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A concept of hydraulic fracturing flowback treatment using electrodialysis reversal

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ABSTRACT

The possibility of desalinated water production from hydraulic fracturing flowback by electrodialysis reversal (EDR) was investigated. To simulate geochemical reactions of hydraulic fracturing fluid with the formation rocks, fluid-gas-rock reaction was performed in autoclave. Next, an EDR of hydraulic fracturing flowback was simulated and the composition of diluate and concentrate was calculated, assuming that maximum possible Langelier Saturation Index (LSI) in a single-pass EDR unit equipped with low residence time variance spacer was +2.3 and maximum gypsum saturation level was 520%. Simulation suggested that the hydraulic fracturing flowback could be desalinated to total dissolved salts (TDS) of 1,352 mg dm^{-3} at water recovery of 89.8%, and it could be reused as a hydraulic fracturing fluid. High LSI and $CaSO_4$ supersaturation indicated that there was a possibility of calcium carbonate and calcium sulfate precipitation from the obtained concentrate.

Keywords: Hydraulic fracturing; Electrodialysis; Industrial waste water

1. Introduction

Hydraulic fracturing is a gas extraction method, in which gas-bearing rock formation is fractured by the injection of pressurized fluid. The technology allows reaching shale gas reserves, and it has already become an important method of natural gas production. In Poland, territories extending from the eastern Pomerania and northern Masovia, Podlasie, southwards to Lublin region, are expected to contain estimated gas reserves of 347–768 billion m^3 [1]. Drilling as well as completion of wells requires large quantities of water. Drilling of the vertical and horizontal components of a well may require 400–4,000 m^3 of water for drilling fluids to maintain downhole hydrostatic pressure, cool the drillhead, and remove drill cuttings. Then, 7,000–18,000 m^3 of water is needed for hydraulic fracturing of each well [2]. Unfortunately, most of shale gas areas in Poland have relatively low resources of fresh groundwater [3]. Around 75% of Poland suffers from the periodic shortages of water, and the situation may get worse. The water scarcity means shale gas industry should reuse as much water as possible. Approximately 10% to 40% of the fracturing fluid returns to the surface during the flowback period [4]. Flowbacks typically contain chemicals naturally present in the rocks, together with some components of the fracturing fluid. Table 1 presents the range of selected parameters and ionic composition of the Barnett and Marcellus Shale flowbacks [5]. Flowbacks from Polish shale gas formations reveal similar characteristic [4]. They have complex composition, high content of organics, hardness and salinity, and as such are problematic for desalination and reuse.

Although the flowback water can be injected back to the gas-bearing formation, salts leached from the rocks accumulate, eventually making the flowback too salinized for its

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Table 1
Selected parameters and composition of Barnett and Marcellus Shale flowback water samples [5]

Parameter	Range
pH	5.8–8.0
Alkalinity, mg dm^{-3} as $CaCO_3$	49–1,630
TDS, mg dm^{-3}	23,600–238,000
TSS, mg dm^{-3}	10.8–3,220
TOC, mg dm^{-3}	3.7–388
BOD, mg dm^{-3}	93–1,480
Oil and grease, mg dm^{-3}	5–1,720
Na^+, mg dm^{-3}	10.7–65,100
Ca^{2+}, mg dm^{-3}	1,440–23,500
Mg^{2+}, mg dm^{-3}	135–1,550
Fe^{2+}, mg dm^{-3}	10.8–180
Ba^{2+}, mg dm^{-3}	21.4–13,900
Cl^-, mg dm^{-3}	26,400–148,000
HCO_3^-, mg dm^{-3}	29.8–162
NH_4^+, mg dm^{-3}	15–242
SO_4^{2-}, mg dm^{-3}	5–200

Table 2
Water quality guidelines for flowback reuse [9]

Parameter	Target
pH	6–8
Iron, mg dm^{-3}	<25
Total hardness, mg dm^{-3} as $CaCO_3$	<15,000
Oxidizing agents	0
Reducing agents	0
Carbonate, mg dm^{-3} as $CaCO_3$	<600
Bicarbonate, mg dm^{-3} as $CaCO_3$	<600
Silica, mg dm^{-3}	<35
Bacteria, CFU cm^{-3}	0
TDS, mg dm^{-3}	<50,000
TSS, mg dm^{-3}	<50

