Treatment and Reuse of Coalbed Methane Produced Water Using a Pervaporation Irrigation Membrane Process

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ABSTRACT

Managing the water that is co-produced during the extraction of oil and natural gas reserves persists as both an environmental and economic challenge for the energy industry. While the specific chemistry and composition of these waters are highly variable they are most frequently characterized as brackish or highly saline waters, with total dissolved solids (TDS) concentrations ranging from 1,000 to 200,000 mg/L. This characteristic typically requires the use of pressure-driven membrane processes, like reverse osmosis (RO), and/or mechanical distillation to dispose of the produced water either through beneficial reuse or other routes. While effective, these treatment processes are infrastructure intensive, expensive and not always a practical option for small energy producers. The objective of this study, and the focus of this paper, is to evaluate the performance of a non-pressure driven pervaporation membrane process for treating coal bed methane (CBM) produced water and reusing it in an irrigation application. The pervaporation membrane that was used in this study is a non-porous hydrophilic polymer that is configured into an irrigation tube, into which the produced water is fed. This design requires that the produced water undergo minimal, to no, pretreatment as the pervaporation membrane serves as both the treatment (organics, salt separation) and reuse (irrigation) process. This presentation will cover performance results for the pervaporation irrigation process when treating model salt solutions and produced water (TDS ~ 2,000 mg/L) from an existing CBM site in Wyoming's Powder River basin. The pervaporation irrigation process has been found to effectively treat source waters having TDS concentrations from 1,000 to 150,000 mg/L while maintaining a permeate flux rate on the order of 5×10^{-4} m^3 m^{-2} day^{-1}. Independent of the feed water TDS the process has maintained an ion rejection rate of > 99%. In contrast to what has been observed for conventional RO processes, no loss of process performance (salt rejection, permeate flux rate) has been observed over time for the pervaporation irrigation process as mineral scaling of the membrane surface proceeds. These, and other, results suggest that the pervaporation irrigation process may be a viable produced water management option for small energy producers.

INTRODUCTION

Produced Water. Produced water is generally defined as water that is co-produced during the extraction of oil and/or natural gas from subsurface geologic formations. Produced water usually contains elevated concentrations of inorganic and/or organic constituents because of its contact with oil reservoirs, drilling mud, and subsurface geologic formations. The composition of inorganic and organic constituents in produced water can vary considerably depending on the geographic location and composition of the geologic formation from which the water is extracted. The depth of an extraction well and type of energy resource being extracted may also determine the composition and chemistry of the produced water. For example, water produced from conventional oil and gas extraction can have a total dissolved solids (TDS) concentrations ranging from 1,000 to 400,000 mg/L, and total oil contents from 40 to 2,000 mg/L (Benko and Drewes 2008).

There are basins all over the United States with significant recoverable amounts of coal bed methane (CBM), mainly the Appalachian and Black Warrior basins in the East, and the Powder River, San Juan, Raton, Greater Green, Piceance, and Uinta basins in the West (National Academic Press, 2010). Approximately 70 percent of CBM reserves are comprised of the San Juan, Raton and Powder River Basins in the Rocky Mountain States (National Academic Press, 2010). The presence of inorganic and/or organic materials in produced waters generally requires some form of treatment prior to disposal or reuse of the water.

Example techniques that are used for disposing of produced waters include deep well injection, discharge into surface water systems without treatment, and evaporation ponds. Process selection is dictated by the composition of the produced water and the intended reuse application. In many cases reducing the TDS concentration, and specifically the sodium concentration, of the CBM produced water is of primary importance to protect the quality of receiving waters, soils (land application), and/or to reuse it for industrial or municipal purposes (Mondal et al., 2008). Removing or reducing the TDS concentration in water requires the use of demineralization or desalination processes. Example desalination technologies that are commonly used in produced water treatment applications include ion exchange, mechanical distillation, pressure driven membrane processes (reverse osmosis), and non-pressure driven membrane processes (forward osmosis). While effective at removing TDS from water, each of the aforementioned technologies is associated with some type(s) of drawback. Important concerns for any desalination system are the specific energy consumption for the process (kWh/1,000 gal water treated) and the feed water recovery rate that may be achieved. This latter concern arises from the fact that as the feed water recovery rate increases there is less of a residual waste stream that must ultimately be disposed of.

