CHAPTER 25

Treatment of high salinity waste water from shale gas exploitation by forward osmosis processes

Xue-Mei Li[a], Gang Chen[a], Hokyong Shon[b], Tao He[a]

[a]Laboratory for Membrane Materials and Separation Technology, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

[b]Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), Level 5 (503), Building 2, City campus, Broadway NSW 2007, Australia

1 Introduction

Hydraulic fracturing has been a key technology in producing shale gases an affordable addition to the United States' energy supply. Hydraulic fracturing is a rather water intensive process which requires 2 million to 5 million gallons of water for a horizontal shale gas well depending on the basin and formation characteristics (Ground Water Protection Council, 2009). After fracturing, the hydraulic fluid begins to flow back through the well casing to the well head. This produced water contains various dissolved constituents and organic matters. Its treatment and recycling has drawn wide attention because of its health, environmental and ecological impacts. Because of the complexity in composition, high TDS, limited footprint and cost issues, new water treatment technologies that can recycle the water as fracturing make-up water, or irrigation water, and in some cases pure process water.

Forward osmosis is an osmotically driven membrane process, where a chemical potential difference acts as the driving force for transferring of water across the membrane from a dilute feed solution to a concentrated draw solution (Cath et al. 2006). The semipermeable FO membrane can block the transfer of a broad range of contaminants including organic matter, dissolved solids, and suspended solids with potential applications in treatment of domestic and industrial wastewater, concentration of beverages and pharmaceutics, and controlled drug release. The most significant characteristics of FO are low energy input, low fouling propensity, high water recovery rate, and highly tolerance to high salinity water streams. FO could potentially provide a new perspective to the disposal of the special wastewater containing high total dissolved solids (TDS).

In this chapter, a review on the state-of-the-art of the treatment of shale gas produced water with the focus on the treatment of shale gas flow-back water (SGW) by forward osmosis. A brief introduction of origin and chemical/physical characteristics of the SGW are given, and the advantages and limitations of potential treatments methods are analyzed. The process parameters, selection of membrane and draw solutions were summarized. Finally, the potential of utilization of FO process for the treatment of SGW in a large scale are discussed.

2 Water management in shale gas exploitation

2.1 Generation, health and environmental impacts

Shale gas is an important unconventional natural resource for the energy thirsty, and its exploitation activities has been increasing. Based on the US EIA data in 2011, the reservation of the shale gas in US was about 2.44 x104 BM^3 and that in China is 3.6 x104 BM^3 (He et al. 2012). As shown in Figure 25.1, the projection of the shale gas productivity in US will be 280 Billion cubic meter by 2015 in America and to 100 Billion cubic by 2020 in China. Between 2003 to 2010, there has been a quick and steady growth of the shale gas output in USA. Based on this fact, it is expected that the shale gas production in China follows a even more drastic increase in coming 10 years.

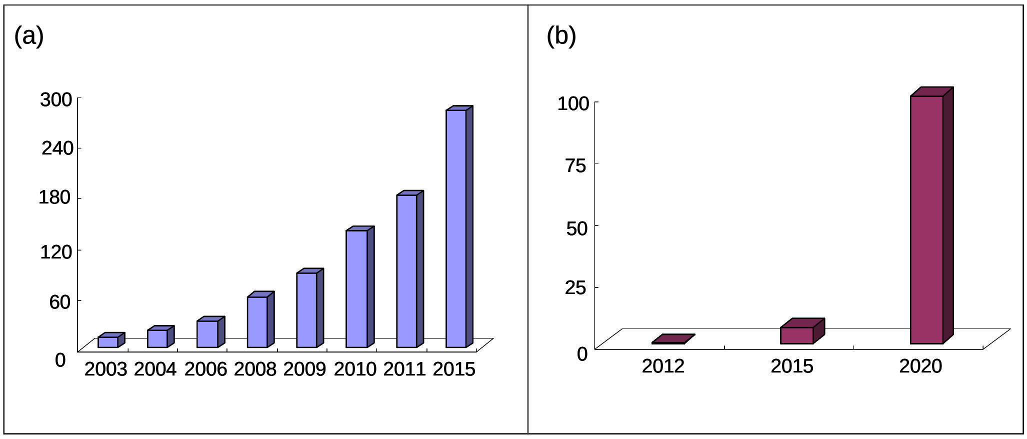

Figure 25.1: Shale gas productivity in USA (a) and China (b) (in Billion cubic meters)

The shale gas resources in many areas had been overlooked because the production economical feasibility was not attractive enough until the development of combination of sequenced hydraulic fracture treatments and horizontal well completions for shale gas drilling. During the hydraulic fracturing process, a fracturing fluid under high pressure is pumped into a shale formation to generate fractures or cracks in the shale layer. The natural gas flows out of the shale to the well. Water and sand make up over 98% of the fracture fluid, with the rest consisting of various chemical additives that improve the effectiveness of the fracturing process as seen in Figure 25.2. Figure 25.2 shows the main compositions of the fracturing fluid, which consists of 90.60% water and about 9% sand and other additives. The additives include biocides (sodium hypochlorite or sodium hydroxide), corrosion inhibitors, scavengers, friction reducers, surfactants, etc. The exact chemical components are the secret of the oil/gas service companies, thus not known in public. The amount of water needed to drill and fracture a horizontal shale gas well generally ranges from about 2 million to 5 million gallons of fresh water, depending on the basin and formation characteristics (Colorado School of Mines. 2009).

After a hydraulic fracture treatment and relief of the pumping pressure from the well, the water-based fracturing fluid, mixed with any natural underground water, begins to flow back through the well casing to the wellhead. The time for recovering the majority of fracturing fluid ranges from several hours to a couple of weeks. In various basins and shale gas plays, the volume of produced water may accounts for 15-40% of the original fracture fluid volume. In some cases, flowback of fracturing fluid in produced water can continue for several months after gas production has begun. If not directly treated, the flow back water is stored in a man-made pond before further treatment or tankering. Figure 25.3 shows a typical site for shale gas mining in a remote area in the northwest China. Next to the crane, shale gas flowback water and domestic wastewater were temporarily stored in separate ponds. Both streams are of different characteristics and remains yet untreated.

