Journal of Membrane Science 560 (2018) 125–131

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Polyacrylamide in hydraulic fracturing fluid causes severe membrane fouling during flowback water treatment

Boya Xiong[a], Selina Roman-White[b], Bethany Piechowicz[b], Zachary Miller[b], Benjamin Farina[b], Travis Tasker[a], William Burgos[a], Andrew L. Zydney[b,*], Manish Kumar[a,b,**]

[a] Department of Civil and Environmental Engineering, The Pennsylvania State University, Greenberg Building, University Park, PA 16802, United States
[b] Department of Chemical Engineering, The Pennsylvania State University, Greenberg Building, University Park, PA 16802, United States

ABSTRACT

Sustainable wastewater management strategies are required to further minimize impacts of high-volume hydraulic fracturing (HVHF) as current practices such as reuse or direct disposal have long term limitations. Membranes can provide superior effluent quality in HVHF wastewater treatment, but the application of these systems is severely limited by membrane fouling. However, the key fouling components in HVHF wastewater have not yet been clearly identified and characterized. Here we demonstrate that fouling of microfiltration membranes by synthetic flowback water is mostly due to polyacrylamide (PAM), a major additive in slickwater fracturing fluids. A synthetic fracturing fluid was incubated with Marcellus Shale under HVHF conditions (80 °C, 83 bar, 24 h) to generate synthetic flowback water. Different HVHF conditions and fracturing fluid compositions generated a fouling index for flowback water ranging from 0.1 to 2000 m^{-1}, with these values well correlated with the peak molecular weight (MW) (ranging from 10 to 1.5×10^4 kDa) and the concentration of high MW components in the water. The lowest fouling index was observed when PAM was further degraded by ammonium persulfate under HVHF conditions, although this is infrequently used with PAM in current fracturing operations. These results highlight the importance of PAM and its degradation products in fouling of subsequent membrane systems, providing insights that can help in the development of effective treatment processes for HVHF wastewater.

1. Introduction

In the past decade, the development of unconventional oil and gas using high-volume hydraulic fracturing (HVHF) has had a significant impact on the U.S. energy landscape. However, the environmental impacts of HVHF have generated tremendous social concerns, largely due to the production of large quantities of wastewater, referred to as flowback and produced water, that contain high salinity (220,000–340,000 mg/L), turbidity, organic constituents (1–5500 mg/L total organic carbon), and radioactivity (gross alpha 50–120,000 pCi/L) [1,2]. In some states, such as Texas, wastewater is primarily disposed of by deep well injection due to the ready availability of class II disposal wells. In Marcellus Shale gas wells in Pennsylvania, 90% of the wastewater (both flowback and produced water) is recycled and reused in subsequent HVHF operations because of the limited number of disposal wells [3]. The influence of such recycling after minimal treatment, particularly the effect of transformed organic additives, on well productivity has not been reported. More importantly, deep well injection is not an environmentally friendly management strategy [4]; the opportunity for recycling will be limited when the number of new fracturing jobs declines. There is a clear need for developing processes that can provide cost-effective treatment of flowback and produced water.

Membrane systems have been proposed by a number of investigators for treatment of flowback water [5,6], both to remove suspended solids and organics using microfiltration (MF) or ultrafiltration (UF) [7,8] and to remove high salinity/hardness using nanofiltration (NF) [9], reverse osmosis (RO) [10] and forward osmosis [11] or membrane distillation [12]. However, membrane fouling by hydrocarbon [10] and polymeric organics [9,13,14], inorganic scaling species [15], microbial [9] and particulate materials [7,14] in flowback water remains a challenge in efficiently treating the wastewater [16]. Our previous work with flowback water from Marcellus Shale gas wells showed a large variation in both water quality and fouling rates during microfiltration with no apparent correlation between the measured fouling index and either the total organic content or turbidity [14]. The exact nature of the key fouling constituents in these wastewaters remains unknown. This knowledge gap makes it

---

[*] Corresponding author.
[**] Corresponding author at: Department of Chemical Engineering, The Pennsylvania State University, Greenberg Building, University Park, PA 16802, United States.
E-mail addresses: zydney@engr.psu.edu (A.L. Zydney), manish.kumar@psu.edu (M. Kumar).

https://doi.org/10.1016/j.memsci.2018.04.055
Received 28 February 2018; Received in revised form 30 April 2018; Accepted 30 April 2018

Nomenclature

HVHF	High volume hydraulic fracturing
FR	Friction reducer
PAM	Polyacrylamide
MF	Microfiltration
UF	Ultrafiltration
MW	Molecular weight
SEC	Size exclusion chromatography

difficult to design treatment processes that are effective for managing fracturing wastewaters.