Pervaporation. Pervaporation is a non-pressure-driven membrane process that relies on differences in vapor pressure between the feed and permeate sides of a membrane to achieve mass transport of water from one phase to another (Marin et al. 1992). Volatile materials (i.e., water) are transported across the membrane as vapors, which then condense in the permeate stream. Non-volatiles (e.g., salts and minerals) are retained on the feed side of the membrane. Pervaporation membranes are non-porous and may be constructed using hydrophilic, hydrophobic, or organophilic materials. The type of membrane material used dictates the type of volatile material that will be transported across the membrane barrier. For instance, a hydrophilic polymer will preferentially transport polar materials like water, while rejecting hydrophobic materials like organic solvents. Regardless of the transporting compound vapor transport will occur in three distinct steps: i) adsorption of the targeted solvent molecule to the membrane surface, ii) diffusion of the solvent molecule through the membrane barrier in vapor form along the vapor pressure gradient, and iii) desorption of the solvent from the posterior (permeate) side of the membrane into the condensing stream. A very low absolute pressure is usually maintained at the downstream side of the membrane in order to ensure continuous mass transport that helps to maintain a concentration difference across the membrane (Shao et al. 2001). To maintain a low absolute pressure on the downstream side of the membrane, either a sweeping gas or vacuum can be used.

Pervaporation has been used in the separation of mixtures of different organic solvents and removal of dilute organic compounds from aqueous streams. Although not widely researched, pervaporation has shown promise in desalination (Korngold et al. 1996, Quionones et al. 2005, Quinones et al. 2006). Of most importance to produced water treatment is the fact that pervaporation is less energy intensive than other processes as it does not require the use of high-pressure pumping systems, and it is capable of achieving relatively high feed water recovery rates. Taking advantage of these attributes requires that a vapor pressure gradient can be easily maintained between the feed and permeate streams. In this regard pervaporation irrigation is an ideal avenue for both treating and reusing saline waters like produced water.

Pervaporation irrigation involves the use of pervaporation membranes, in the form of tubes, for subsurface irrigation applications. The pervaporation membranes are constructed of a non-porous hydrophilic polymer membrane. The feed water, which in this case is the produced water, is fed into the tubular membranes using the pressure head that exists between the feed tank at ground level and the membranes, which are buried at some depth underground. Water permeates across the membrane as a result of the vapor pressure gradient that exists between the feed solution and the surrounding soil (< 100% moisture content). All other constituents (e.g., salts, minerals, organics) are retained on the feed side of the membrane. If the surrounding soil becomes saturated, and the partial pressures are balanced on either side of the membrane, water transfer across the membrane ceases. The pervaporation membrane tubes are arranged to form a drain field, with the tube depth and spacing being a function of environmental (soil type, vegetative cover), feed water, and membrane performance characteristics. The pervaporation process serves as a subsurface irrigation process for either the natural vegetative cover and/or for commercial crops. Water uptake by the root systems of the vegetative cover aids in creating the vapor pressure difference between the soil and the interior (feed side) of the pervaporation membranes. Pervaporation irrigation is therefore well suited for regions characterized by low humidity, water intensive crops, and high elevation, such as Wyoming.

METHODS AND MATERIALS

CBM Produced Water. Produced water samples were collected from a detention pond at an operating CBM site (Dutch Creek) outside of Sheridan, WY (**Fig. 1**). The detention pond, and current water treatment system, is managed by BeneTerra, LLC of Sheridan, WY. The detention pond contains water from several CBM wells in the surrounding area.

Figure 1. Aerial photo of the planned field site on which the pervaporation (PV) irrigation process will be evaluated for its ability to treat coal bed methane produced water.

The physical and chemical properties of the produced water samples were characterized by the University of Wyoming and Wyoming Analytical Laboratory (Laramie, WY). Results from the Dutch Creek produced water quality analysis analyzed by the Wyoming research team, along with known historical values for the area, are summarized in **Table 1**. The high pH value means that the water is alkaline water, as evidenced by the high concentration of bicarbonates present. The current water treatment method that is used for the CBM water is acidification using sulfuric acid, which precipitates the bicarbonates out of solution. Sodium is the primary cation present in the CBM water, with trace amounts of dissolved metals.