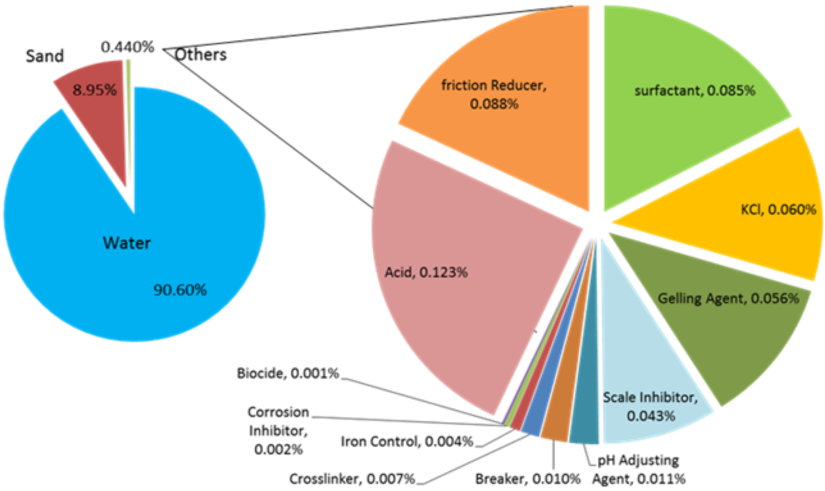

Figure 25.2: Compositions of the fracturing fluid, consisting of 90.60% water and about 9% sand and other additives. The additives include biocides (sodium hypochlorite or sodium hydroxide), corrosion inhibitors, scavengers, friction reducers, surfactants, etc.

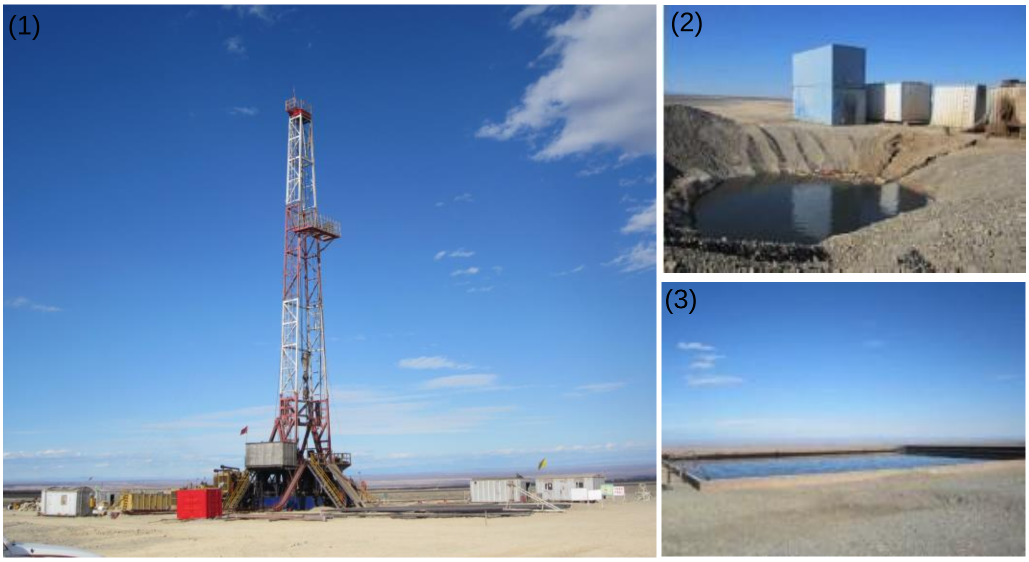

Figure 25.3: Photos of one typical shale gas exploitation site in west China. (1) Shale gas exploitation well pad; (2) domestic wastewater; (3) wastewater storage.

The SGW contain various dissolved constituents. Initial produced water can vary from fresh (TDS <5,000 mg/L) to varying degrees of salinity (TDS from 5,000 mg/L to 100,000 mg/L or higher). The dissolved constituents are naturally occurring compounds and vary from one shale site to the other.

Table 25.1 listed the constituents of produced water in a Shale play in Marcellus Shale and the southwest China. The composition varies significantly as compared to the composition of produced water from Marcellus Shale drilling. The TDS in the wastewater changes with time as well. Initial TDS of 38500-238000 mg/L was found in the produced water from wells drilled in Marcellus Shale at 5 days post hydraulic fracturing and was in the range of 3010-261000 mg/L at 14 days of post drilling. This high TDS makes the treatment of such produced water a great challenge. In the case of south west China, the saline content appears to be much lower than that in the US. The difference is a strong reflection of the geological variation from region to region.

It is a common concern to the public that the flowback water from shale gas drilling is a major environmental issue. Compatibility of the land use is the first concern. Contamination of the surface water and ground water as well as the release of toxic pollutants are critical to the environment. Most of the shale gas sites, particularly in southwest China, are densely inhabited farming fields. Although no specific regulations yet for the shale gas, the discharge of industrial wastewater guidelines are restricted as well. Therefore, a post-treatment of the flowback and produced water from shale gas exploitation is of crucial for the sustainable development of the oil and gas industry.

Table 25.1: Chemical constituents in produced water from Marcellus shale play and Southern China.

Chemical constituent or surrogate parameter	Unit	Marcellus Shale at 5 days post hydraulic fracturing	Typical flowback water from southwest China (initial stage)
TSS	mg/L	10.8-3220	-
Turbidity	NTU	2.3-1540	630-640
TDS	mg/L	38500-238000	6706
Specific Conductance	umhos/cm	79500-470000	-
TOC	mg/L	37-388	-
Conductivity	µS/cm	-	11300
DOC	mg/L	30.7-501	-
COD	mg/L	195-17700	259
BOD	mg/L	37.1-1950	-
Alkalinity	mg/L	48.8-327	-
Acidity	mg/L	<5-447	
pH	-	-	7.5
Hardness (as $CaCO_3$)	mg/L	5100-55000	277
TKN	mg/L as N	38-204	
NH3-N	mg/L as N	29.4-199	
NO3-N	mg/L as N	<0.1-1.2	
Chloride	mg/L	26400-148000	4033
Bromide	mg/L	185-1190	<1.0
Sodium	mg/L	0700-65100	2072
Sulfate	mg/L	2.4-106	2.3
Oil and Grease	mg/L	4.6-655	-
Barium	mg/L	21.4-13900	N.D
Strontium	mg/L	345-4830	5.0
Lead	mg/L	Non-detect-0.606	N.D.
Calcium as Ca	mg/L	-	128
Iron	mg/L	21.4-180	<1.0
Manganese	mg/L	0.88-7.04	N.D.
Boron as B	mg/L	-	16.5
Silica as Si	mg/L	-	19.6

2.2 Water management in shale gas exploitation

The potential targets for the treatment of the SGW are listed as follows:

(1) brine volume reduction with the possibility for reuse to future fracturing purpose

(2) removal of the organic polymeric additives

(3) oil and grease control

(4) removal of suspended solids

(5) microbial control

(6) soluble organics

Management of the shale gas wastewater depends on multidimensional criteria, e.g. the local regulation, site conditions, produced water quality and the most important issue, economic feasibility. Approaches used for the treatment of high salinity waste water include (1) deep well injection; (2) transport and centralized treatment; (3) treatment and disposal (4) reuse. Selection of different approaches is not a pure technical choice. However, it is a common paradigm that deep well injection and treatment and disposal is one of the first choices. centralized treatment is a high cost and last choice if an economical reuse alternative exists. The main targets of the reuse include reduce of total suspended solids (TSS), oil and grease, hydrocarbons, hardness, iron, boron etc.