reuse. Ma et al. [6] have investigated the water management in major U.S. shale plays; most of them do not reuse flowback water, with the exception of Marcellus shale gas play, where oil/water separation, filtration and dilution allow 90% of flowback water to be reused. Potentially limiting factors for reuse are the chemical stability of the viscosity modifiers and other constituents of hydraulic fracture water in the brine solution and the potential of precipitation of divalent cations in the wellbore [2]. Hydraulic fracturing fluids contain friction reducers, the effectiveness of which may be decreased at high TDS [2,7]; this limits the possibility of reusing highly concentrated flowback. Hagshenas and Nasr-El-Din [8] have investigated the impact of salinity on the possibility of flowback reuse. They found that magnesium and sodium ions contents were the limiting factor, preventing direct flowback reuse and creating the need for desalination. In case of guar-based fracturing fluid, the maximum acceptable concentrations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ were approximately 600, 750, 11,000, and 2,300 mg dm^{-3}, respectively; higher concentrations significantly affected the fluid viscosity. The Petroleum Technology Alliance Canada has laid a set of general guidelines for flowback reuse [9] – see Table 2 – in terms of total dissolved salts (TDS) content, bicarbonate content and pH. The excessive TDS may prevent the gelling agent from fully uncoiling and hydrating, which in turn may result in the formation of "fish eyes", as well as cause the insolubility of the gelling agents and/or potential precipitation within the water-based cross-linked fluid. The excessive bicarbonate content may delay cross-linking of some fluids, whereas too high pH impede the rate and quality of hydration of the water-based cross-linked fluid, while too low pH accelerates the rate of hydration of the water-based cross-linked fluid, creating gel balls, lumping or fish eyes.

Various methods can be applied for flowback treatment. Thiel et al. [10] have investigated several thermal desalination methods, as well as reverse osmosis. Coday et al. [11,12] have compared deep well disposal with forward osmosis, concluding the latter can be significantly cheaper. Miller et al. [13] have operated a pilot ultrafiltration-reverse osmosis flowback treatment plant and tried to modify membrane surface with polymeric coatings to decrease fouling. Michel et al. [14] have proposed an integrated system, consisting in pretreatment and pressure-driven method (nanofiltration and reverse osmosis), which proved effective in a pilot scale. In the Marcellus basin, in order to reuse the produced water, a mobile electrocoagulation unit was used to remove iron and turbidity, oil emulsions and biological activity from the flowbacks [15].

One of the possible methods of flowback desalination is electrodialysis (ED). The process is based on the phenomenon of ion migration in the electric field and exclusion of co-ions by the charged group fixed in a polymeric matrix of an ion-exchange membrane. A salt solution flows between the alternately placed cation- and anion-exchange membranes. When an electric field is applied in the direction perpendicular to the solution flow, cations migrate through cation-exchange membranes and are retained by anion-exchange membranes, whereas anions migrate through anion-exchange membranes and are retained by cation-exchange membranes. Thus, a salt solution stream is split into desalinated stream (diluate) and concentrated stream (concentrate). ED is widely recognized as a method for brackish water desalination, but it is also applied for the treatment of more concentrated solutions: seawater or brines. McGovern et al. [16] have proposed a 10-stage ED system for treatment of high salinity flowbacks and showed that ED treatment could generate lower costs than the evaporation. Hao et al. [17] have proposed an integrated coagulation-electrodialysis system for flowback treatment; they reach water recovery of 85%. Previously, we have proposed an integrated electrodialysis-reverse osmosis system [18], which could desalinate flowback of conductivity of 123.4 mS cm^{-1} down to RO permeate level at water recovery 41%–69% and energy consumption of 25–35 kWh m^{-3}.

In this work, we present a concept of the application of ED for desalination of hydraulic fracturing flowbacks. Application of ED should decrease the volume of the hazardous wastes generated by the shale gas industry. ED has an important advantage over pressure-driven methods for flowback treatment: it desalinates the hydraulic fracturing flowback without removal of uncharged, organic species present in the fracturing fluids, which makes the reuse of produced diluate possible. Moreover, ion-exchange membranes are more resistant to fouling and biofouling than NF/RO membranes, less sensitive to chlorine, able to operate at higher feed SDI and are easier to clean up. Because they are less prone to fouling, they require less sophisticated feed stream pretreatment, which makes them a better choice for flowback treatment. ED can sustain higher temperature than NF/RO; in fact, temperature increase may be beneficial, as it decreases the electric resistance and viscosity of the solution.