Table 1. Summary of the water quality analysis performed by the University of Wyoming research team (Mean Value), the Wyoming Analytical Laboratory (WAL), and known historical values for the site. The mean value determined by the Wyoming research team is displayed, and the number of samples for each parameter was either 5 or 6.

Water Quality Parameter	Units	Mean Value	WAL Analysis	Historical Value
pH	-	7.91 ± 0.28		8.1
Conductivity	mS/cm	2.12 ± 0.03	2570	2.08
Total dissolved solids	mg/L	1418 ± 1.71	1230	1290
Total organic carbon	mg C / L	-	19	
Cations / Anions				
Na^+	mg/L	-	444	539
Ca^{2+}	mg/L	-	10	6
Mg^{2+}	mg/L	-	10	3
Cl^-	mg/L	-	6	6
SO_4^{2-}	mg/L	-	36	7
HCO_3-	mg/L	-	1234	1440
Trace metals				
B	mg/L	-	0.229	0.1
Fe	mg/L	-	0.3	0.47
Li	mg/L	-	0.151	0.2
Zn	mg/L	-	0.002	0.01

* The Wyoming research team's water samples were collected in June 2011
* The sample analyzed by WAL was collected in August 2011
* The historical data was collected by BeneTerra October 2010

Pervaporation Membrane. The pervaporation membrane used in this research is a hydrophilic polymeric non-porous membrane from DuPont. Tests were carried out using both flat-sheet and tubular membrane samples. Field emission scanning electron microscope (FESEM) images were collected of the flat-sheet membrane surface in order to characterize its morphology. Images were taken of both dry and wet membrane samples in order to assess any changes in surface morphology that might occur as the polymer swelled. Wet membrane samples were soaked in doubly deionized water (pH ~ 5.5) for over 24 hours prior to imaging. Representative FESEM images of the dry (left image) and wet (right image) flat-sheet pervaporation membrane are shown in **Fig. 2**. Note that at least three different areas were imaged per sample. As can be seen in **Fig. 2** the membrane surface is characterized by hexagonal features, which upon wetting swell and become smoother. The dimensions of the hexagons do not appear to change upon swelling.
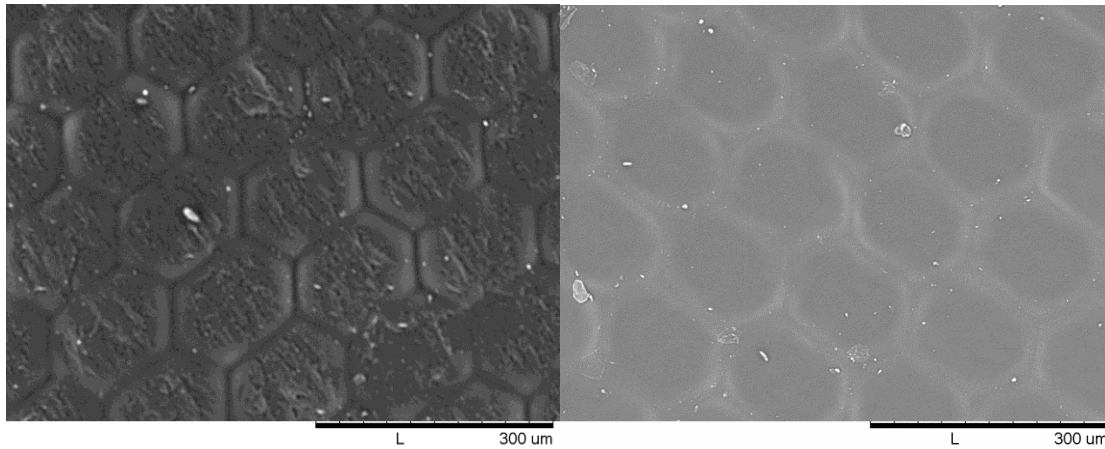
Figure 2. Representative FESEM images of the dry (left) and wet (right) flat-sheet pervaporation membrane samples. The scale bar for both samples is 300 μm.

Assessment of Salt Rejection. The rejection efficiency for the pervaporation membranes was assessed using simple diffusion experiments and bench-scale performance studies. The diffusion experiments were performed using flat-sheet membrane samples to assess the ion rejection efficiency of the pervaporation membranes and to determine if salts were able to penetrate into. The flat-sheet membrane was used to separate two different compartments. One compartment contained the feed solution (produced water or a concentrated sodium chloride solution), while the second compartment was either a sweeping gas or a concentrated sodium chloride solution.