For the removal of the TDS, evaporation, distillation and reverse osmosis are the main candidates. Although the water quality is of the highest level, cost per cubic of wastewater becomes most important. Membrane based process such as reverse osmosis, nanofiltration, membrane distillation, and forward osmosis. However, injection eliminates water permanently from water cycle and at some areas this is critical environmental issue. Some processes are highly energy intensive and may require intensive pretreatment, leading to rather high OPEX due to the membrane replacement. Nevertheless, membrane-based process has seen promising due to the advantages in simple/automatic operation, small foot-print and high efficiency, etc. Table 25.2 lists the several typical membrane technologies which show potential applications in the shale gas wastewater treatment. A summary of the advantages and disadvantages for the present treatment technologies for the shale gas flowback water is listed in Table 25.2.

For nanofiltration, reverse osmosis and membrane distillation, a pre-treatment facilities to remove completely or partially the inorganic or organic contaminants are necessary as listed in Table 25.3. Usually, membrane fouling is primarily caused by organics such as humic acid and alginate (Kim and Dempsey 2013; Resosudarmo et al., 2013; Ghouas et al., 2012; Peter-Varbanets et al., 2011; Sioutopoulos et al., 2010; Zazouli et al., 2010), which can reduce the efficiency of salt removal. Consequently, pre-treatment is often compulsory to control water chemistry and reduce fouling. For TDS concentrations of up to 20,000 mg/L, RO is the preferred method. membrane distillation is used for waters with TDS concentrations of 40,000-100,000 mg/L. FO technology was widely reported in treatment of brackish water and brine (Tang and Ng 2008; Zhao and Zou 2011; Li et al. 2013).

FO systems do not need external hydraulic pressure as the driving force. it has a high rejection rate of contaminates, and more importantly a lower propensity for membrane fouling, comparing to pressure driven osmotic processes (Cath and Bamaga 2011). In case the draw solution is directly reusable without any further post-treatment, the forward osmosis is essentially working at low energy consumption. Success in the utilization of forward osmosis technology has been reported in literatures (Hickenbottom et al., 2013). A summary of the technical assessment of the several membrane technologies are listed in Table 25.4. Forward osmosis was a low energy and simple process for the reuse of the shale gas flowback water. Therefore, the following section will mainly focus on the application of forward osmosis for the reuse of the shale gas wastewater.

Table 25.2: Summary of advantages and challenges of the present treatment technologies for the shale gas flow back water.

	Advantages	Challenges
Deep well injection	Low cost: \$1.5-2/Bbl; well established and accepted for public	limited deep injection well/capacity; transportation may be costly
Thermal distillation	Pure water obtained, reusable for industry and irrigation or for discharge	Bulky and complicated system, high cost alternative
Evaporation/crystallization	No extra energy input, water reusable; cheap choice	Large footprint, possible for limited area
Reverse osmosis	Relatively pure water permeate; mature technology,	system cost high, limited salinity< 3.5%; high energy cost
Electrodialysis	Mature technology, high water recovery rate; suitable for water with high SDI, TOC; removal of heavy metals, cyanide, chloride, less fouling, scaling and chemical addition	Limit is TDS <15000 ppm; pre-treatment required; no removal of bacteria, colloidal matters, boron, silica etc
Capacitive Deionization (CDI)	Minimum pre-treatment, low fouling scaling, low operating voltages/pressures	Low adsorption capacity; energy loss in regeneration; suitable for TDS < 1500 mg/L
Ion exchange	High water recovery	Limit for low salinity water; generation of waste; chemical usage for regeneration; cost
Membrane distillation	Very high permeate water quality; less chemical interaction between membranes and solutions; no hydraulic pressure needed	Heat sources needed; high cost in energy; membrane wetting; technology not yet mature; limited membrane supplier
Forward osmosis	Tolerable to High salinity; Low energy consumption, very good quality permeated water; reusable for fracturing job	Suitable draw solute, limited membrane supplier; immature technology

194 **Table 25.3**: Summary of technical assessment of membrane-based technologies

Criteria	Membrane-based technologies			
	NF	RO	MD	FO
TDS of feed water	500-25,000 mg/L	1000-35000 mg/L	40,000-100,000 mg/L	>35,000 mg/L
Product water quality	High rejection (>99%) of larger divalent ions and metals with moderate rejection (<90%) of monovalent is expected.	94% rejection of TDS	Equal to distilled water	The product of FO is a diluted draw solution. To obtain pure water from the process a secondary system is required to exact pure water from the draw solution, and to re-concentrate the draw solution.
Recovery	75-90%	>90%	60-90%	>96%
Energy use	Approximately 2 kWh/kgal of energy is required to power the system’s high-pressure pumps	No data is currently available	Require some energy input	Just need power to circulate solution across FO membrane.
Chemical use	Use of NaOH, Na_4EDTA, HCl, $Na_2S_2O_4$, or H_2O_2 for cleaning.	Use of NaOH, Na_4EDTA, HCl, $Na_2S_2O_4$, or H_3PO_4 for cleaning.	Use of NaOH, Na_4EDTA or HCl for cleaning.	Less cleaning frequency, possible to use the same chemicals as RO for the cleaning purpose
Pretreatment of feed water	Require pretreatment to mitigate harmful water quality constituents.	Require pretreatment to mitigate harmful water quality constituents.	Removal of constituents that may wet the hydrophobic, microporous pores of the MD membranes is required	Prefilter is required to remove large debris; antiscalant may be required for high recovery operation.
Post-treatment of product water	Product water may require remineralization	Product water may require pH stabilization or remineralization	Product water may require remineralization and pH stabilization	diluted draw solution requires further separation to produces pure water and reconcentrate the draw solution for reuse.
Capital and O&M costs	Capital cost:\$0.8 to \$4/gpd;O&M cost: \$0.7.kgal	Capital cost:\$4/gpd;O&M cost: \$ 0.7 kgal	\$3.34/gpd with operating costs \$1.4/kgal for a 1 MGD DCMD plant	unknown

3 Forward osmosis for treatment of wastewater produced from Shale gas exploitation

3.1 Overview

Forward osmosis is an osmotically driven membrane process, where a chemical potential difference acts as the driving force for water transfer across the membrane of a dilute feed solution to a concentrated draw solution. The semipermeable FO membrane can block the transfer of a broad range of contaminants including organic matter, dissolved solids, and suspended solids with application potentials in treatment of domestic and industrial wastewater, concentration of beverages and pharmaceutics, and controlled drug release. The most significant characteristics of FO are no or little energy input, low fouling propensity, high water recovery rate, and highly tolerant to high salinity and TDS. FO could potentially provide a new perspective to the disposal of the special wastewater containing high concentrated TDS (McGinnis et al. 2013; Hickenbottom et al. 2013).

