Submitted for publication in the
International Journal of Greenhouse Gas Control
Special Issue: Nexus of Water and Carbon Capture and Storage

**Treatment of produced water from an oilfield and selected coal mines
in the Illinois Basin**

Seyed A. Dastgheib*, Chad Knutson¹, Yaning Yang², Hafiz H. Salih

*Illinois State Geological Survey, University of Illinois, 615 East Peabody Drive,
Champaign, Illinois 61820, USA*

* Corresponding author. Tel: +1 217 265 6274; Fax: +1 217 333 8566; *E-mail address:* seyed@illinois.edu (S.A. Dastgheib).

¹ Present address: Wolfram Research Inc., 100 Trade Center Drive, Champaign, IL 61820, USA.

² Present address: GHD, 1755 Wittington Place, Suite 500, Dallas, TX 75234, USA.

Abstract

If large-scale CO₂ sequestration operations are implemented in oilfields or coal mines, large volumes of water (i.e., produced water) could potentially be generated that would need to be properly managed. In this work, produced water samples with total dissolved solids (TDS) values of 18,000–102,000 mg/L (ppm) were collected from an oilfield, a coal-bed methane field, and a coal mine in the Illinois Basin of the United States and were treated by selected conventional pretreatment processes followed by a reverse osmosis desalination process. Pretreatment processes included coagulation by lime, ferric chloride, or aluminum sulfate; filtration by sand, walnut shells, anthracite coal, or microfiltration; and adsorption by organoclay, activated carbon, or ion-exchange resins. Selected pretreatment processes were sufficient for removing most of the contaminants, but the high sodium background of the high-TDS produced water (102,000 ppm) limited the effectiveness of the ion-exchange pretreatment in removing scale-forming species. Reverse osmosis was a practical process for desalination of pretreated produced water samples tested (by reducing the TDS more than 96%) except for the high-TDS produced water. Reported bench-scale produced water treatment data might be beneficial for the design and operation of pilot-scale plants for treating produced waters with similar properties.

Keywords: Produced water, Water treatment, Pretreatment, Reverse osmosis, Desalination, Carbon sequestration

1. Introduction

Available techniques for natural gas and crude oil extraction that are also attractive options for CO₂ geological sequestration and storage include CO₂-enhanced oil and gas recovery (CO₂-EOR and CO₂-EGR; Holtz et al., 2001) and CO₂-enhanced coal-bed methane (CBM) recovery (CO₂-ECBMR; Gunter et al., 1997). If large-scale CO₂ sequestration operations are implemented in oilfields and coal mines, large volumes of water (i.e., produced water) could be generated that would need to be properly managed.

The term “produced water” refers to the water obtained from geological formations during the production of fossil fuels. Produced water constitutes the single largest waste stream in the oil and gas industry (Sirivedhin and Dallbauman, 2004). The national average water-to-oil ratio estimated from the onshore production-weighted ratios of 14 states was 7.6 (barrel per barrel). However, this ratio can be significantly higher for mature oilfields: an average water-to-oil ratio of 41.2 has been reported for Illinois oilfields (Dastgheib et al., 2014). From 1988 to 2007, the estimated annual amount of produced water generated from onshore oil and gas activities in the United States varied between 14 and 21 billion barrels (Veil et al., 2004). Larger volumes of produced water may be available, depending on the future production of fossil fuels. For oilfields, CO₂-EOR could produce large volumes of water, especially if the objective is to maximize subsurface CO₂ storage. Potential water production from CO₂-EOR in the 20 largest oilfields in the Illinois Basin is estimated at 4.1 billion barrels. Present volumes of produced water from CBM production in the Illinois Basin are not large, but significant

volumes of water could be available if CO₂-ECBMR is practiced extensively (Knutson et al., 2012).

Depending on the quality of the produced water, current practice for produced water management includes reinjection into underground formations, surface discharge into receiving waters, and treatment for beneficial reuse. Water from surface mines and overflowing underground mines typically is discharged to surface streams, whereas reinjection is the most common approach for managing onshore oil and gas produced water. More than 98% of produced water from onshore wells was injected underground in 2007, of which 59% was injected into producing formations to maintain reservoir pressure and for EOR and another 40% was injected into nonproducing formations for disposal (Clark and Veil, 2009).

Various conventional and advanced water treatment technologies have been applied to treat produced water. These technologies might be also applicable to treatment of produced water from Illinois Basin. Each technology has its advantages and disadvantages with respect to treatment efficiency, requirements for chemicals, equipment and energy, environmental footprint, and cost. Evaluation and selection of the best technologies available for treatment of produced water from a particular source must take into consideration the types of contaminants to be removed, the levels of total dissolved solids (TDS), and the goal of treatment required for potential end use. Treatment of produced water includes pretreatment and main treatment (or desalination) stages. Conventional pretreatment includes using various technologies to remove residual

oil (e.g., by hydrocyclone and gas floatation), organic compounds (e.g., by organoclay and activated carbon adsorption), suspended solids (e.g., by coagulation/sedimentation and filtration), and scale-forming species (e.g., by lime softening or by using ion-exchange resins).

A large volume of publications on conventional coagulation–flocculation processes for the drinking water and wastewater treatment can be found. However, a limited number of reports on produced water treatment by these processes can be identified in the open literature. For pretreatment by coagulation and sedimentation, a significant removal of suspended and colloidal oil can be achieved in addition to removal of organic and natural organic matter species, as reported for treatment of an oilfield produced water (Zhong et al., 2003). Coagulation and flocculation are processes for aggregating colloidal species and small particles in the water into larger, heavier clusters that settle out in a short time. In coagulation, a coagulant (usually an aluminum or iron salt) is added to raw water and mixed in the rapid mix chamber. According to the water pH, the iron or aluminum ions will hydrate to give rise to a variety of mononuclear and polynuclear species. These emerging species will interact with the suspended particles and accelerate their coagulation and sedimentation. The suspended and colloidal particles in produced water can be removed by coagulation–flocculation processes. However, this process is not effective for removing dissolved constituents unless they precipitate at the treatment conditions (e.g., pH, temperature, concentration and distribution of dissolved species) of the coagulation process.

Some innovative coagulation–flocculation approaches have been also proposed for produced water treatment (Fakhru’l-Razi et al., 2009). For instance, a steam generator-quality feedwater was produced by treating produced water containing 2,000 ppm of hardness, 500 ppm of sulfides, 10,000 ppm of TDS, and 200 ppm of oil by using a modified hot lime process (Garbutt, 1997). Other methods include using an inorganic mixed metal (Fe, Mg, and Al), a polynuclear polymer (Zhou et al., 2000), ozone-enhanced coagulation (Cheng et al., 2011), and electrocoagulation (Zhao et al., 2014).

