



Research article

Pilot-scale study on the treatment of basal aquifer water using ultrafiltration, reverse osmosis and evaporation/crystallization to achieve zero-liquid discharge



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ABSTRACT

Basal aquifer water is deep groundwater found at the bottom of geological formations, underlying bitumen-saturated sands. Some of the concerns associated with basal aquifer water at the Athabasca oil sands are the high concentrations of hardness-causing compounds, alkalinity, and total dissolved solids. The objective of this pilot-scale study was to treat basal aquifer water to a quality suitable for its reuse in the production of synthetic oil. To achieve zero-liquid discharge (ZLD) conditions, the treatment train included chemical oxidation, polymeric ultrafiltration (UF), reverse osmosis (RO), and evaporation-crystallization technologies. The results indicated that the UF unit was effective in removing solids, with UF filtrate turbidity averaging 2.0 NTU and silt density index averaging 0.9. Membrane autopsies indicated that iron was the primary foulant on the UF and RO membranes. Laboratory and pilot-scale tests on RO reject were conducted to determine the feasibility of ZLD crystallization. Due to the high amounts of calcium, magnesium, and bicarbonate in the RO reject, softening of the feed was required to avoid scaling in the evaporator. Crystals produced throughout the testing were mainly sodium chloride. The results of this study indicated that the ZLD approach was effective in both producing freshwater and minimizing brine discharges.

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1. Introduction

The Athabasca oil sands in northern Alberta, Canada, are one of the largest reserves of crude oil in the world, with approximately 168 billion barrels of recoverable bitumen available (ERCB, 2013). For shallow deposits, the recovery methodology relies on surface mining and aqueous extraction technologies to facilitate the separation of bitumen from the oil sands ore. As the overburden and bitumen deposits are removed, the underlying basal aquifer water becomes depressurized, flooding the open-mine pit. In order to reduce the risk of pit-wall failure, depressurizing of the McMurray basal aquifer has been implemented as a key strategy for achieving a safe and productive mining operation. To do that, dewatering wells have been installed to minimize the upwelling of the basal water to the mine pit. Currently, the dewatered basal water is stored in ponds. However, reliable alternatives to manage the water

from dewatering system are needed.

Some of the main concerns associated with the basal aquifer water at the Athabasca oil sands are the high concentrations of hardness-causing compounds, alkalinity, and total dissolved solids as well as high levels of soluble metals (Kim et al., 2013; Loganathan et al., 2015). Typically, the total dissolved solids of the McMurray formation waters vary from non-saline (<240 mg/L) to brine (279,000 mg/L) (Cowie et al., 2014). Because of its proximity to bitumen, the McMurray formation water also has naturally elevated concentrations of dissolved hydrocarbons (Lemay, 2002).

Treating basal aquifer water using efficient and cost-effective methods to remove organic and inorganic components will allow recycling it to process bitumen and reducing the need for freshwater resources. Previously, Kim et al. (2013) treated McMurray basal aquifer water using coagulation-flocculation-sedimentation followed by electro dialysis (ED). The results showed that ED yielded a constant quality product, with average rejection ratios of ionic species (i.e., final/original electrical conductivities) of 99.2% at room temperature and ambient pressure. The use of electro dialysis reversal (EDR)-reverse osmosis (RO) combined with a low-

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temperature evaporator/crystallizer was also investigated to treat basal aquifer water for a near-zero liquid discharge approach, achieving promising results in terms of freshwater production and minimization of brine volume (Loganathan et al., 2015). Nano-filtration (NF) and RO membranes have also been used for the desalination of groundwater due to their strong separation capabilities (Afonso et al., 2004; Walha et al., 2007) and because these technologies are significantly more energy efficient than other deionization methods (Ahmad and Williams, 2011). However, the membrane lifetime and permeate flux of RO systems are affected by the phenomena of concentration polarization and fouling at the membrane surface (Goosen et al., 2004). In addition, one of the major drawbacks for the adoption of pressure-driven membrane processes is the need for additional treatment of the concentrate stream (Chelme-Ayala et al., 2009).

Several treatment alternatives have been used to treat membrane concentrate; some of them have been designed to achieve zero liquid discharge (ZLD) and recover valuable compounds from the concentrate streams (Morillo et al., 2014; Pérez-González et al., 2012). Thermal-based technologies such as vertical tube falling film evaporator followed by a forced-circulation crystallizer are capital intensive and consume a significant amount of energy (Greenlee et al., 2009). Membrane-based technologies are less energy intensive when compared to thermal-based technologies. However, their applications are limited when treating complex water matrices (Subramani and Jacangelo, 2014). Emerging technologies such as forward osmosis are promising for the reduction of effluent volume and have low pollution potential (Cath et al., 2005). Membrane distillation coupled with crystallization (MDC) has also been successfully used to treat brines from seawater RO units at the bench-scale level (Ji et al., 2010; Van der Bruggen, 2013). Nonetheless, the applicability of these emerging technologies on an industrial scale-level has not been proved so far.

