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

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#### ABSTRACT

If large-scale CO<sub>2</sub> 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.

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#### 1. Introduction

Available techniques for natural gas and crude oil extraction that are also attractive options for CO<sub>2</sub> geological sequestration and storage include CO<sub>2</sub>-enhanced oil and gas recovery (CO<sub>2</sub>-EOR and CO<sub>2</sub>-EGR; Holtz et al., 2001) and CO<sub>2</sub>-enhanced coal-bed methane (CBM) recovery (CO<sub>2</sub>-ECBMR; Gunter et al., 1997). If large-scale CO<sub>2</sub> 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 aver-

age water-to-oil ratio of 41.2 has been reported for Illinois oilfields (Dastgheib et al., 2014). From 1988–2007, 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, CO<sub>2</sub>-EOR could produce large volumes of water, especially if the objective is to maximize subsurface CO<sub>2</sub> storage. Potential water production from CO<sub>2</sub>-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 CO<sub>2</sub>-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).

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S.A. Dastgheib et al. / International Journal of Greenhouse Gas Control xxx (2016) xxx-xxx

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). 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 2000 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 (TDS < 1000 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 Louden 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<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, and Sr<sup>2+</sup>) and anions (Cl<sup>-</sup>, Br<sup>-</sup>, and HCO<sub>3</sub><sup>-</sup>), ammonia, and dissolved organic carbon (DOC) concentrations by using standard methods described

2

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