Pervaporation Membrane Performance Tests. Bench-scale tests were performed using the pervaporation irrigation process that simulated the future field tests, but under controlled environmental conditions. A schematic of the bench-scale system (i.e., soil box) is given in **Fig. 3**. The pervaporation tubing was placed inside the box and surrounded by washed silica sand. Feed water was placed in the feed water tank from which it traveled into the pervaporation tubing. The feed tank was placed on a scale and the amount of water that was being processes by the tubing was determined from the change in mass of the feed tank. The feed tank was placed at an elevation above the tubing to provide some pressure head to the pervaporation tubing. Conductivity, pH and temperature probes were placed in the feed tank to monitor these parameters for the duration of the experiment. Soil probes were placed within the sand box to monitor soil moisture, soil conductivity and the soil temperature. Probes were also placed in the head space within the box to measure the temperature and relative humidity of the air above the sand. One probe was attached to the lid of the box and the other probe was placed on the sand surface to see if there was a humidity gradient within the box. An airline was used to flow air through the box as a means to keep the humidity in the soil box as low as possible. Samples were periodically drawn from inside the pervaporation tubing using a sample line that was fed into the tubing. The conductivity of the drawn samples was measured as a way of monitoring the increase in salt concentrations during the test.
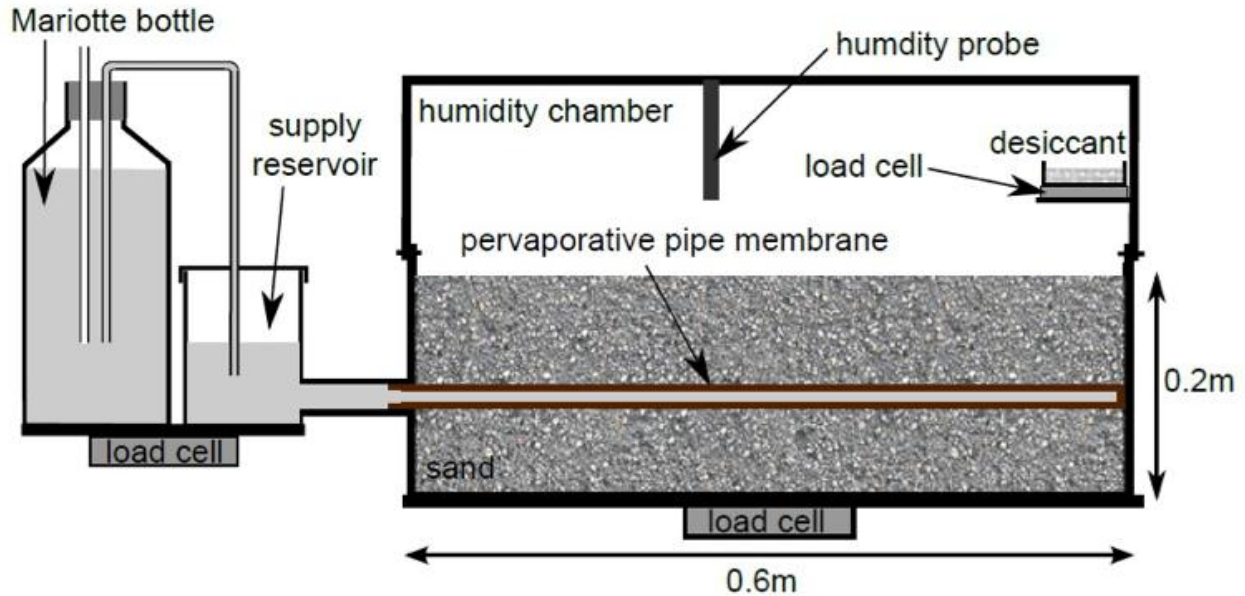
Figure 1. Experimental set-up for the bench-scale pervaporation irrigation tests (soil box).