These inherent advantages make FO a promising candidate for wastewater treatment. Consequently, studies were performed to examine the effectiveness of FO in the treatments of high salinity wastewater produced from shale gas exploitation.

3.2 Membranes

Hydration Technologies Inc. (HTI) has commercialized their CTA membranes for application in an FO process. The HTI FO membranes made of cellulose triacetate (CTA) supported by embedded polyester webs were widely reported in desalination of brackish water (Zhao et al. 2012; Zhao and Zou 2011; Phuntsho et al. 2013) and seawater (Yangali-Quintanilla et al. 2011; Li et al. 2012; Boo et al. 2013). Few investigations were for disposal of high saline wastewater generated from Shale gas exploitation (Hickenbottom et al. 2013). In addition, thin-film composite (TFC) FO membranes were also used in desalination of high salinity wastewater derived from shale exploitation (McGinnis et al. 2013). Characteristics of different FO membranes used in shale gas exploitation wastewater treatment are summarized in Table 25.4. TFC membranes appear to show higher water flux than CTA membranes.

Table 25.4: Summary of cellulose triacetate and polyamide TFC FO membrane mass transfer for the membrane used in treatment of wastewater from shale gas exploitation

	HTI	CTA[a]	TFC[a]	TFC[b]
Water Permeability A ($L/m^2.hr.bar$)	0.79±0.07	0. 97±0.1	3.5	N.A.
Rejection (%)	89.06±0.03	0.91	95	N.A.
B value (10^{-7} m/s)	2.69	3.25	3.16	1.76±0.22
S value (10^{-4} m)	4.12	8.3	7.96	2.66±0.46
Jw ($L/m^2.h$)	8.7	6.7	12	N.A.
Js/Jw (g/L)	1.17	1.04	0.3	N.A.

[a] Cellulose triacetate and thin-film composite fabricated by our lab (He et al. 2012)
[b] Product developed by Oasys (McGinnis et al. 2013).

3.3 *Draw solution*

Draw solutions, composing a draw solute and water, provide the driving force for the water to transfer across the membrane. Draw solution is a key component for a successful FO application. In general, an ideal draw solute should have a series of characters: (1) high solubility in water; (2) high osmotic pressure upon dissolution; (3) no reaction to the membrane; (4) highly rejected by the membrane; (5) nontoxic; (6) low cost. It is even more desirable that the draw solutes can be recovered in an energy efficient process (Achilli et al. 2010). Various chemicals have been tested and compared as draw solutes, such as NaCl, $MgCl_2$, and Na_2SO_4, even fertilizers (Phuntsho et al. 2011). For SGW treatment, the general selecting rules hold, but special focus should be paid on high rejection, high osmotic pressure, scaling and cost.

Hickenbottom et al (Hickenbottom et al. 2013) employed sodium chloride solution (NaCl, 4.5mol/L) as draw solution in FO process for concentration of drilling mud and fracturing wastewater from oil and gas operations. Moreover, McGinnis et al (McGinnis et al. 2013) used ammonium bicarbonate (NH_4HCO_3) as draw solution in desalination of high salinity (>70,000 ppm TDS) produced waters from shale gas exploration in order to produce clear water. This product water generated in the process was found to meet surface water discharge quality criteria (<500 mg/L TDS, <250 mg/L chlorides, <10 mg/L barium, <10 mg/L strontium) for the Site of Pennsylvania. However, ammonium bicarbonate is alkaline in nature, may deteriorate membrane.

Sodium chloride, magnesium chloride ($MgCl_2$) and disodium ethylenediaminetetraacetate (EDTA) were compared as draw solutes in concentration of shale gas wastewater (SGW) using different FO membranes (HTI, CTA and TFC) (He et al. 2012). CTA and TFC FO membranes were tailor-made (Li, G. et al. 2013). Both in AL-DS and AL-FS test mode (Figure 25.4), TFC FO membrane showed better performance in the process of SGW concentration than that of HTI and CTA FO membranes using sodium chloride draw solution (3.26 mol/L).

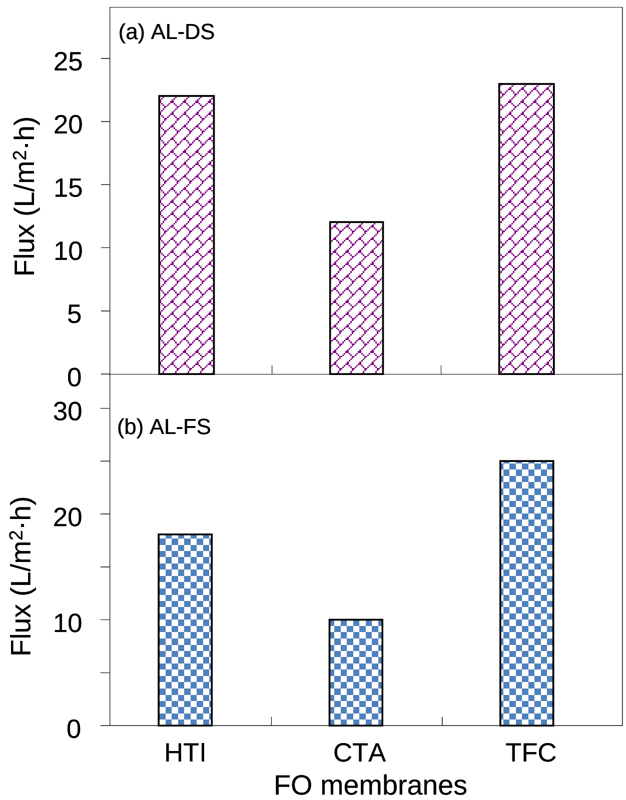

Figure 25.4: Water fluxes of three different FO membranes used in SG wastewater treatment by FO process. (3.26M NaCl as the draw solution and SG waste water as the feed, (a) AL-DS mode; (b) AL-FS mode)

However, when $MgCl_2$ draw solution (1.74 mol/L) was used, the FO fluxes of three different FO membranes differed quite much in the order of $J_{w\text{-}TFC} > J_{w\text{-}HTI} > J_{w\text{-}CTA}$ in the AL-DS mode and $J_{w\text{-}HTI} > J_{w\text{-}CTA} > J_{w\text{-}TFC}$ in AL-FS mode (Figure 25.5).