Filtration has been used extensively in water treatment plants for removing finite-size particles from water. In granular filtration, the porous medium is a thick bed of granular material such as sand. The transport and deposition of particles in a sand filter are highly affected by the electrostatic interactions between these particles and the filter media. Normally, sand filters are negatively charged in most water treatment processes (Jaradat et al., 2009). In depth filtration, contaminant particles accumulate throughout the filter bed by colliding with and adhering to the media; thus, the captured particles can be much smaller than the smallest pore size in the bed. Deep-bed filters (e.g., sand, anthracite coal, walnut shell filters) can be used to remove larger suspended solids and coagulated particles from water. In the case of walnut shells, some residual oil may also be removed along with the suspended solids (Hayes and Arthur, 2004; Rahman, 1992; Srinivasan and Viraraghavan, 2008). Adsorption has been widely applied to remove organic compounds from produced water. Materials used as adsorbents include activated

carbon, organoclay, zeolite, natural organic materials, and synthetic polymers (Ahsan et al., 2001; Allen, 2008).

Available desalination technologies include reverse osmosis (RO) and thermal distillation processes, which produce freshwater and a brine by-product. Reverse osmosis is a practical technology for desalination of produced water with low and medium TDS values (e.g., lower than ~50,000 ppm), but current RO technology is restricted by the maximum osmotic pressure limit of 1200 psi (Bourcier et al., 2011) for the RO membranes. Several projects have demonstrated the use of RO to treat oilfield produced water and generate freshwater for agricultural and potable use (e.g., Tao et al., 1993). The RO membranes are prone to fouling by scale-forming species and by biofilm development, which is promoted by dissolved organic compounds (Hayes and Arthur, 2004). Therefore, pretreatment processes are essential as initial stages of produced water treatment to minimize membrane fouling at the RO desalination stage.

The existing thermal seawater desalination technologies include Multi-Effect Distillation, Multi-Stage Flash, and Mechanical Vapor Compression. These technologies are not designed to treat highly saline brines mainly due to corrosion and fouling issues. For high-TDS brine, only evaporation and crystallization (for zero liquid discharge) appear to be available practical technologies. High-TDS brines are typically disposed of by deep well injection. Treatment of high-TDS brine is only commonly practiced when environmental regulations require the implementation of a zero liquid discharge process to minimize or eliminate liquid waste.

Potentially significant volumes of produced water in the Illinois Basin might be available and could be considered as valuable nontraditional water resources (Dastgheib et al., 2014) if they can be properly treated. The main objective of this research is to investigate the treatability of selected types of produced water samples collected from an oilfield and selected coal mines in the Illinois Basin of the United States by conventional water treatment processes to generate water that is suitable for beneficial uses. The treatment objective is to treat water for beneficial use as cooling water ($\text{TDS} < 1,000$ ppm). Selected pretreatment processes were used to remove residual oil by filtration, organic impurities by organoclay and activated carbon adsorption, scale-forming species by an ion-exchange process, and suspended matter and colloids by coagulation (using lime, ferric chloride, or aluminum sulfate) and filtration (by sand, walnut shells, anthracite coal, or microfiltration). Reverse osmosis is used as the main desalination process for water purification. Various pretreatment processes are used to minimize membrane fouling during the main RO desalination stage.

2. Materials and methods

2.1. Produced water sampling and characterization

Produced water samples were collected from the Loudon oilfield (Fayette, Illinois), the Galatia coal mine (Saline, Illinois), and the ACT CBM project (Posey, Indiana). One to three samples from each site were collected and characterized but only one sample from each site was used for the experimental work presented here. It should

be noted that water quality parameters of collected samples from each site were relatively similar, however some variations were also observed (Knutson et al., 2012). Produced water samples were analyzed for pH, conductivity, turbidity, TDS, total suspended solids (TSS), alkalinity, total petroleum hydrocarbons (TPH), selected cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , and Sr^{2+}) and anions (Cl^- , Br^- , and HCO_3^-), ammonia, and dissolved organic carbon (DOC) concentrations by using standard methods described elsewhere (Knutson et al., 2012). Quality assurance for analyses was provided by analyzing selected duplicate samples, blank samples, and spiked samples.

2.2. Produced water treatment methods

The treatment processes were designed to remove organic impurities, suspended solids, and dissolved salts from the water. The conventional treatment processes investigated were (1) coagulation–flocculation–sedimentation using lime, ferric chloride, or aluminum sulfate; (2) filtration by microfiltration or through a bed media filter packed with sand, walnut shells, or anthracite coal; (3) adsorption onto activated carbon, organoclay, or an ion-exchange resin; and (4) membrane desalination by RO. Some additional softening by lime treatment followed by recarbonation (CO_2 bubbling) was also performed for pretreated samples prior to the RO treatment. All treatment processes, except RO, are considered pretreatment steps and were used to remove organic impurities as well as scale-forming species and suspended solids that negatively affect the performance of RO desalination. An overview of various treatment experiments

conducted for each type of produced water is provided in Table 1. A brief description of each method is presented below.

Table 1

Overview of different treatments conducted for each type of produced water sample.

Treatments	Coagulation			Filtration			Adsorption		Ion exchange		Softening	Reverse Osmosis				
	Lime only	Lime + alum	Lime + FeCl ₃	Sand	Anthracite coal	Microfiltration	Walnut shells	GAC	organoclay	MAC-3	Marathon C	Lime softening + recarbonation	TCF XR	TCF HR	XLE	SW30HR
Oilfield produced water (Louden)	X	X	X	X	X	X	X	X	X	X	X	-	-	X	-	-
Coal mine produced water (Galatia)	X	X	X	X	X	X	-	X	-	X	X	X	X	-	X	X
CBM produced water (ACT)	X	X	X	X	X	X	-	X	-	X	X	X	X	-	X	-

2.2.1. Coagulation, flocculation, and sedimentation

The optimal dose (i.e., the dose resulting in the lowest turbidity) and type of coagulant were obtained by jar tests. Ferric chloride and aluminum sulfate coagulants were obtained from Sigma-Aldrich (St. Louis, Missouri). The lime (calcium oxide) used in this study was obtained from Fisher Scientific (Pittsburgh, Pennsylvania). Lime solutions were added to the samples for pH adjustment. After addition of the coagulant, the sample was stirred vigorously at 1,000 rpm for 1 min and then slowly mixed for 20 min at 60 rpm with a 4-cm-diameter stirrer. Samples were then allowed to settle for 24 hr, and the supernatant was sampled for turbidity analysis. Selected filtered samples were also analyzed by inductively coupled plasma-mass spectroscopy.