RESULTS AND DISCUSSION

The permeate flux rate as a function of time for the tubular pervaporation membrane treating the CBM produced water is reported in **Fig. 4**. During these tests the feed reservoir was maintained at a constant level by refilling it with fresh CBM produced water. This was done to maintain a constant hydraulic head for the buried pervaporation tubing. As a consequence of this the CBM produced water became concentrated in the pervaporation tubing over time (i.e., the TDS/conductivity concentration in the pervaporation tubing increased over time). From **Fig. 4** there is an initial drop in the permeate flux rate before it reaches a relatively stable value of approximately 5×10^{-4} m^3 m^{-2} day^{-1}. This initial drop is attributed to the polymer swelling following the introduction of water into the system. A steady-state condition is reached in less than one day. The conductivity of the water within the pervaporation tube is reported in **Fig. 5** as a function of time. As shown in **Fig. 5** the conductivity of the feed water has increased by nearly 300% as a result of salts and minerals being retained by the pervaporation membrane. Interestingly, despite the increase in the feed water conductivity, and the corresponding increase in the osmotic pressure of the feed water, the permeate flux rate remained relatively constant (**Fig. 4**).
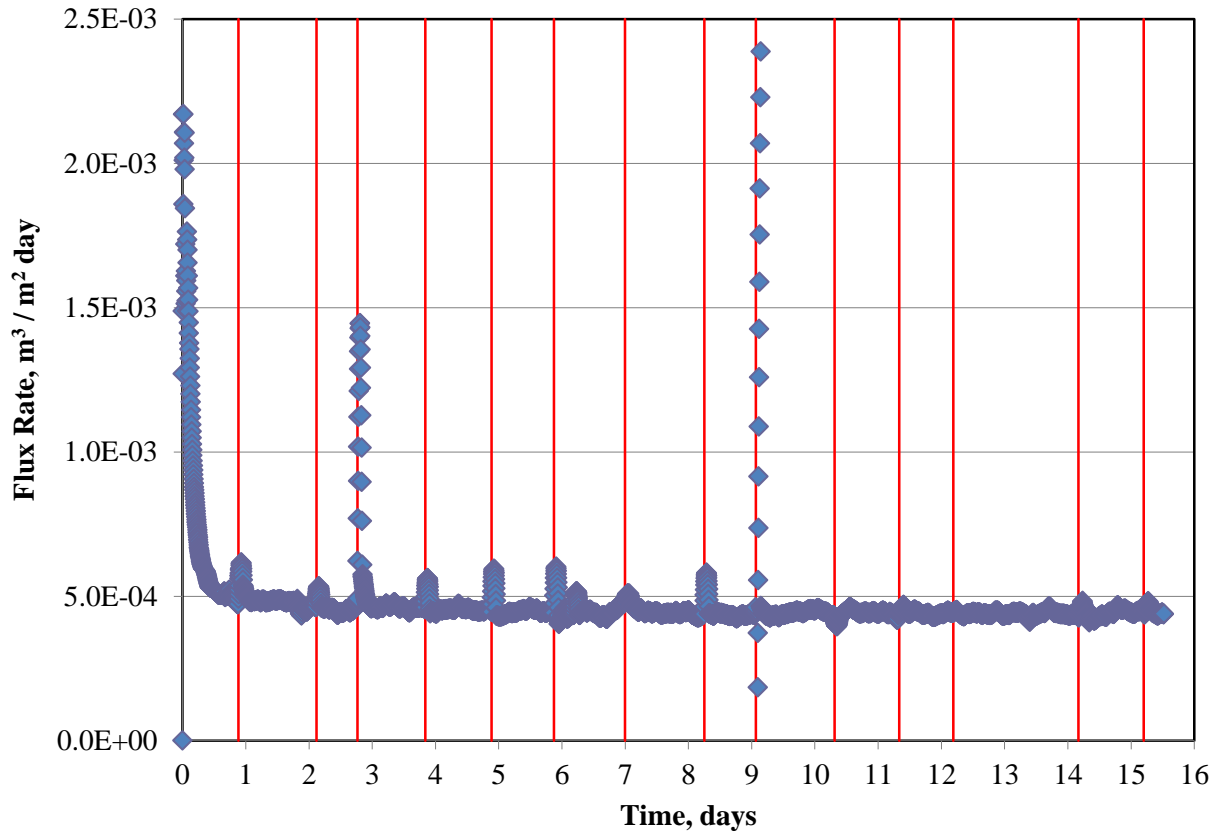
Figure 4. Permeate flux rate for the pervaporation membrane process using CBM produced water as a feed source (T = 30°C, pH$_{initial}$ = 8.55, Starting Feed Conductivity = 2.11 mS/cm). The red lines correspond to when the feed reservoir was refilled in order to maintain a consistent head of 1 ft of water in the pervaporation tube.
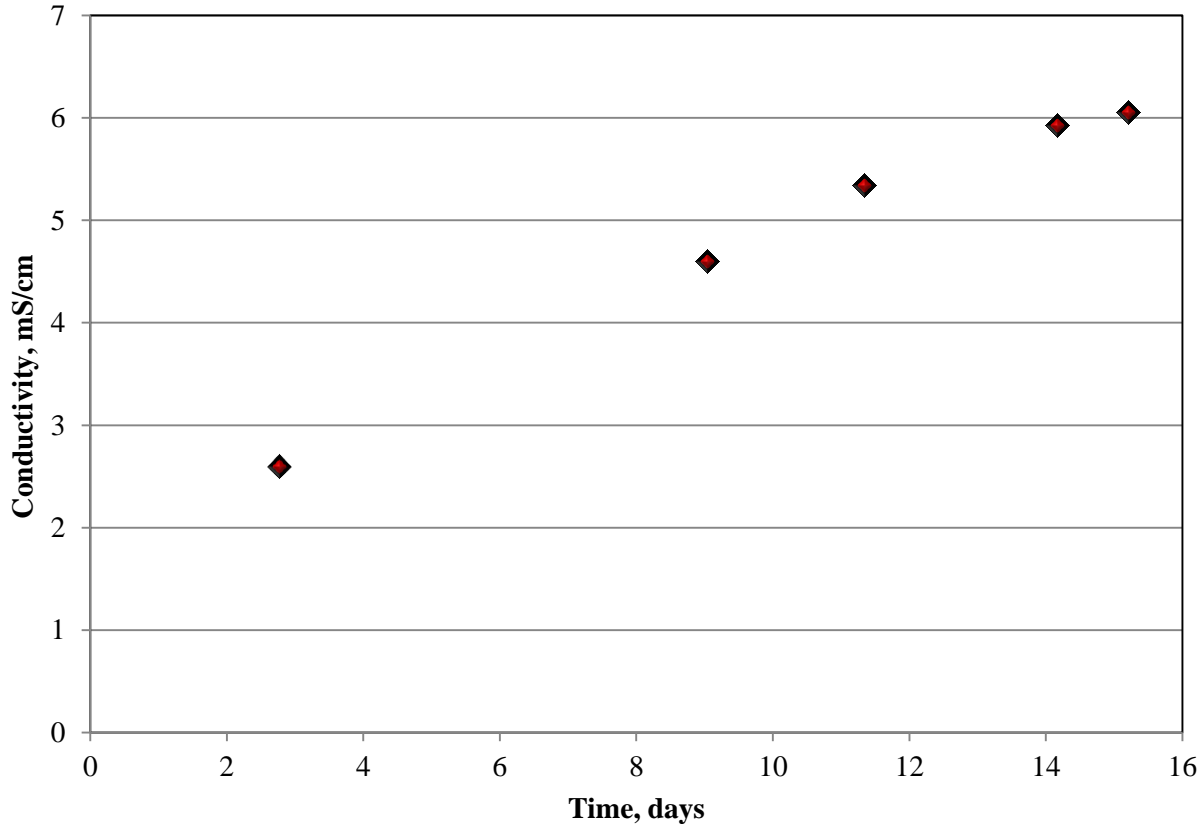
Figure 5. Conductivity of the produced water within the pervaporation tube as a function of time. The initial conductivity of the produced water ($t = 0$ days) was 2.11 mS/cm. Water samples were collected over the duration of the soil box experiment reported in Fig. 4.