The organics in flowback water come from both the chemical additives used in the hydraulic fracturing fluid and the hydrocarbons extracted from the shale. Over 1000 chemicals [17], some of which are proprietary, have been used in hydraulic fracturing, and many of these have been detected in flowback and produced water [18,19] as well as in contaminated surface water / groundwater samples [20–22]. Many of these analyses utilized advanced gas chromatography coupled with mass spectroscopy, which can identify hydrophobic and volatile organics such as hydrocarbons; however, components that are hydrophilic and larger than 1 kDa, such as polyacrylamide (PAM) used as a friction reducer (FR) and guar gum used as a gelling agent, cannot be detected in these analyses [21]. Two very recent studies found that 90% of the organic matter in fracturing wastewater is hydrophilic, and some wastewaters have been shown to contain 20–40% biopolymers [13,23]. These polymers, including high MW PAM, can be significant membrane foulants. For example, PAM was found to be the major contributor to the total membrane resistance in fouling tests performed with synthetic oil-field polymer flooding wastewater [24]. Wang *et al.* [25] reported that PAM used as a coagulant caused MF fouling predominantly by surface pore blockage, with the rate of fouling determined by the molecular weight and concentration of the polymer solution. Liu *et al.* [26] utilized atomic force microscopy to correlate intermolecular forces with the fouling resistance provided by hydrolyzed polyacrylamide during filtration through a polyvinylidenefluoride UF membrane. This study concluded that fouling was dominated by the resistance from the concentration polarization layer formed by intermolecular attraction, rather than the gel layer formed by polymer-membrane attraction, where both attractive forces are attributed to hydrophobic interactions involving the polymer backbone in combination with hydrogen bonding. However, it is not possible to directly extrapolate from these studies to the fouling characteristics of PAM in flowback water, particularly given the complex transformation of PAM that can occur under HVHF conditions due to interactions with the solid shale and with other additives present in the fracturing fluid. Recent work in our laboratory has demonstrated that PAM undergoes significant degradation via a free radical mechanism at the high temperatures, where the free radicals are generated by reactions involved dissolved oxygen present in the fracturing fluid and dissolved Fe^{2+} from shale at low pH [27]. There is a critical need to evaluate the fouling of degraded PAM characteristic of the materials in flowback / produced water from HVHF operations.

The primary objectives of this work were to: 1) quantify the effect of downhole pressure and temperature on fouling indices of PAM compared to ‘raw’ fracturing fluid and flowback water; 2) evaluate the effect of combinations of PAM and other additives on the fouling index; and 3) examine the correlation between the fouling index and PAM size and concentration. These results aim to provide new insights into the fouling characteristics of flowback water, while also identifying possible strategies to reduce membrane fouling. The data also suggest possible concerns regarding plugging of the micro/nano-scale pores in shale formations (similar in size to those in porous membranes) during reuse of flowback water.

2. Materials and methods

2.1. Synthetic fracturing fluid

Stock chemicals of friction reducer (FR), biocide, corrosion inhibitor, crosslinker, and surfactant were provided by Weatherford Chemical, Inc. and are commercial products used in HVHF operations. Each additive contains a mixture of chemicals as provided by the supplier (see Table SI); the exact composition and concentration of individual components are proprietary. FR contains PAM and petroleum distillate. Vacuum incubation of a neat FR stock solution yielded a nonvolatile (polymer) portion of approximately 40% by mass. A previous study reported that raw FR fluid contained roughly 0.7 g/L PAM with a peak MW of 15 MDa based on size exclusion chromatography analysis [27]. Ammonium persulfate (breaker), citric acid (iron control), and potassium hydroxide and sulfuric acid (pH adjustment) were purchased from Sigma-Aldrich (St. Louis, MO) and were prepared using deionized (DI) water from a Barnstead Nanopure water purification system with a resistivity of > 18 MΩ cm. This work primarily considers a slickwater fracturing fluid, which mainly contains FR, biocide, corrosion inhibitor, surfactant and iron control agents, given that 84% fracturing operations in the Marcellus utilized slickwater frac based on a review of 100 drilling logs and 97% nationwide utilized FR based on a review of 750 drilling logs on FracFocs.org. Hybrid frac combines slickwater and gel frac, where both FR and a gelling agent (such as guar gum) are used. We also performed limited experiments simulating a hybrid fracturing fluid by adding breaker and crosslinker to the fluid; critically, gelling agent could be another significant source that contributes to membrane fouling, which will be discussed in detail in a separate paper. Gel frac without the use of FR is rare and thus was not considered in the current study. The concentrations of the fracturing additives used to prepare the synthetic fracturing fluid (Table 1**)** were based on FracFocus.org and literature sources [17,28]. Additive concentrations tend towards the high ranges reported in the literature. Synthetic fracturing fluids were prepared by mixing appropriate additives with DI water. The

Table 1
Chemicals used to prepare the synthetic fracturing fluid.

Chemical additives	Specific compounds (provided by supplier)	Concentration
Friction Reducer[a]	Polyacrylamide, petroleum distillate	0.15% v/v
Biocide[a]	2,2-Dibromo- 3-Nitrilopropionamide (DBNPA)	0.0017% v/v
Corrosion Inhibitor[a]	Isopropanol, Ethylene glycol, N,N-Dimethylformamide, 2-Butoxyethanol, Cinnamaldehyde, Tar Bases, 1-Decanol,1-Octanol, Triethyl phosphate	0.0007% v/v
Crosslinker[a]	Sodium tetraborate pentahydrate , Glycerine, Potassium hydroxide	0.03% v/v
Breaker	Ammonium Persulfate	0.011% w/v
Iron Control	Citric Acid	0.0014% w/v
Surfactant[a]	Ethoxylated alcohol (C6-C12), Ethylene Glycol, Isopropyl Alcohol, D-limonene, 1-Octanol	0.075% v/v
pH Adjustment	Potassium hydroxide and sulfuric acid	pH adjusted to 7.2

[a] indicates chemical is provided by Weatherford Chemical, Inc. Final concentrations are based on the volume fraction of the liquid chemical stock (e.g., % volume of chemical stock/volume of water).