2.2.2. Packed-column filtration

Filtration experiments were conducted with a bench-scale column test conducted using 2.5 cm I.D. $\times$ 30 cm Kontes Chromaflex columns obtained from Fisher Scientific. Produced water was pumped through the packed columns at a preset flow rate of 2.5 mL/min using a Masterflex peristaltic pump. A pressure gauge was installed at the inlet of the column to monitor the head loss. Effluent samples were collected at the outlet of the columns at selected time intervals until certain head loss occurred (0.03 or 0.07 bar for different produced waters). Turbidity, conductivity, and DOC were monitored at the column outlets. Treatment design parameters such as removal efficiency, breakthrough time, and adsorption capacity were obtained. The continuous treatment with a series of columns packed with different filtration/adsorption media was also examined.

Filtration media included crushed walnut shells, sand, and anthracite coal. Black walnut shells (12 $\times$ 16 mesh, i.e., 1.19–1.68 mm) were supplied by Siemens Water Technologies Corp. (Rothschild, Wisconsin). The sand (0.35–0.45 mm) and anthracite coal (0.60–0.80 mm) filtration media were obtained from Carbon Enterprises, Inc. (Circleville, Ohio). The walnut shells and anthracite coal particles were crushed and passed through 40- and 50-mesh screens to obtain a consistent particle size between 0.30 and 0.42 mm. The typical diameter of slow sand filtration media is 0.30–0.45 mm (Crittenden et al., 2012a).

2.2.3. Adsorption and ion exchange

Rapid small-scale column tests were used to evaluate the adsorption characteristics and breakthrough behavior of different impurities in small packed-bed columns (Knappe et al., 1997). This method can be used to obtain critical parameters for the ultimate design and operation of full-scale adsorption columns. For produced water from the Loudon field, walnut-shell-filtered effluent from the previous filtration experiments was used for the adsorption experiments. For other produced waters, no filtration was performed before the adsorption experiments. The adsorption media tested included organoclay, granular activated carbon (GAC), and ion-exchange resin. OilSorb organoclay (8×30 mesh, i.e. 0.60–2.38 mm) was obtained from Biomin, Inc. (Ferndale, Michigan). The organoclay has a density of 0.98 g/cm^3 , a porosity of 0.3, and a surface area of $3.54 \text{ m}^2/\text{g}$. A coal-based GAC (20×50 mesh, i.e., 0.30–0.84 mm) was obtained from CEI-Carbon Enterprises, Inc. (Circleville, Ohio). The GAC has a density of $0.4\text{--}0.7 \text{ g/cm}^3$, a bulk porosity of 0.7–0.8, and a surface area of $295 \text{ m}^2/\text{g}$. To minimize the chances of channeling in an adsorption column, the inner column diameter should be at least 25 times greater than the particle diameter (Crittenden et al., 2012b). Therefore, both the organoclay and GAC were crushed and passed through 40×50 meshes to obtain a consistent particle size between 0.30 and 0.42 mm.

The rapid small-scale column tests were performed using a Kontes Chromaflex column (1.0 cm I.D. $\times$ 15 cm length) at a feed flow rate of 2.0 mL/min and an empty bed contact time of 6 min. Adsorption experiments were conducted with a GAC column, an

organoclay column, and an organoclay column followed by a GAC column (organoclay–GAC). High removal efficiency of hydrocarbon from produced water was reported when organoclay was used in combination with GAC adsorption (Alther, 1997). The conductivity and DOC content of the effluents were monitored at the outlet of the columns until breakthrough occurred.

Batch ion-exchange equilibrium tests were performed using a Dowex MAC-3 weak acid resin and a Dowex MARATHON C strong acid resin, both manufactured by Dow Water & Process Solutions (Midland, Michigan) and obtained from Sigma-Aldrich. Both resins are recommended for water softening, but the Na-form of weak acid resins exhibits a much higher affinity for hardness ions than does that of strong acid resins. Results from the equilibrium tests were used to estimate the removal efficiency and optimize the design of the ion-exchange column tests. An aliquot of the resin was mixed with produced water samples in amber bottles and shaken overnight at room temperature (25 °C). The ratio of resin to water for the experiment was estimated, assuming that the ion-exchange capacity of the resin would be fully used. The produced water used in the ion-exchange experiments had been treated with the walnut shell filter and the organoclay–GAC columns. The concentrations of Ca and Mg in the water samples before and after the ion-exchange experiments were analyzed by inductively coupled plasma-mass spectroscopy.

Cation-exchange breakthrough curves were obtained by monitoring the concentrations of Ca and Mg in water passing through small columns packed with cation-

exchange resins. The column tests were performed with Kontes Chromaflex columns (1.0 cm I.D. $\times$ 15 cm length) at a flow rate of 2.0 mL/min. An aliquot of 6 mL of H-form MAC-3 was packed into the column. A 100-mL volume of 10% NaOH solution was passed through the column to exchange the resin from H-form to Na-form. The column was washed with pure water until the effluent pH reached neutral.

The breakthrough curves of the Na-form MARATHON C (SAC) resin alone and of the SAC resin followed by the Na-form MAC-3 (WAC) resin were determined by a continuous-flow system using produced water treated with a sand filter and a GAC column. The SAC resin was used as the roughing stage, and the WAC resin was used as a polishing bed. Effluents from the first column (SAC resin) and the second column (WAC resin) were collected and analyzed for Ca and Mg concentrations to obtain the breakthrough curves for a one-column (SAC) or two-column (SAC–WAC) system.

2.2.4. Membrane filtration

The membrane filtration studies were conducted using a bench-scale RO setup equipped with a cross-flow 316 stainless steel membrane cell (SEPA CF II) obtained from Sterlitech Corporation (Kent, Washington). The active cross-sectional area of the membranes is 139 cm², and the system can operate at pressures up to 69 bar. The pump and a control valve regulate pressure across the membrane. The RO system was run in a recycle mode by returning both permeate and the reject streams to the feed tank. The procedure for membrane experiments is described in detail in Ladner et al. (2010). A

membrane sheet was cut to fit the membrane holder and then soaked in deionized (DI) water for at least 24 hr. The membrane was then compacted with DI water containing NaCl at the operating pressure for the produced water experiment for approximately 24 hr. The NaCl solution had the same concentration as the salt concentration in the produced water sample to be tested. The pretreated produced water was then pumped through the system for 1 min to flush out the residual NaCl water. After the residual NaCl water was fully removed, the pressure and flow rate were increased to operating conditions. The RO system was run with the produced water sample for approximately 24 hr in the recycle mode. Then either the experiment was stopped or the produced water was flushed out of the system and replaced with a new produced water sample. Permeate flow rate and conductivity were monitored. The membrane filtration system was cleaned thoroughly after each experiment by using a dilute phosphoric acid solution wash and a final rinse with DI water until the conductivity of the outlet was equal to that of the inlet.