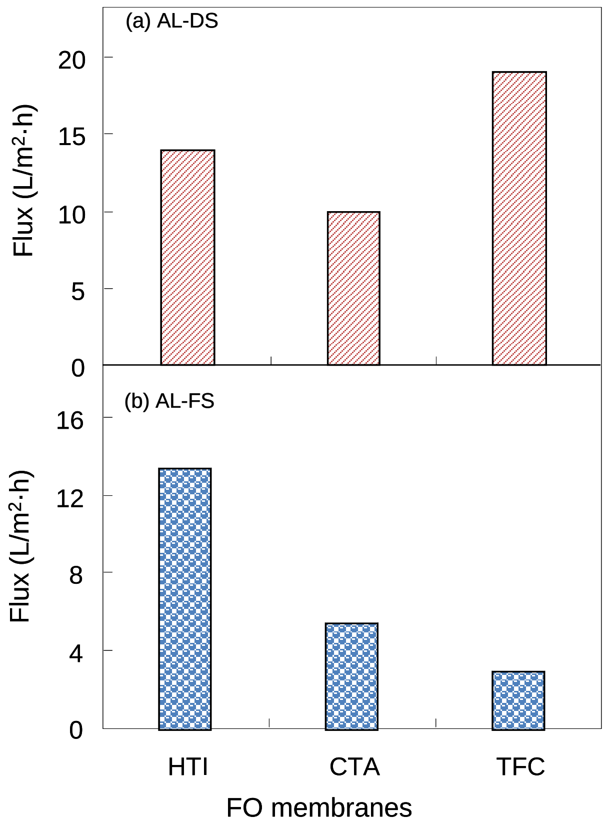

Figure 25.5: The water fluxes of three different membranes used in SG wastewater treatment by FO process. (1.74M $MgCl_2$ as the draw solution and SG waste water as the feed, (a) Water flux under AL-DS mode; (b) Water flux under AL-FS mode)

In AL-DS mode, using EDTA (1 mol/L) as draw solution, the flux of TFC FO membrane was similar to that of HTI, which was obviously higher than that of CTA FO membrane. In contrast, the TFC FO membrane showed higher flux than that of HTI and CTA FO membrane in AL-DS mode (Figure 25.6).

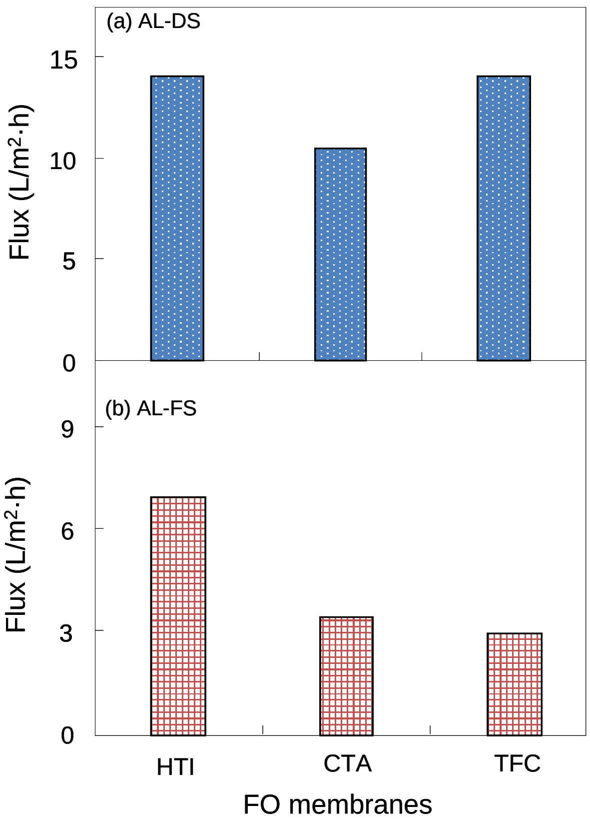

Figure 25.6: The water fluxes of three different membranes used in SG wastewater treatment by FO process. (1M EDTA as the draw solution and SG waste water as the feed, (a) Water flux under AL-DS mode; (b) Water flux under AL-FS mode)

Difference in the FO flux between AL-DS and AL-FS mode is mainly caused by the internal concentration polarization (ICP). In case of AL-FS mode, the draw solute diffusivity mainly determines the extent of ICP. Overall, in terms of economy and efficiency, NaCl still appears to be the best choice as the draw solute. Moreover, the recycling of NaCl in an energy efficient manner remained a great challenge. Recently, temperature and pH sensitive draw solutes have received much attention. Temperature sensitive hydrogels have been published (Li, D. et al 2011), but their application in shale gas produced water treatment still needs further confirmation.

3.4 Operating conditions

3.4.1 Feed and draw solution temperatures

Several studies have investigated the effect of temperature on water flux and salts permeation (You et al. 2012; Phuntsho et al. 2012; Zhao and Zou 2011) in the FO process. Generally, it was concluded that water flux and salt permeation increased with increasing temperature in the FO process (McCutcheon and Elimelech 2006; Nayak and Rastogi 2010; Phuntsho et al. 2012; Zhao and Zou 2011). Recent studies have also focused on the impact of the temperature difference between the feed and draw solutions on water and draw solute permeation across FO membranes. Phuntsho et al. (Phuntsho et al. 2012) examined the water flux change with feed and draw solutions of different temperature and found that water flux increased significantly by increasing draw solution temperature. You et al. (You et al. 2012) proposed that the heat flux generated by the temperature difference between the feed and draw solutions could enhance the water flux due to the decrease in feed solution viscosity and the increase in water diffusivity.

Nevertheless, so far, no attention is paid to the effect of temperature on the water flux in concentration of waste stream from shale gas exploitation, which is a significant aspect to the application of the FO process in high saline wastewater reclamation. Recently, in the authors' laboratory, it was demonstrated that concentration flux of shale gas wastewater tested in AL-FS mode (Figure 25.7) increased dramatically as the system temperature increased from 15 to 45°C. In AL-FS mode, the exponential increase in the diffusivity against the temperature may effectively decrease in the ICP, resulting in high FO flux. This result indicates that concentration water flux of high saline wastewaters in AL-FS model can be improved through increasing system temperature of the FO process.