2. Experimental

The scheme of the proposed solution is presented in Fig. 1. Traditionally (Fig. 1(a)), the flowback is recycled and reused as the fracturing fluid; however, the flowback salinity gradually increases up to a point where, it losses the required rheological properties and has to be discharged. In the proposed solution (Fig. 1(b)), the flowback is reused as long as it meets the assumed criteria for fracturing fluid; when the salinity build-up is too high, flowback is treated with electrodialysis reversal (EDR) and the diluate is reused. Such a treatment should decrease the water consumption of the shale gas drilling plant. EDR of hydraulic fracturing flowback was simulated and the composition of diluate and concentrate was calculated under following assumptions:

- The energized hydraulic fracturing fluid was used to obtain artificial flowback solution in a reaction with samples of gas-bearing rock formation. To simulate geochemical reactions of hydraulic fracturing fluid with the formation rocks, fluid-gas-rock reaction was performed in autoclave.
- Flowback could only be reused if the following criteria were met: TDS <50,000 mg dm^{-3}, bicarbonate concentration <600 mg dm^{-3}, pH 6-8, concentrations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ lower than 600, 750, 11,000, and 2,300 mg dm^{-3}, respectively.
- Flowback flow rate was 1 m^3 h^{-1}; it was used as a feed for both, diluate and concentrate compartments of an EDR unit, working in a counter-current, single-pass mode.
- Membrane was perfectly selective: it completely rejected co-ions, while the univalent counter-ions had the same transport numbers as bivalent ones.
- Diffusion of large, organic species across the ion-exchange membranes was very slow and therefore negligible in a single-pass mode.
- Water flux was caused solely by electroosmosis, and depended only on hydration numbers of sodium chloride in the membrane, calculated basing on previous experiments [19].
- Maximum Langelier Saturation Index (LSI) of the concentrate was +2.3, as proven experimentally in a single-pass EDR unit equipped with low residence time variance spacer [20].
- The obtained pH stemmed from CO_2-bicarbonate-carbonate equilibrium (dissolved ammonia was neglected).
- Maximum gypsum saturation level was 520%, as proven previously [20].
- Maximum ratio of diluate to concentrate feed flow rate was 91:9, as it was impractical to have either very low concentrate flow rate (very long residence time, high concentration polarization) or very high diluate flow rate (very high pressure drop).

EDR was chosen over conventional ED because of the scaling risk: the treated flowbacks characterized with high calcium, sulfate and bicarbonate ions concentrations. Two cases were investigated: (1) regular operation, in which the flowback was desalinated to the level allowing its reuse as a hydraulic fracturing fluid; (2) final treatment, in which the fracturing process stopped and the remaining flowback was deeply desalinated by EDR. The deeply desalinated EDR diluate could then be passed to an organics removal unit operation.

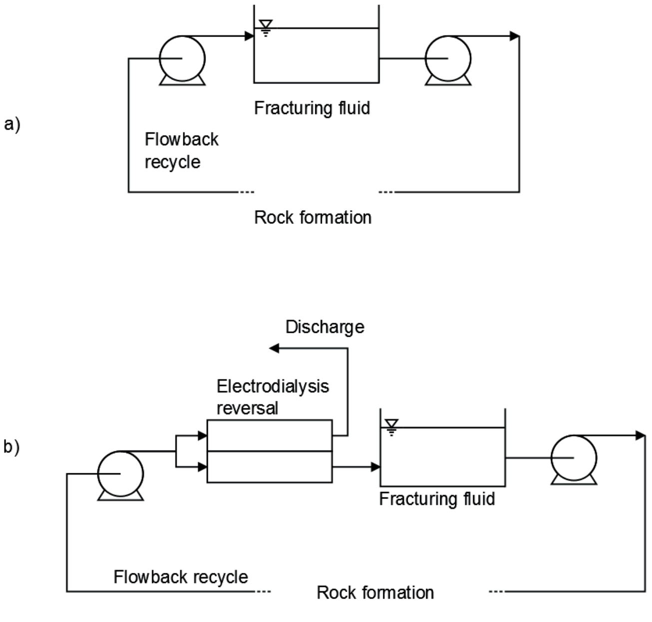

Fig. 1. A scheme of flowback recycle (a) without EDR (b) with EDR (proposed solution).