The membranes tested in this study were provided by Koch Membrane Systems, Inc. (Wilmington, Massachusetts) and Dow Water & Process Solutions–FilmTec Corporation (Edina, Minnesota). Operating pressures for each experiment were based on the manufacturers' guidelines. For some membranes, experiments using two different operating pressures were performed to compare their treatment performance at the same pressure. The RO pressure range was from 28 to 69 bar. Table 2 lists the different membranes tested in this study along with the key parameters or information for each membrane.

Table 2

Membranes used for the membrane desalination experiments.

Manufacturer	Membrane	Description
Dow	SW30HR	RO membrane for seawater desalination with 99.7% salt rejection for 32,000 mg/L of NaCl and 8% recovery at 55 bar, pH 8, and 25 °C.
Dow	XLE	RO membrane for brackish water with 99.0% salt rejection and 15% recovery for 500 mg/L of NaCl at 7 bar and 25 °C.
Koch	TCF HR	RO membrane for brackish water at low pressure. Typical operating pressure is 10–17 bar.
Koch	TCF XR	RO membrane for brackish water with high rejection at low pressure. Typical operating pressure is 16–31 bar.

A number of pretreatment steps before the RO membrane treatment stage were investigated to improve the RO performance. Filtration was performed using 0.22- μ m nitrocellulose membranes for the majority of samples. Some experiments were performed using water that had been pretreated with sand filtration, GAC, and an ion-exchange resin. For most samples, the pH was adjusted to 6 by adding 0.1 N HCl. Lime softening was performed for selected experiments. For this step, CaO was added to the sample until the pH was approximately 10. The solution was stored in a tank overnight to allow the solids to settle. The supernatant was decanted into another tank, and CO₂ was bubbled into the water until the pH was 8.7. The lime-softened water was then filtered through a 0.22- μ m filter. Finally, HCl was added to reduce the pH to 6.

3. Results and discussion

3.1. Produced water characterization

Different water quality parameters (i.e., pH, turbidity, conductivity, TDS, TSS, alkalinity, DOC, and ammonia content) of the produced water samples showed

significant variation in physical and chemical properties of the water samples (Table 3). Total dissolved solids concentrations ranged from 17,982 to 101,734 mg/L, TSS from 5.4 to 57.0 mg/L, alkalinity from 260 to 636 mg/L, and DOC from 7.3 to 8.5 mg/L. The concentration of ammonia (primarily in the form of NH_4^+ within the sample pH ranges) ranged from 6.3 to 25.4 mg of N/L.

The TPH content of the sample collected from the Loudon oilfield was 26.4 mg/L and was reduced by 71% after the sample was passed through the 0.7- μm filter, which indicates that the majority of TPH in the water samples was associated with suspended small droplets, colloids, and particles. The TPH concentrations in the samples collected from the Galatia coal mine and the ACT CBM project were less than 0.1 mg/L.

Table 3

Characterization of produced water samples.

Produced water	pH	Turbidity (NTU)	Conductivity (mS/cm)	TDS (mg/L)	TSS (mg/L)	Alkalinity (mg/L as CaCO ₃)	DOC (mg/L)	Ammonia (mg of N/L)	TPH (mg/L)
Oilfield (Louden)	7.4	33.0	120	101,734	8.5	285	8.5	25.4	26.4
CBM (ACT)	7.5	5.9	34	25,114	57.0	636	7.3	11.2	NM ^a
Coal mine (Galatia)	7.9	11.0	31	17,982	5.4	260	8.0	6.3	NM

^aNM, not measurable.

Concentrations of selected cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , and Sr^{2+}) and anions (Cl^- , Br^- , and HCO_3^-) in the produced water samples are presented in Table 4. Na^+ was the dominant cation in all samples, followed by Ca^{2+} , whereas Cl^- was the most abundant anion in all samples. Concentrations of HCO_3^- were calculated from alkalinity and pH values. The HCO_3^- concentration ranged between 314 and 773 mg/L in the produced water samples.

Table 4

Concentrations (mg/L) of trace elements in the produced water samples.

Produced water	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ba^{2+}	Sr^{2+}	Cl^-	Br^-	HCO_3^-
Oilfield (Louden)	33,568	101	2,603	969	610	219	60,341	95	346
CBM (ACT)	7,235	28	124	68	6	5	10,418	37	773
Coal mine (Galatia)	6,312	33	266	150	1	8	9,487	30	314

As expected, produced waters under investigation contained high concentrations of organic and inorganic impurities because of their contact with hydrocarbon compounds and minerals in geological formations. Sodium chloride was the most dominant salt in all the produced waters studied, whereas calcium ions were the dominant divalent cations that could contribute to scale formation. Concentrations of the majority of the measured divalent cations in oilfield produced water were about one order of magnitude higher than those in the CBM and coal mine produced waters.

3.2. Coagulation, flocculation, and sedimentation

Results of the coagulation–flocculation studies for different types of produced water are presented below. For the Loudon oilfield water, the initial turbidity was 33 nephelometric turbidity units (NTU) and the pH was 7.4 (Table 3). After the addition of a relatively small amount of lime (<60 mg/L), the pH change was minimal, remaining near 7.4. The addition of ~150–200 mg/L of lime, without the addition of alum or ferric chloride, increased the solution pH to 8.9–9.4 (Table 5). The final turbidity of oilfield water samples, coagulated by using different combinations of lime and coagulants, ranged from 0.2 to 10.6 NTU. Several different combinations resulted in the lowest turbidity values, including high alum/low lime (204 mg/L of alum and 12 mg/L of lime), moderate alum/high lime (136 mg/L of alum and 196 mg/L of lime), and moderate ferric chloride/low lime (124 mg/L of ferric chloride and 12 mg/L of lime). For the lime-only tests, the turbidity decreased with increasing lime concentration to a minimum value of 0.5 NTU at the maximum lime dose, but the pH increased substantially as well.

The pH of the water sample is a critical parameter for water treatment. The influence of pH on the coagulation process is due to the influence of the water pH on hydrolytic dissociation of the coagulant and speciation of metal ions as a function of solution pH. For instance, the concentration of Fe^{3+} in solution as a function of pH (or pOH) can be calculated from its solubility product K_{sp} (Eq. 1):

$$K_{\text{sp}} = [\text{Fe}^{3+}] [\text{OH}^-]^3 = 10^{-39}. \quad (1)$$

Table 5

Coagulation tests using different doses of lime, alum, and ferric chloride.