An additional soil box experiment was carried out to assess the performance of the pervaporation irrigation process as the feed water becomes concentrated over time. Results from these experiments speak to the recovery rate that may be achieved using the pervaporation irrigation process. The source water used in these tests was made to have a similar composition to the CBM produced water, but only more concentrated. The starting TDS and conductivity for the pervaporation feed water for these tests were 4,284 mg L^{-1} and 4.064 mS cm^{-1}, respectively. The permeate flux rate as a function of time for this second series of tests are reported in **Fig. 6**, while the conductivity of the water within the pervaporation tubing over time is reported in **Fig. 7**. It is important to point out that these tests were carried out at 24°C instead of 30°C, which was the temperature used in the first series of tests. The lower flux rate that was measured during the second series of tests (3.56×10^{-4} m^3 m^{-2} day^{-1}) was attributed to the reduction in temperature, which reduces the vapor pressure difference between the inside and outside of the pervaporation membrane. Note, however that the flux values are still of the same order of magnitude. Inspection of **Figs. 6 and 7** finds that despite the initial and continued increase in TDS concentration within the pervaporation irrigation tube there was no noticeable decrease in permeate flux rate. In other words, after a recovery of approximately 50 percent (starting value relative to the CBM produced water) the performance of the pervaporation irrigation process was unaffected.
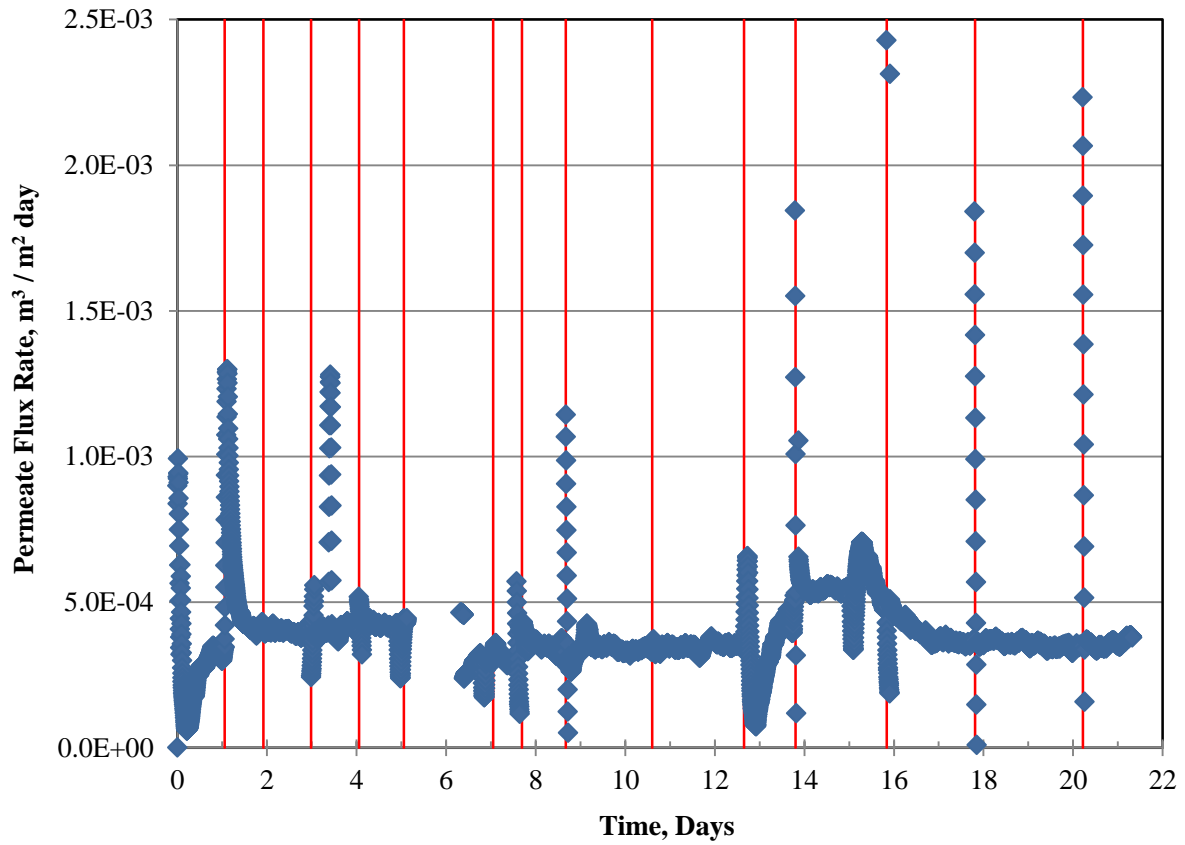