3. Results

The composition of energized hydraulic fracturing fluid and the obtained flowback is presented in Table 3. Although,

Table 3
The composition of energized fracturing fluid and the flowback obtained after the fluid-gas-rock reaction in the autoclave

Parameter	Energized fracturing fluid	Flowback
Cl^-, mg dm^{-3}	174	1,539
Br^-, mg dm^{-3}	17.15	30.99
SO_4^{2-}, mg dm^{-3}	38.8	558
Na^+, mg dm^{-3}	120.6	1,412
NH_4^+, mg dm^{-3}	68.8	48.2
K^+, mg dm^{-3}	32.4	249.4
Mg^{2+}, mg dm^{-3}	13.5	104
Ca^{2+}, mg dm^{-3}	67.7	715
HCO_3^-, mg dm^{-3}	515.8	3,622
pH		6.5

Table 4
Estimated parameters of diluate and concentrate after EDR treatment compared with water quality guidelines for flowback reuse

Parameter	Flowback (feed water)	Regular operation		Final treatment		Water quality guidelines
		Diluate	Concentrate	Diluate	Concentrate	
Cl^-, mg dm^{-3}	1,539	251	12,820	62.4	14,364	–
Br^-, mg dm^{-3}	30.99	5.12	261	1.27	293	–
SO_4^{2-}, mg dm^{-3}	558	91.1	4,648	22.6	5,208	–
Na^+, mg dm^{-3}	1,412	230	11,762	57.3	13,179	<11,000 [8]
NH_4^+, mg dm^{-3}	48.2	7.87	402	1.96	450	–
K^+, mg dm^{-3}	249.4	40.7	2,078	10.1	2,328	<2,300 [8]
Mg^{2+}, mg dm^{-3}	104	17.0	866	4.22	971	<750 [8]
Ca^{2+}, mg dm^{-3}	715	117	5,956	29.0	6,673	<600 [8]
HCO_3^-, mg dm^{-3}	3,622	592	30,150	147	33,935	<600 [9]
pH	6.5	6.54	6.58	6.54	6.58	6–8 [9]
LSI	+0.74	<0	+2.0	<0	+2.1	–
Relative gypsum saturation, %	–	–	390	–	420	–
TDS, mg dm^{-3}	8,279	1,352	68,954	336	77,412	<50,000

the obtained flowback was not highly salinized, and the sodium, potassium, magnesium concentration, and pH criteria were met, it did not meet the HCO_3^- and Ca^{2+} concentration criteria, so it had to be treated to be reused. Acidification could remove the excessive $CaCO_3$, but the flowback would then require addition of base to meet the pH criterion. Bicarbonate and calcium content increase could be explained as a result of dissolving the limestone and other minerals present in the gas-bearing rock formation and probably sorption of CO_2 present in gas phase in case of HCO_3^-. The obtained flowback was supersaturated in respect to calcium carbonate (LSI +0.74), but it did not show any signs of crystallization. We were not able to prepare a model solution of flowback of the same composition, what suggested that the liquid obtained after rock-fluid-gas reaction in the autoclave was stabilized by organic substances present in the energized fracturing fluid.

The estimated results of ED are presented in Table 4. During the regular treatment, the flowback could be desalinated to TDS of 1,352 mg dm^{-3}, at initial flowback TDS of 8,279 mg dm^{-3}, that is, it could be reused as a hydraulic fracturing liquid, especially considering that the majority of non-ionic, organic components of the flowback would be kept in the produced diluate. The obtained diluate fulfilled the water quality guidelines for the flowback reuse in terms of bicarbonate content and salinity [9]. The obtained concentrate had a LSI of +2.1 and gypsum saturation level of 390%. If the fracturing operation was stopped, the final flowback could be desalinated to TDS of 336 mg dm^{-3} and passed to further treatment in order to remove organic substances. The obtained concentrate had a LSI of +2.1 and gypsum saturation level of 420%. The results showed that the initial ratio of diluate to concentrate volumes had to be 91:9, which we assumed was the maximum ratio from a practical point of view. Water flux across the ion-exchange membranes, would increase the concentrate flow rate by ca. 15% during the course of the ED – see Table 5.

Table 5
Estimated changes in volumetric flow rate caused by water flux across the ion-exchange membranes

Volumetric flow, m^3 h^{-1}	Regular operation		Final treatment	
	Diluate	Concentrate	Diluate	Concentrate
Inlet	0.910	0.090	0.910	0.090
Outlet	0.898	0.102	0.897	0.103

4. Conclusions

Simulation suggests that the hydraulic fracturing flowback can be desalinated to TDS of 1,352 ppm at water recovery of 89.8% and reused during regular operation of EDR plant. If the hydraulic fracturing stops, the remaining flowback can be deeply desalinated (down to TDS of 336 mg dm^{-3}) and passed forward to organics removal. The obtained results are based on the assumption that without antiscalants the maximum LSI is +2.3 and maximum gypsum saturation is 520%, as in our previous work [20]. However, because the flowback already contains a lot of antiscalants (typically up to 0.043% v/v of ethylene glycol [2,4]), we believe that even higher LSI and gypsum saturation is possible to be achieved, which will improve water recovery.