Coagulant	Oilfield produced water				CBM produced water				Coal mine produced water			
	Coagulant dose (mg/L)	Lime dose (mg/L)	pH	Turbidity at 24 hr (NTU)	Coagulant dose (mg/L)	Lime dose (mg/L)	pH	Turbidity at 24 hr (NTU)	Coagulant dose (mg/L)	Lime dose (mg/L)	pH	Turbidity at 24 hr (NTU)
None	0	155	8.9	1.7	0	155	9.2	2.1	0	155	10.7	2.0
None	0	196	9.4	0.5	0	196	9.5	2	0	196	10.7	0.4
Alum	136	58	7.3	10.6	136	58	8.2	2.4	136	58	8.6	0.8
Alum	136	196	7.6	0.3					136	196	9.8	0.7
Alum	204	12	7.5	0.5	204	155	8.8	1.6	204	0	6.8	0.4
Ferric chloride	62	12	7.4	1	68	12	7.7	1.2	62	12	7.5	2.0
Ferric chloride	62	58	7.4	0.9	68	58	7.9	0.7	62	155	9.5	0.4
Ferric chloride	124	12	7.4	0.2	136	12	8.4	2.9	124	12	6.8	0.4
Ferric chloride	124	58	7.3	0.4								

Often, when the coagulants are added, the pH values of treated water decreases because of the acidic character of the Fe^{3+} or Al^{3+} cations (both Lewis acids). Under basic conditions resulting from addition of lime, more precipitation of metal species will occur that may coagulate and coprecipitate with other suspended solids.

The initial turbidity of the CBM (ACT) water was 5.9 NTU, and this water had a pH value of 7.5. For the coal mine produced water (Galatia), the initial turbidity and pH were 11 NTU and 7.9, respectively (Table 3). Similar to the oilfield produced water, for both the CBM and coal mine water, a large addition of lime decreased the turbidity significantly but increased the pH to values above 9. The turbidity of the coagulated and settled CBM and coal mine produced water ranged from 0.4 to 2.9 NTU. The lowest turbidity value was observed for the low ferric chloride and lime doses (68 mg/L of FeCl_3 and 58 mg/L of CaO) for the CBM water and the low ferric chloride/high lime dose (62 mg/L of FeCl_3 and 155 mg/L of CaO) or the high alum dose without addition of lime for the coal mine produced water (Table 5). Lime by itself may be used as a coagulant, but the pH increases to more than 9 when acceptable coagulation is achieved. The use of lime as the main coagulant may have some drawbacks, such as increasing the sample pH and hardness. High pH values will likely cause scaling problems on RO membranes.

Table 6 shows concentrations of the major divalent cations and Si (potential scale-forming species) in the filtered produced water and water after coagulation. Barium concentration in the oilfield produced water was about two orders of magnitude higher

than that in the CBM and coal mine produced waters. It was significantly reduced by alum coagulation. Alum and ferric chloride coagulation (with addition of lime) of the oilfield and coal mine produced waters did not decrease or even slightly increase the Ca content, whereas a reduction in Ca concentration for the coagulated CBM was observed. Addition of lime contributed to the increase in Ca^{2+} in the solution, and precipitation of Ca species during the coagulation and flocculation processes decreased the Ca concentration. Concentration of Mg in coagulated water samples did not noticeably decrease (considering the measurement errors) for the oilfield and CBM water samples, but a reduction in Mg concentration was observed for the alum-coagulated coal mine water. Strontium concentrations in all coagulated water samples appeared to be similar to those of filtered raw produced water samples. Silicon was partially removed from the coagulated oilfield water and from the alum-coagulated CBM water.

Table 6

Ion concentrations in selected produced water with and without the addition of coagulants.

Coagulant	Ba	Ca	Mg	Sr	Si
Oilfield produced water					
None	610	2,603	969	219	5
Alum (136 mg/L), lime (196 mg/L)	480	2,700	960	220	2
Ferric chloride (124 mg/L), lime (58 mg/L)	580	2,800	990	220	3
CBM produced water					
None	6	124	68	5	4
Alum (204 mg/L), lime (155 mg/L)	4	77	64	3	1
Ferric chloride (68 mg/L), lime (12 mg/L)	7	110	66	4	3
Coal mine produced water					
None	1	266	150	8	1
Alum (136 mg/L), lime (196 mg/L)	1	260	100	7	2
Ferric chloride (124 mg/L), lime (12 mg/L)	1	270	140	8	2

3.3. Packed column filtration

Slow sand filters typically never reach breakthrough and are always replaced when the head loss reaches the maximum acceptable head in the system; therefore, for bench-scale tests, the filtration experiments were performed for 7–8 days until the head loss in filters reached 0.07 bar (1 psi). The choice of 0.07 bar was due to the limited water volume and the experimental time scale. The suspended particles and oil droplets in the water were collected at the top layer of the filter beds.

The change in effluent turbidity of the oilfield produced water over time is shown in Fig. 1a. The effluent turbidity decreased from 33 to 0.02 NTU, remained stable for 80 hr, and increased to 0.07 NTU after 119 hr for the walnut shell filter. The effluent

turbidity after sand filtration decreased to 0.03 NTU after 10 hr, increased to 0.08 NTU between 18 and 27 hr, decreased again to 0.02 NTU after 37 hr. This result may have been due to the ripening effect normally observed in newly packed filters. A filter with a newly installed medium typically has a ripening period that can last several days, during which the captured particles gradually provide a better collector surface and improve the overall efficiency of the filter (Crittenden et al., 2012a). The effluent turbidity after coal filtration decreased to 0.02 NTU.

The ultimate low turbidities of the effluents suggest that all three filters were effective at removing particles and fine oil droplets from oilfield produced water. The sand and anthracite coal filters had better removal efficiencies than the walnut shell filter, based on a comparison of their effluent turbidities, which can be attributed to the smaller, more spherical-shaped sand particles (physical entrapment) and the higher affinity of coal particles for hydrocarbon droplets.

Fig. 1. Filtration effluent turbidity versus time for the produced water samples tested: (a) Louden oilfield water and (b) ACT CBM and Galatia coal mine water.

The filtration experiments on the CBM and coal mine produced water samples were performed for 3–4 days until the head loss in the two types of tested filters (sand and anthracite coal) reached 0.03 bar. The choice of 0.03 bar as the cutoff was due to the limited water volume available. The low initial turbidity of the effluents suggests that both filters were effective at removing particles in the produced water. However, the anthracite coal filter had better particle removal efficiency than did the sand filter before breakthrough occurred (Fig. 1b).

Fig. 2a illustrates the DOC removal efficiency [effluent DOC divided by the influent DOC (or DOC_0)] from the oilfield water by the three filter media. The anthracite coal filter had a stable DOC removal of ~70% after 15 hr—higher than those of the walnut shell (~60%) and sand (~45%) filters. The higher DOC removal efficiency of the coal filter was attributable to its higher affinity for dissolved hydrocarbons. A ripening period was again observed for the sand filter in terms of its DOC removal efficiency.