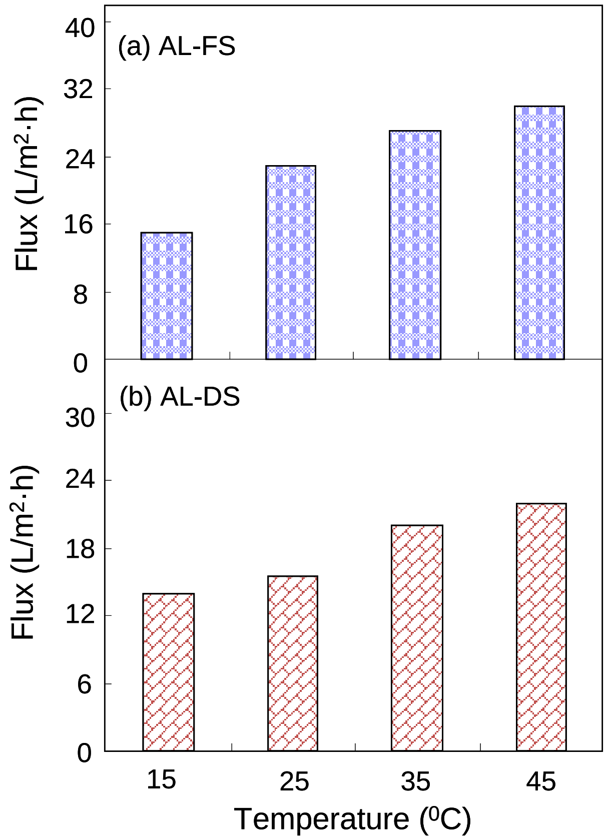

Figure 25.7: effect of temperature on concentration of shale gas wastewater using the HTI CTA membrane. Draw solution: 20wt% KCl; Feed solution: shale gas wastewater; (a) AL-FS, (b) AL-DS.

3.4.2 **Flow velocity**

The flow velocity affects the hydraulic status of the FO system, which is very important for the determination of the scale of the FO plant as well as the cost. Recently, He (He 2013) reported the effect of the flow rate on the FO flux in concentrating shale gas wastewater in the AL-FS mode (Figure 25.8). It was found that the FO flux did not change with the flow velocity, but in AL-DS mode, an obvious increase of FO flux was observed. This phenomenon is most probably ascribed to the internal concentration polarization in the AL-FS mode where the porous support layer is facing the DS. Moreover, the flux in AL-FS mode was higher than that in AL-DS mode. Literature has shown that AL-FS mode has shown much steady performance than in the AL-DS mode for feed solutions of complicated compositions especially those tend to foul the membranes, thus, for shale gas produced water treatment, the AL-FS mode should be the primary choice.

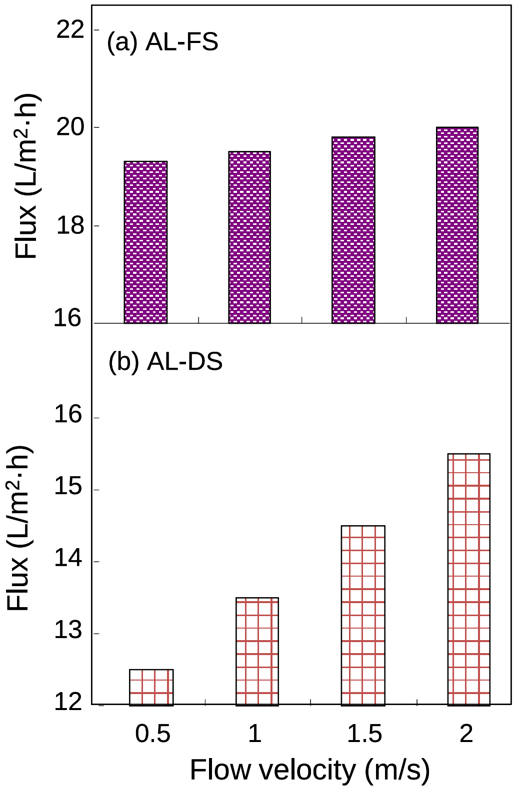

Figure 25.8: Relationship between the draw solution concentration and the FO flux with shale gas wastewater as the feed using HTI membranes at different flow velocity. Note:DS, 20wt% KCl; (a) AL-FS, (b)AL-DS.

3.5 Membrane fouling

The shale gas flowback water may contain various contaminants which is particularly detrimental to the FO membrane surfaces. Organic compounds, such as oil, surfactants and other particle based colloids are the main cause for the membrane fouling. Two main factors may influence the fouling in forward osmosis:

(1) Surface roughness may affect the fouling behavior; A rough top surface tends to trap micro or submicro-size pollutants, especially the particulate aggregates or foulants of potential to form a particulates, but not a smooth surface (Hashina et al. 2011). Moreover, once trapped, they are difficult to be washed away by the tangential flow. For a smooth surface, the possibility for the trapping of the particles is lower than the rough surface, thus less aggregation of the foulant to the membrane surface. It is thus probable that the HTI CTA membranes of a smooth surface is less accessible to the foulants in the SGW wastewater; However, for a rough membrane surface as TFC membranes, it is most likely to form a fouling layer during the FO process for the concentration of the SGW wastewater.

(2) The concentration of the particles in the feed solution; a large amount of particles and the aggregation of the particles can result in the instantaneous decline in the flux, for feed solutions with low concentration of particulates, there may be a

certain time duration before significant reduction in flux is visualized.

Figure 25.9 shows the schematic of the fouling mechanism of fouling in an FO process for smooth and rough surface membranes. The particles are illustrated as the foulants and are negatively charged. The negatively charged membrane surface may repulse the foulants away from approaching the surface, denoted as F_R. Other forces that may prevent the fouling include the tangential sweeping force given by the flow rate across the membrane surface, denoted as F_T. These two forces are the main factors to prevent the adherence of the foulants to the membrane surface. However, due to water diffusion in the FO process from the bulk to the membrane surface, there exists a force which pushes the foulants towards the membrane surface, denoted as F_{FO}. This is the only force which may lead to the formation of a fouling layer during the FO process as shown in Figure 25.9(A). For a smooth membrane surface as HTI CTA membranes, both F_R and F_T act as the factors to reduce the fouling formation, and the adherence of the foulants to the membrane surface driving by F_{FO} may not be strong enough, thus, swept away by the surface flow.

In case of a rough membrane surface, as seen in Figure 25.9(B), when the foulants follows the water diffusion direction approaching the FO membrane surface, they tend to be trapped by the valley-like surface structures. Beneath the layer adjacent to the membrane surface, the F_T is counter-balanced by the blocking microstructures in the membrane surfaces. Thus, foulants preferentially aggregate to the membrane surface, resulting in a cake layer. Once the membrane surface morphology is filled up with the foulants, the membrane may behave as a smooth surface again and no significant fouling is possible anymore. It is therefore theoretically preferred to have a membrane of smooth surface instead of a rough membrane surface in order to decrease the fouling tendency during the FO process for SGW treatment.

