalania modelowych roztworów zawierających sole w stężeniach charakterystycznych dla płynu powrotnego ze szczelinowania złóż gazu z łupków. Na podstawie otrzymanych wyników badań prowadzonych w skali pilotowej, stwierdzono, że zintegrowany układ NF/RO pozwala na zadowalające zmniejszenie mineralizacji roztworu modelowego płynu powrotnego. Można zatem założyć, iż zastosowanie układu NF/RO umożliwi ponowne wykorzystanie ścieku rzeczywistego podczas szczelinowania hydraulicznego.