The DOC removal efficiency by the sand or coal filter from the CBM and coal mine produced water samples showed a stable DOC removal of ~20–30% (Fig. 2b), considerably lower than that for the oilfield water. The DOC_0 values of the three tested produced water samples were similar (~8 mg/L), but the observed differences in DOC removal efficiency from the oilfield water versus the CBM and coal mine water were likely due to the different compositions of dissolved hydrocarbons and the preferential

removal of heavier dissolved hydrocarbons from the oilfield water compared with the CBM and coal mine water.

Fig. 2. DOC removal by filtration processes from (a) the Louden oilfield produced water and (b) the ACT CBM and Galatia coal mine produced water.

3.4. Adsorption and ion exchange

Produced water samples were treated by the adsorption columns before the ion-exchange treatment. For the oilfield produced water, it was first filtered with the walnut

shell filter, which removed about 98% of the oil components, including free oil, emulsified oil droplets, and oil associated with particulate matter. Organoclay adsorption was then used as a prepolymer for the GAC adsorption to remove residual oil from the oilfield produced water. After the filtered Louden water was passed through the organoclay column, TPH in the effluent was negligible. The removal of DOC by adsorption to both organoclay and GAC is shown in Fig. 3. Adsorption to organoclay reached complete breakthrough ($\text{DOC}/\text{DOC}_0 = 1$) within 4 hr, whereas adsorption to GAC reached half breakthrough ($\text{DOC}/\text{DOC}_0 = 0.5$) after 23 hr. The data in Fig. 3 clearly show that GAC was more effective than organoclay at removing DOC from the Louden oilfield produced water. This result was mainly due to the higher internal surface area of the GAC. As expected, the GAC adsorption was found to be effective in removing DOC from the Galatia coal mine and CBM produced water. The breakthrough curve was still below 55% after a 24-hr experimental period (Fig. 3).

Fig. 3. Removal of dissolved organics from produced waters by GAC and organoclay sorbents.

According to the preliminary batch ion-exchange tests for the high-TDS Loudon produced water, the introduction of the MARATHON C resin resulted in 38% and 18% reductions in the concentrations of Ca and Mg, respectively. However, when the MAC-3 resin was used, the concentrations of Ca and Mg were reduced by only 4% and 3%, respectively.

The preliminary tests indicated that cation-exchange resins were inefficient for softening the Loudon water, which had a high TDS value (~102,000 mg/L) and a high Na content. In the ion-exchange softening process, Ca and Mg ions in the water are exchanged for Na ions. However, the high Na level in produced water from the Loudon field inhibited the ion-exchange process for removing hardness ions. Results of the preliminary tests suggested that ion-exchange columns would be neither practical nor efficient for pretreatment of the produced water from the Loudon field. In contrast, the preliminary batch ion-exchange tests showed high removal of Ca and Mg from both the CBM and coal mine produced water with TDS values of ~25,000 and ~18,000 mg/L, significantly lower than the TDS values of the oilfield produced water. The Na-form SAC resin removed 93.1% and 84.0% of Ca and Mg, respectively, from the ACT CBM water. The WAC resin removed 99.9% and 99.7% of Ca and Mg, respectively, from the ACT CBM water. However, the H-form MAC-3 resin was not effective at removing Ca and Mg.

Fig. 4 shows cation-exchange breakthrough curves of the SAC resin in a single column, and of the SAC resin followed by the WAC resin for the two continuous columns. For both the Galatia and ACT produced water, breakthroughs of Ca and Mg began almost immediately in the SAC resin column. After passing about 70 bed volumes (BV) of water, the Mg reached almost complete breakthrough for both water types. For Ca, we observed relatively stable breakthrough levels of about 80% for Galatia and 60% for CBM after about 150 BV.

Breakthroughs of Ca and Mg occurred after ~100 BV of Galatia water had passed through both the SAC and WAC resin columns. The initial breakthrough for the ACT water began at ~200 BV (twice the Galatia value), roughly correlating with the Ca and Mg concentrations of the ACT water, which were almost half those of the Galatia water (Table 4). After about 550 BV of Galatia water had passed through both resin columns, Mg and Ca reached breakthrough values of approximately 100% and 80%, respectively. For the ACT water, we observed breakthrough values of approximately 30-60% for Ca and 85% for Mg at 550 BV (Fig. 4).

The results of the preliminary cation-exchange tests and the column tests suggest that cation-exchange columns may be a practical pretreatment process for produced water with relatively low salt contents, for example, the CBM water, coal mine water, and oilfield water with salt contents similar to those of brackish water or seawater (e.g., <40,000 mg/L).

Fig. 4. Removal of Ca and Mg by ion-exchange resin columns: (a) Galatia and (b) ACT produced water.

3.5. Membrane filtration

Reverse osmosis experiments using selected membranes and NaCl solutions with concentrations ranging from 15,000 to 32,000 mg/L were performed to produce a baseline and characterize the membranes for produced water treatment (Table 7 and Fig.

5). The permeate flux decreased between 11% and 23% during the first 24 hr for all experiments. Membrane salt rejection values at the end of the compaction phase were more than 97%.

Table 7

List of bench-scale RO experiments using NaCl dissolved in deionized water.

Experiment	Membrane	Feed flow rate (mL/min)	Hydraulic pressure (bar)	Feed tank conductivity (mS/cm)	Rejection at 20 hr (%)
HR 4	TFC HR	980	41	29	97.0
XR 2	TFC XR	1300	41	41	97.4
XR 4	TFC XR	740	62	54	98.9

Fig. 5. Baseline testing of RO membranes during initial compaction with NaCl solutions (experimental conditions are provided in Table 7).

After pretreatment by filtration through a 0.22- μ m nitrocellulose filter, the Louden oilfield produced water was treated with the RO system by using a TFC HR membrane at an operating pressure of 69 bar. A low flow rate of 0.52 mL/min (equal to a

flux of 2.2 kg/m²·h) was initially observed that was further decreased to 0.43 mL/min (equal to a flux of 1.9 kg/m²·h) after 29 hr of treatment. Observed flux values were one order of magnitude lower than the baseline RO results for the baseline low-salinity NaCl solution by the same membrane (Fig. 5). A poor salt rejection of 63% was also measured for this negligible water flux. As expected for the Loudon water with a high TDS value of ~102,000 mg/L, the observed near-zero flux was due to the required high osmotic pressure, which exceeded the operating pressure of 69 bar and the practical pressure range of the existing membrane materials.

Membrane types, experimental conditions, and applied pretreatments for the ACT produced water, before the RO experiments, are listed in Table 8. The ACT water had a significant quantity of suspended solids that were filtered out by the 0.22-μm filter (listed as a microfiltration pretreatment in Table 8) in most cases. In some cases, other pretreatments were used, such as lime softening and ion-exchange adsorption (Table 8).