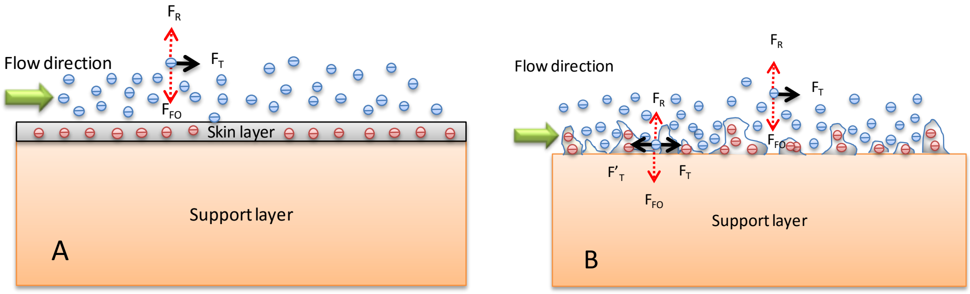

Figure 25.9: Mechanism of the deposition of the foulants on to the membrane surface; (A) smooth surface, representing an HTI membrane; (B) rough surface, representing a thin-film composite membrane. Notice that the surface charges were omitted due to the high saline concentration in the feed solution. The black arrow points to the direction for the main flow and the red dashed arrow points to the direction of water flowing to the membrane surface due to osmosis.

Similar to other FO processes, the FO performance in shale gas produced water treatment especially water flux is highly dependent on membrane orientation, operation temperature and fluid velocity. Although FO process has the capability to treat highly concentrated waste streams such as oil and gas wastewater, membrane fouling has been observed. Some foulants absorbed on FO membrane surface can be washed off through increasing flow rate. In most cases, the cleaning is performed without the use of chemicals. Several studies demonstrated successful restoration of water flux through FO membranes by increasing flow rate of membrane surface (Cath et al. 2009; Holloway et al. 2007; Sagiv et al. 2010).

4 Application cases

4.1 Osmotic dilution

Recently, Bear Creek Services and Hydration Technology Innovations (HTI) (Albany, OR) developed a new water reclamation system, Green Machine, for the deposal of oil field related wastewaters (HTI. 2010). The Green machine is a portable, modular and scalable system, as shown in Figure 25.10. It was claimed that the technology could dramatically reduce the environmentally damage and cost for tankering. The basis of this machine is osmotic dilution. In an osmotic dilution process, the draw solution is diluted by the water from the waste streams and then reused as the process liquid. It was reported that the Green machine had been operated in the Haynesville Shale exploitation play in North Louisiana and East Texas. Over 20% of the water required for hydraulic fracturing of new wells are supplied by the waste water utilizing the osmotic dilution process (Hickenbottom et al. 2013). This operation reduces significantly the fresh water demand in the hydraulic fracturing site, recycles the shale gas wastewater as well.

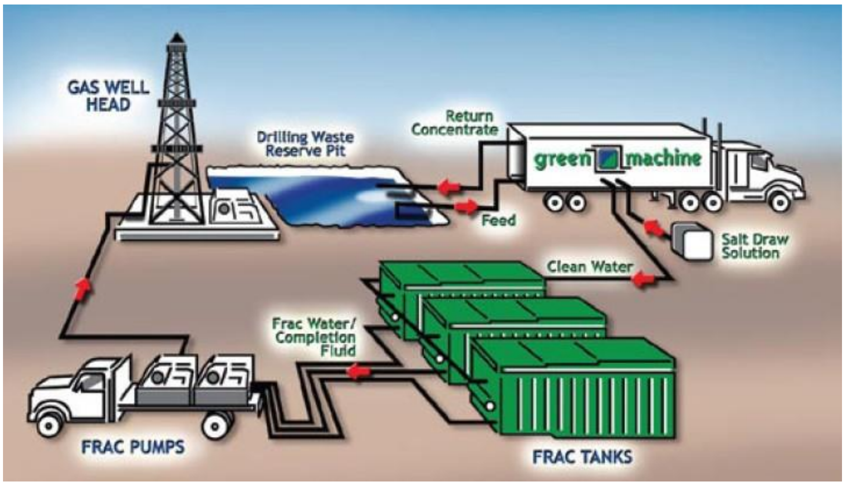

Figure 25.10: Schematic of Green machine FO process for treatment of the wastewater produced from hydraulic fracturing (HTI. 2010).

4.2 FO-Distillation Process

Although osmotic dilution can reduce the water demand in the hydraulic fracturing process, it does not generate fresh water that meets the discharge standards. Moreover, because of the operation principle, solely an individual FO membrane process can never produce water that meets discharge standards (Cath et al. 2006). To purify the flowback wastewater from shale gas wastewater, a hybrid FO-MD process was investigated by McGinnis et al (McGinnis et al. 2013). They demonstrated a pilot scale integral FO-MD concentrator (shown in Figure 25.11) to desalinate fracturing flowback and produced waters from natural gas extraction operations in the Marcellus shale region. Compared to initial concentration of wastewater with TDS of 73,000±4200 mg/L, the salt concentration of the product was 300±115 mg/L TDS that meet surface water discharge quality criteria for the State of Pennsylvania.

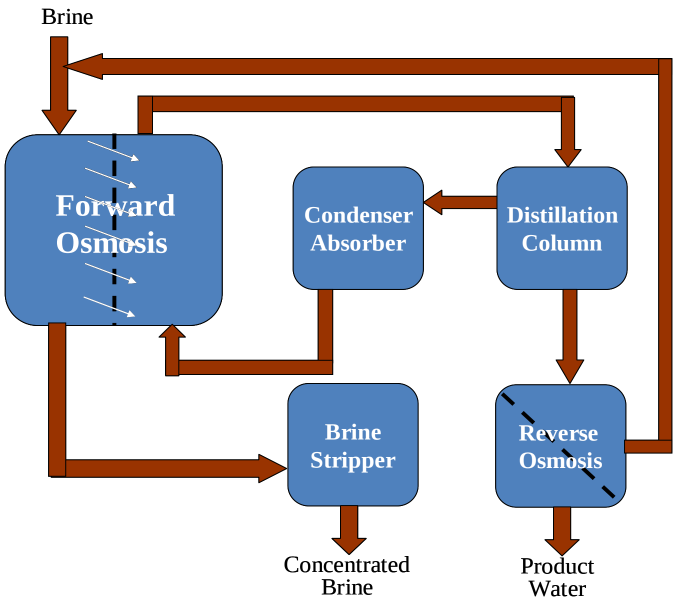

Figure 25.11: Block flow diagram of the FO membrane brine concentrator setup (McGinnis et al. 2013)

The conventional evaporation process and the FO process combined with membrane brine concentrator are shown in Figure 25.12 for energy consumption comparison. Compared with evaporative desalination methods, producing 1 kg of water product by evaporating water from a 73,000 mg/L NaCl solution to a recovery of 50% (identical to the recovery of the FO MBC pilot during specific energy testing), in a similarly configured evaporative brine concentrator (open cycle, single stage, no energy recovery) is estimated to require an energy input of approximately 633 kWth/m3 of thermal energy. This is 2.3 times the energy measured in the FO MBC pilot (275 kWth/m^3), measured in the FO MBC pilot.