The main objective of this pilot study was to treat basal aquifer water to a quality suitable for its reuse in the production of synthetic oil and to minimize the volume of liquid waste. To achieve zero-liquid discharge (ZLD) conditions, the treatment train included chemical oxidation, polymeric ultrafiltration (UF), RO, and evaporation-crystallization. Other objectives of this study were: to optimize the operating condition; to identify the maximum sustainable recovery rates and fouling characteristics of the UF and RO membranes; and to evaluate the effectiveness of the cleaning procedures. Membrane autopsies were also conducted to identify the primary foulants on the UF and RO membranes. The final purpose of this study was to determine the feasibility of ZLD crystallization of basal water RO reject.

2. Materials and methods

2.1. Basal aquifer water and pilot plant

McMurray basal aquifer water from the Canadian Natural Horizon Mine was trucked directly from the basal water wellheads into a 60 m³ storage tank used as the plant influent water source. The pilot facility was located at the Canadian Natural Resources Limited (CNRL) Horizon site. The pilot study took place between June 7th and October 8th, 2012. The pilot plant was designed to treat up to 83 L/min of feed water.

As shown in Fig. 1, the pilot treatment system consisted of chemical oxidation, polymeric UF, single pass RO, and evaporation-crystallization (off-site). The oxidation step (i.e., potassium permanganate) was added before the UF treatment to precipitate out substances such as iron, manganese and sulfides that could foul the membranes. A coagulant (i.e., ferric chloride) was added upstream of the UF system to destabilize colloidal particles. The basal aquifer

water was then treated by the polymeric UF system (PVDF hollow fiber outside-in membrane with a nominal pore diameter of 0.03 μm; DOW SFD 2860 module) operated in dead-end mode for solids removal. Crossflow operation was also tested briefly at the end of the piloting period to address the limitations of dead-end UF operation. The UF filtrate was pumped through a 5-μm cartridge filter which protected the RO membranes from any suspended solids present in the feed water; the water was then treated using a RO system. The RO unit consisted of a three-stage design (Fig. S1 in the Supplementary Material) with fiberglass pressure vessels containing polyamide thin-film composite elements (DOW Filmtec SW30-4040). Detailed specifications of the UF and RO membranes are provided in Table S1.

Antiscalant (Hydrex 4102) was also added upstream of the RO system to address mineral scaling, while organic fouling was mitigated by the application of biocide (Nalco Permaclean PC-11) to prevent biological growth (Herzberg and Elimelech, 2007). Backwashes (BWs), chemically enhanced backwashes (CEBs), and clean-in-place (CIP) procedures were conducted according to the membrane manufacturer's recommendations. A summary of the UF BW and CEB sequences are provided in Tables S2 and S3, respectively.

2.2. Evaporation and ZLD crystallization of the RO reject

RO reject from the pilot plant was shipped to Veolia Water Solutions & Technologies Laboratory in Plainfield, IL, for an evaporation/crystallization study. The as-received basal water RO reject was first treated with lime (Ca(OH)₂) in order to reduce the calcium, magnesium, and silica in the feed water. After lime treatment, the solids were allowed to settle and the supernatant was used as feed to a Veolia's pilot-scale single tube falling film evaporator. The concentrate from the falling film evaporator was further concentrated in a Veolia's forced circulation evaporator. The forced circulation testing was performed solely to preconcentrate the feed and reduce the test length.

The concentrate from the forced circulation evaporator was used as feed to a Veolia's laboratory-scale evaporative crystallizer. The crystallizer consisted of a feed tank, evaporator body, condenser, distillate cooler, and a distillate receiver. The evaporator body was a three-liter glass cylindrical vessel with a hemispherical bottom and was heated with an external electrical heating mantle. The apparatus was fed continuously and distillate was removed continuously. The feed was pumped in using a peristaltic pump. The crystals were separated from the mother liquor using a basket centrifuge with a 10–15 μm filter cloth. The mother liquor was then recycled back to the crystallizer in order to concentrate impurities in the mother liquor.

2.3. Membrane autopsy and deposit analyses

Autopsy of the UF and RO membranes was conducted to identify the condition of the membranes and to determine the nature of the fouling. Scanning electronic microscopy (SEM) was used to determine the deposit morphology, while SEM-energy dispersive X-ray spectroscopy (SEM/EDX) was utilized to analyze the atomic composition of the deposits. Measurements of mineral elements were conducted by inductively coupled plasma (ICP). Deposit analyses were conducted by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to obtain the structural characteristics of the foulants.

2.4. Analytical analyses

Samples were collected on a daily basis and analyzed in the onsite laboratory. A key aspect of this pilot study was the collection

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