Table 8

Bench-scale membrane desalination experiments performed using ACT produced water.

Run ID	Membrane	Pressure (bar)	Pretreatments
xle1	XLE	65	Microfiltration
xle2	XLE	65	Lime softening, microfiltration, pH 6
xle4	XLE	65	Microfiltration, pH 6
xle5	XLE	65	Lime softening, microfiltration, pH 6
xle8	XLE	65	Lime softening, microfiltration, pH 6
xle9	XLE	65	Sand filtration, activated carbon and ion-exchange adsorption, pH 6
xr1	TFC XR	65	Microfiltration
xr2	TFC XR	65	Microfiltration, pH 6

To evaluate the impact of pretreatments on membrane fouling and performance, the relative permeate flow values (flow rate at a given time divided by the initial flow rate) of different experiments were calculated and compared (Figs. 6 and 7). As expected, the best relative permeate flow performance was observed with the NaCl solution. The best relative permeate flow for ACT produced water desalination resulted from the microfiltration and pH adjustment run (xle4), whereas the worst result was observed for the microfiltration-only pretreatment (xle1) without any pH adjustment. Lime softening (xle2, xle5, xle8) and ion exchange (xle9) did not improve membrane performance for these short-term experiments.

For the TFC XR membrane (Fig. 7), the relative permeate flow decreased by 37% after 26 hr when the micro-filtered water was used without pH adjustment (xr1). For the reduced pH and micro-filtered run (xr2), the relative permeate flow declined by less than 4% throughout the duration of the experiment. The relative flow decreased significantly between 48 and 53 hr because the pH of the feed water had increased to 7.5. Hydrochloric acid was added to again reduce the pH to 6, and the permeate flow increased, following the previous trend.

The two membranes tested for purification of the ACT CBM produced water showed similar salt rejection performance. The typical salt rejection observed for the XLE membrane experiments was 97%, and the permeate TDS concentration was ~400 mg/L. For the TFC XR membrane, the salt rejection ranged from 98 to 99%, corresponding to permeate TDS of approximately 120 to 300 mg/L.

Fig. 6. Relative permeate flows for ACT produced water using XLE membranes with the different pretreatment steps listed in Table 8.

Fig. 7. Relative permeate flows for microfiltered ACT produced water using TFC XR membranes with pH adjustment to 6 for the xr2 run and without any pH adjustment (pH 7.6) for the xr1 run.

Membrane desalination experimental conditions and results for the Galatia produced water are shown in Table 9 and Figs. 8 and 9. For experiment xle5, the

permeate was bled off at the end of day 2 and the beginning of day 3 to increase the salt concentration in the feed tank.

Table 9

Membrane experiments performed using Galatia coal mine produced water.

Run ID	Membrane	Pressure (bar)	Duration (days)	Pretreatments
xle1	XLE	65	3	Microfiltration, pH 6
xle2	XLE	65	3	Lime softening, microfiltration, pH 6
xle4	XLE	65	3	Filtration by anthracite coal, pH 6
xle5	XLE	65	3	Microfiltration
xle6	XLE	65	2	pH 6
SW301	SW30	65	1	Microfiltration, pH 6
TFC XR1	TFC XR	65	1	Microfiltration, pH 6

The relative permeate flows with time for the XLE membrane filtration studies conducted with Galatia produced water are shown in Fig. 8. For comparison, data from an experiment using a 17,000 mg/L NaCl solution are also included. Relative permeate flow values were greater than 80% for all experiments except xle6, which produced water used for the experiment without any filtration. The best relative flow at the end of day 3 was observed for the xle1 run (microfiltration, pH-adjusted) at a 90% value.

Fig. 8. Relative permeate flow rates for membrane treatment of Galatia produced water for various pretreatment steps (see Table 9) using the XLE membrane.

The relative permeate flow results shown in Fig. 8 suggest that only filtration and perhaps pH adjustment are needed to obtain good performance with the XLE membrane. Microfiltration (runs xle1, xle2, xle5) appears to give slightly better results compared with filtration with the anthracite coal column (run xle4), but the difference might not be significant. Results of the xle6 run (no filtration pretreatment) showed an immediate and continuous decrease in relative permeate flow over time, possibly caused by an accumulation of suspended solids on the membrane.

Fig. 9 shows the relative permeate flow over time for experiments with the Galatia produced water using the three different membranes but the same pretreatment method. Good membrane performance was observed for the 24-hr experiments, as indicated by relative permeate flow values of more than 85%. Initial flux values of 66,

32, and 37 kg/m²·h were observed for the XLE, SW30, and TFC XR membranes, respectively. The typical salt rejection observed for the XLE membrane experiments for Galatia water was 98%, and the permeate TDS concentration was ~300 mg/L. For the SW30 membrane, the salt rejection was approximately 99.5%, and permeate TDS values were less than 100 mg/L. For the TFC XR membrane, the salt rejection ranged from 96% to 97%, corresponding to a permeate TDS of ~600 mg/L.

Fig. 9. Relative permeate flow rates for three different membranes (XLE, SW30, and TFC XR) for Galatia produced water pretreated with microfiltration and pH adjustment.

4. Conclusions

Selected conventional water treatment processes were evaluated for their suitability for treating three produced water samples, with TDS values of 18,000–102,000 ppm, collected from the Illinois Basin of the United States. Samples were treated by

selected conventional pretreatment processes followed by a reverse osmosis desalination process. Pretreatments included coagulation by lime, ferric chloride, or aluminum sulfate; filtration by microfiltration or packed beds of sand, walnut shells, or anthracite coal; and adsorption by organoclay, activated carbon, or ion-exchange resins. Pretreatment steps were effective in removing suspended impurities, organic contaminants, and scale-forming species (for the low-TDS water) that cause membrane fouling during the RO desalination stage. Coagulation by a high dose of lime (196 mg/L) without addition of alum or ferric chloride, or a low dose of lime (12 mg/L) and a medium dose of alum or ferric chloride was effective in lowering the turbidity of produced water to about 1 NTU or lower. Filtration through a media filter (sand, walnut shells, anthracite coal) column reduced the turbidity of the filtered produced water to ~0.02 NTU for oilfield produced water, less than 0.1 NTU for CBM produced water, and less than 0.8 NTU for coal mine produced water.

The high sodium background of the high-TDS oilfield produced water (102,000 ppm) limited the effectiveness of the ion-exchange pretreatment in removing scale-forming calcium and magnesium species. However, it was effective for treatment of low-TDS coal mine and CBM produced water (18,000 ppm and 25,000 ppm).