Figure 6. Permeate flux rate for the pervaporation membrane process using a concentrated salt solution as a feed source whose composition approximated that of the CBM produced water (T = 24°C, $pH_{initial}$ = 8.43, Starting Feed Conductivity = 4.06 mS/cm). The red lines correspond to when the feed reservoir was refilled in order to maintain a consistent head of 1 ft of water in the pervaporation tube.
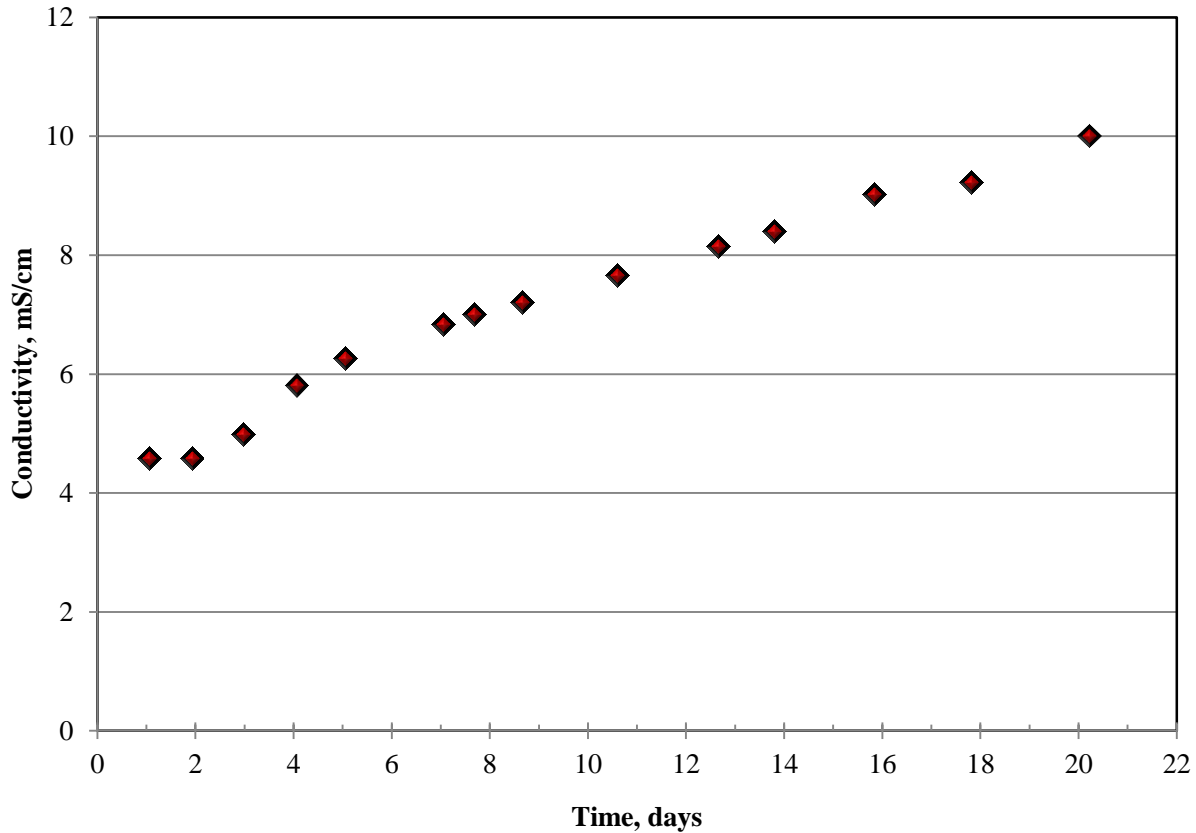
Figure 7. Conductivity of the synthetic produced water within the pervaporation tube as a function of time. The initial conductivity of the produced water ($t = 0$ days) was 4.06 mS/cm. Water samples were collected over the duration of the soil box experiment reported in Fig. 6.

CONCLUSIONS

Based on the preliminary data collected thus far for the pervaporation irrigation membrane process we can draw the following conclusions:

- The permeate flux rate for the pervaporation membrane process is little affected by the feed water TDS concentration. Constant permeate flux rates on the order of 5×10^{-4} m^3 m^{-2} day^{-1} were achieved regardless of the TDS concentration for the produced water.

- Permeate flux rate for the pervaporation irrigation process is affected by vapor pressure differences between the inside and outside of the pervaporation tubing, which is a direct function of temperature.

- Ion rejection efficiencies of ≥ 99 percent were measured for the pervaporation irrigation process (data not shown) up to a feed TDS concentration of 150,000 mg/L.

- Pervapopration irrigation is a viable treatment technology for CBM produced waters and other saline source waters.

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