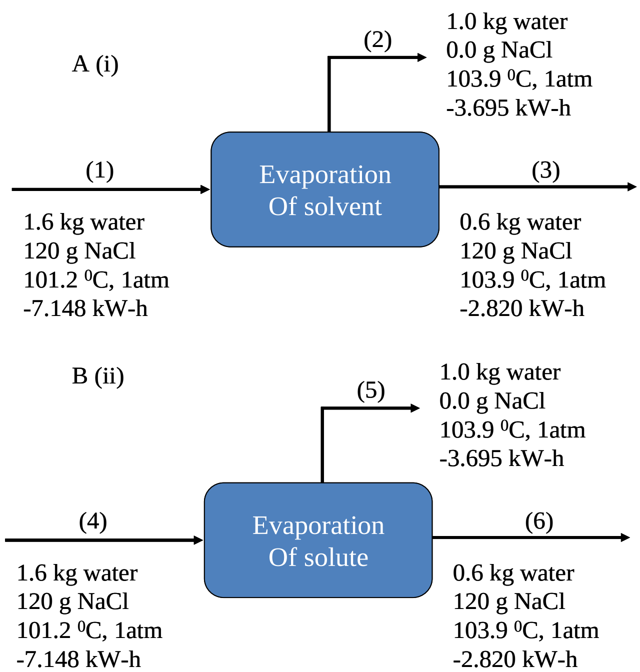

Figure 25.12: Mass and enthalpy balance diagrams based on thermophysical modeling. (A) Case (i), production of 1 kg of pure water through evaporation of the

solvent (water) from a saline source. (B) Case (ii), production of 1 kg of water through evaporation of the solute (shown here as molar flows of C and N, which are equivalent to molar flows of CO_2 and NH_3 in stream (5)) from a draw solution diluted by permeate from an FO membrane process

4.3 Forward osmosis-vacuum membrane distillation

Application of forward osmosis-vacuum membrane distillation (FO-VMD) for the reuse of the shale gas wastewater has been investigated in the authors' laboratory. A schematic of the hybrid process is shown as in Figure 25.13. HTI CTA membrane was used as the FO membrane and a KCl 20 wt% solution was used as the draw solution. The composition of the feed water was as listed in Table 25.1. Before test, the feed water was pre-treated using coagulation and ultrafiltration. The quality of the permeate water was listed in Table 25.5. In comparison to the local potable water, the permeate from the FO-VMD process contains much less ions. The conductivity of MD permeate was 5 µs/cm, which was similar to that of a deionized water.

In this hybrid process, the organic contaminants are removed by FO membranes and the MD membrane faces only the single salt solution. It is therefore probable that the fouling of the MD is significantly low. The draw solute is inorganic salt, which does not decompose upon heating, and thus cannot go through the MD membrane, which guarantees a hig product water quality.

The disadvantages of the hybrid process is the high energy consumption due to the evaporation stage in the membrane distillation. This process is most probably suitable for arid regions where water is more precious than energy. For regions where the solar power is abundant, it is possible to reduce the cost to an acceptable level.

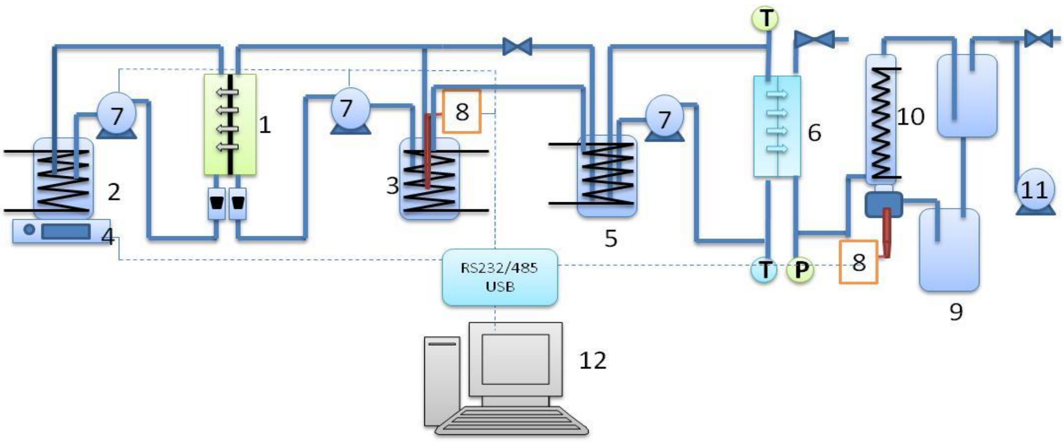

Figure 25.13: Schematic of the hybrid forward osmosis-membrane distillation hydride setup.

Table 25.5: Comparison of the water quality between the potable water and the permeation from FO-MD process treating the shale gas flowback water.

	Potable water in Shanghai	FO-MD permeate
Conductivity（µs/cm）	43.6	5.0
pH	7.88	7.38

COD_{Cr}(mg/L)	1.1	0.9
Turbidity（NTU）	0.09	0.07
K(mg/L)	3.74	0.48
Ca(mg/L)	0	0
Mg(mg/L)	0	0
Na(mg/L)	0.3	0.12
B(mg/L)	0.02	0
As(mg/L)	0	0
Sr(mg/L)	0	0
Mn	0	0

5 Conclusions

This chapter provides an overview on the application of forward osmosis as a potential technology to treat wastewater produced from shale gas exploitation. The choice of draw solution, operating conditions including membrane orientation, flow velocity are discussed. The relationship between the fouling and the membrane surface morphology was hypothetically provided: smooth top surface tends to be more preferentially antifouling in SGW application. The advantages and limitations of osmotic dilution, FO-distillation and FO-VMD hybrid processes are analyzed. Osmotic dilution remains as the least energy intensive process for the treatment of the shale gas wastewater. Hybrid processes show better permeate water quality at higher energy cost. Overall, FO processes have shown potential in the treatment of waste waters of very complicated compositions, especially the treatment of oil and gas drilling wastewater. Further development of membranes with better performance and the search for a draw solutes that can be regenerated at low cost are the future research directions.

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