Reverse osmosis was able to desalinate all the produced water samples tested except the high-TDS water from the Loudon oilfield site. For the high-TDS sample, the TDS value of 102,000 ppm was well above the practical limit of ~50,000 ppm for the RO treatment. For the low-TDS produced water samples, four commercial membranes were

tested at different pressures ranging from 41 bar to 65 bar and showed salt rejection values of 96.0-99.5% and initial flux values of 32-66 kg/m².h. Depending on the pretreatment of the tested produced water, these membranes showed different percentages of flux reduction, due to fouling, during the 24-75 hr tests. Bench-scale experimental results suggest that suspended solids and pH of the incoming water are among the factors that significantly affect the rate of fouling.

Some of the data provided in this work (e.g., coagulant dose for pretreatment, and salt rejection and flux under tested operational conditions for different tested membranes) might be considered first treatment estimations when designing pilot-scale facilities for treating produced waters with similar properties.

Acknowledgments

This research was funded by the U.S. Department of Energy, National Energy Technology Laboratory (Cooperative Agreement DE-NT0005343) and the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute (Grant 08-1/US-3). Any opinions expressed in this paper are those of the author(s) and do not necessarily reflect the views of the funding agencies; therefore, no official endorsement should be inferred. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

- Ahsan, S., Kaneco, S., Ohta, K., Mizuno, T., Kani, K., 2001. Use of some natural and waste materials for waste water treatment. *Water Res.* 35, 3738–3742.
- Allen, E.W., 2008. Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. *J. Environ. Eng. Sci.* 7, 123–138.
- Alther, G., 1997. Organoclay cost effectively removes oil from produced water. *Oil Gas J.* 95, 54–55.
- Bourcier, W.L., Wolery, T.J., Wolfe, T., Haussmann, C., Buscheck, T.A., Aines, R.D., 2011. A preliminary cost and engineering estimate for desalinating produced formation water associated with carbon dioxide capture and storage. *Int. J. Greenh. Gas Control* 5, 1319–1328.
- Cheng, L., Bi, X., Ni, Y., 2011. Oilfield produced water treatment by ozone-enhanced flocculation. Presented at the 2011 International Conference on Computer Distributed Control and Intelligent Environmental Monitoring (CDCIEM), pp. 1589–1593. DOI:10.1109/CDCIEM.2011.515.
- Clark, C., Veil, J., 2009. Produced Water Volumes and Management Practices in the United States. Report ANL/EVS/R-09/1. Argonne National Laboratory, Lemont, Illinois.

- Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G., 2012a. Granular filtration, in: MWH's Water Treatment: Principles and Design, third ed. John Wiley & Sons, New York, pp. 727–818.
- Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G., 2012b. Ion exchange, in: MWH's Water Treatment: Principles and Design, third ed. John Wiley & Sons, New York, pp. 1263–1334.
- Dastgheib, S.A., Knutson, C., Yang, Y., 2014. Produced water from CO₂-EOR in the Illinois Basin. *Energy Procedia* 63, 6878–6886.
- Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L.C., Biak, D.R.A., Madaeni, S.S., Abidin, Z.Z., 2009. Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.* 170, 530–551.
- Garbutt, C.F., 1997. Innovative Treating Processes Allow Steamflooding with Poor Quality Oilfield Water. Technical Paper SPE38799. Society of Petroleum Engineers, Richardson, Texas, pp. 491–499. <http://dx.doi.org/10.2118/38799-MS>.
- Gunter, W.D., Wiwehar, B., Perkins, E.H., 1997. Aquifer disposal of CO₂-rich greenhouse gases: Extension of the time scale of experiment for CO₂-sequestering reactions by geochemical modelling. *Mineral. Petrol.* 59, 121–140.
- Hayes, T., Arthur, D., 2004. Overview of emerging produced water treatment technologies. Presented at the 11th Annual International Petroleum Environmental Conference, Albuquerque, New Mexico, pp. 12–15.

- Holtz, M.H., Nance, P.K., Finley, R.J., 2001. Reduction of greenhouse gas emissions through CO₂ EOR in Texas. *Environ. Geosci.* 8, 187–199.
- Jaradat, A.Q., Grimberg, S.J., Holsen, T.M., 2009. Colloid transport through natural filter media. *J. Environ. Eng.* 135, 544–550.
- Knappe, D.R.U., Snoeyink, V.L., Roche, P., Prados, M.J., Bourbigot, M.-M., 1997. The effect of preloading on rapid small-scale column test predictions of atrazine removal by GAC adsorbers. *Water Res.* 31, 2899–2909.
- Knutson, C., Dastgheib, S.A., Yang, Y., Ashraf, A., Duckworth, C., Sinata, P., Sugiyono, I., Shannon, M.A., Werth, C.J., 2012. Reuse of Produced Water from CO₂ Enhanced Oil Recovery, Coal-Bed Methane, and Mine Pool Water by Coal-Based Power Plants. Final Report for U.S. Department of Energy Project DE-NT0005343. Illinois State Geological Survey, Champaign, Illinois.
- Ladner, D.A., Subramani, A., Kumar, M., Adham, S.S., Clark, M.M., 2010. Bench-scale evaluation of seawater desalination by reverse osmosis. *Desalination* 250, 490–499.
- Rahman, S., 1992. Evaluation of filtering efficiency of walnut granules as deep-bed filter media. *J. Pet. Sci. Eng.* 7, 239–246.
- Sirivedhin, T., Dallbauman, L., 2004. Organic matrix in produced water from the Osage-Skiatook petroleum environmental research site, Osage County, Oklahoma. *Chemosphere* 57, 463–469.

- Srinivasan, A., Viraraghavan, T., 2008. Removal of oil by walnut shell media. *Bioresour. Technol.* 99, 8217–8220.
- Tao, F., Curtice, S., Hobbs, R., Sides, J., Wieser, J., Dyke, C., Tuohey, D., Pilger, P., 1993. Reverse osmosis process successfully converts oil field brine into freshwater. *Oil Gas J.* 91, 88-91.
- Veil, J.A., Puder, M.G., Elcock, D., Redweik Jr., R.J., 2004. A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane. Report for U.S. Department of Energy/National Energy Technology Laboratory Project W-31-109-Eng-38. Argonne National Laboratory, Lemont, Illinois.
- Zhao, S., Huang, G., Cheng, G., Wang, Y., Fu, H., 2014. Hardness, COD and turbidity removals from produced water by electrocoagulation pretreatment prior to Reverse Osmosis membranes. *Desalination* 344, 454–462.
- Zhong, J., Sun, X., Wang, C., 2003. Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration. *Sep. Purif. Technol.* 32, 93–98.
- Zhou, F.S., Dang, Y.S., Lu, F.J., 2000. Inorganic polymeric flocculant FMA for purifying oilfield produced water: Preparation and uses. *Oilfield Chem.* 17, 256–259.