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References

[1] Polish Geological Institute-National Research Institute, Assessment of Shale Gas and Shale Oil Resources of the Lower Paleozoic Baltic-Podlasie-Lublin Basin in Poland, First Report, Tech. Rep. 2012.

[2] K. Gregory, R. Vidic, D. Dzombak, Water management challenges associated with the production of shale gas by hydraulic fracturing, Elements, 7 (2011) 181–186.

[3] B. Uliasz-Misiak, A. Przybycin, B. Winid, Shale and tight gas in Poland – legal and environmental issues, Energy Policy, 65 (2014) 68–77.

[4] P. Dydo, K. Labus, M. Turek, Membrane Treatment of Flowback from Fracturing of Shale Gas Formations, Monographs of the Environmental Engineering Committee Polish Academy of Sciences, Vol. 119, 2014, pp. 299–308.

[5] T. Hayes, Characterization of Marcellus and Barnett Shale Flowback Waters and Technology Development for Water Reuse, Hydraulic Fracturing Technical Workshop #4 USEPA Meeting Facilities, Arlington, Virginia, USA, 2011.

[6] G. Ma, M. Geza, P. Xu, Review of Flowback and Produced Water Management, Treatment and Beneficial Use for Major Shale Gas Development Basins, Proc. 2014 Shale Energy Engineering Conference, 2014, pp. 53–62.

[7] A. Kamel, S.N. Shah, Effects of salinity and temperature on drag reduction characteristics of polymers in straight circular pipes, J. Pet. Sci. Eng., 67 (2009) 23–33.

[8] A. Haghshenas, H.A. Nasr-El-Din, Effect of dissolved solids on reuse of produced water at high temperature in hydraulic fracturing jobs, J. Nat. Gas Sci. Eng., 21 (2014) 316–325.

[9] R. Wasylishen, S. Fulton, Reuse of Flowback and Produced Water for Hydraulic Fracturing in Tight Oil, Tech. Rep., The Petroleum Technology Alliance Canada (PTAC), 2012.

[10] G.P. Thiel, E.W. Tow, L.D. Banchik, H.W. Chung, J.H. Lienhard V, Energy consumption in desalinating produced water from shale oil and gas extraction, Desalination, 366 (2015) 94–112.

[11] B.D. Coday, N. Almaraz, T.Y. Cath, Forward osmosis desalination of oil and gas wastewater: impacts of membrane selection and operating conditions on process performance, J. Membr. Sci., 488 (2015) 40–55.

[12] B.D. Coday, L. Miller-Robbie, E.G. Beaudry, J. Munakata-Marr, T.Y. Cath, Life cycle and economic assessments of engineered osmosis and osmotic dilution for desalination of Haynesville Shale pit water, Desalination, 369 (2015) 188–200.

[13] D.J. Miller, X. Huang, H. Li, S. Kasemset, A. Lee, D. Agnihotri, T. Hayes, D.R. Paul, B.D. Freeman, Fouling-resistant membranes for the treatment of flowback water from hydraulic shale fracturing: a pilot study, J. Membr. Sci., 437 (2013) 265–275.

[14] M.M. Michel, L. Reczek, M. Granops, P. Rudnicki, A. Piech, Pretreatment and desalination of flowback water from the hydraulic fracturing, Desal. Wat. Treat., 57 (2016) 10222–10231.

[15] Fracking with treated water, Shale Play Water Management, 2 (2014) 53–55.

[16] R.K. McGovern, A.M. Weiner, L. Sun, C.G. Chambers, S.M. Zubair, J.H. Lienhard V, On the cost of electrodialysis for the desalination of high salinity feeds, Appl. Energy, 136 (2014) 649–661.

[17] H. Hao, X. Huang, C. Gao, X. Gao, Application of an integrated system of coagulation and electrodialysis for treatment of wastewater produced by fracturing, Desal. Wat. Treat., 55 (2014) 2034–2043.

[18] M. Turek, K. Mitko, P. Dydo, A. Jakóbik-Kolon, K. Labus, A Concept of Fracking Flowback Desalination in an Integrated Electrodialysis-Reverse Osmosis System, IDA World Congress, San Diego, California, USA, 2015.

[19] M. Turek, K. Mitko, M. Chorążewska, P. Dydo, Use of the desalination brines in the saturation of membrane electrolysis feed, Desal. Wat. Treat., 51 (2013) 2749–2754.

[20] M. Turek, J. Waś, K. Mitko, Scaling prediction in electrodialytic desalination, Desal. Wat. Treat., 44 (2012) 255–260.