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CHAPTER 25

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

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## 20 1 Introduction

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

32 Forward osmosis is an osmotically driven membrane process, where a  
33 chemical potential difference acts as the driving force for transferring of water across  
34 the membrane from a dilute feed solution to a concentrated draw solution (Cath et al.  
35 2006). The semipermeable FO membrane can block the transfer of a broad range of  
36 contaminants including organic matter, dissolved solids, and suspended solids with  
37 potential applications in treatment of domestic and industrial wastewater,  
38 concentration of beverages and pharmaceuticals, and controlled drug release. The most  
39 significant characteristics of FO are low energy input, low fouling propensity, high  
40 water recovery rate, and highly tolerance to high salinity water streams. FO could  
41 potentially provide a new perspective to the disposal of the special wastewater  
42 containing high total dissolved solids (TDS).

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

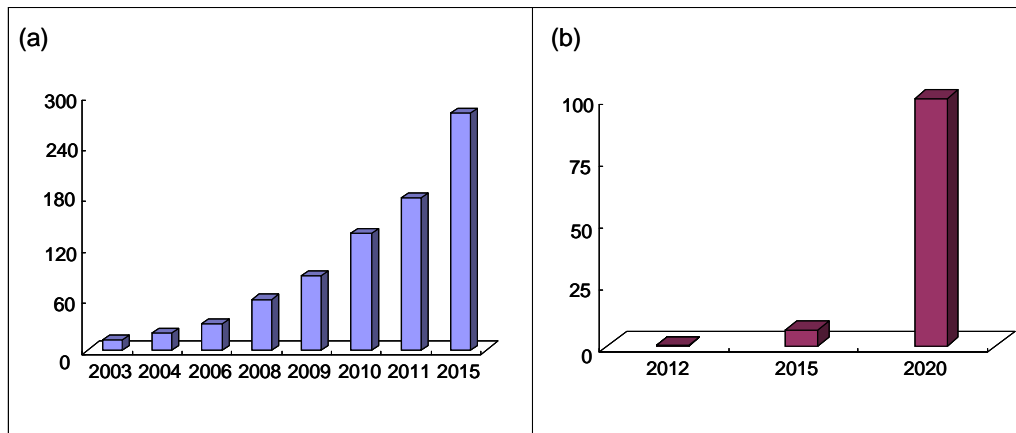
## 50 2 Water management in shale gas exploitation

### 51 2.1 *Generation, health and environmental impacts*

52 Shale gas is an important unconventional natural resource for the energy  
53 thirsty, and its exploitation activities has been increasing. Based on the US EIA data in  
54 2011, the reservation of the shale gas in US was about  $2.44 \times 10^4$  BM<sup>3</sup> and that in  
55 China is  $3.6 \times 10^4$  BM<sup>3</sup> (He et al. 2012). As shown in Figure 25.1, the projection of the  
56 shale gas productivity in US will be 280 Billion cubic meter by 2015 in America and  
57 to 100 Billion cubic by 2020 in China. Between 2003 to 2010, there has been a quick  
58 and steady growth of the shale gas output in USA. Based on this fact, it is expected  
59 that the shale gas production in China follows a even more drastic increase in coming  
60 10 years.

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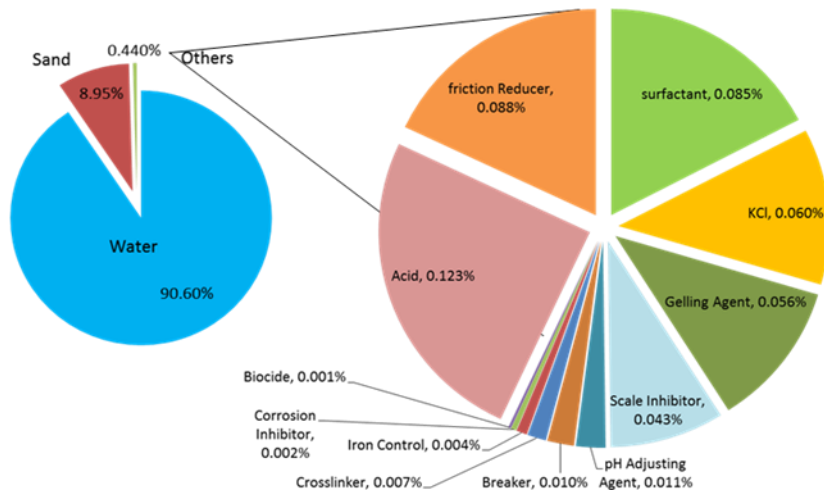
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64 **Figure 25.1:** Shale gas productivity in USA (a) and China (b) (in Billion cubic  
65 meters)

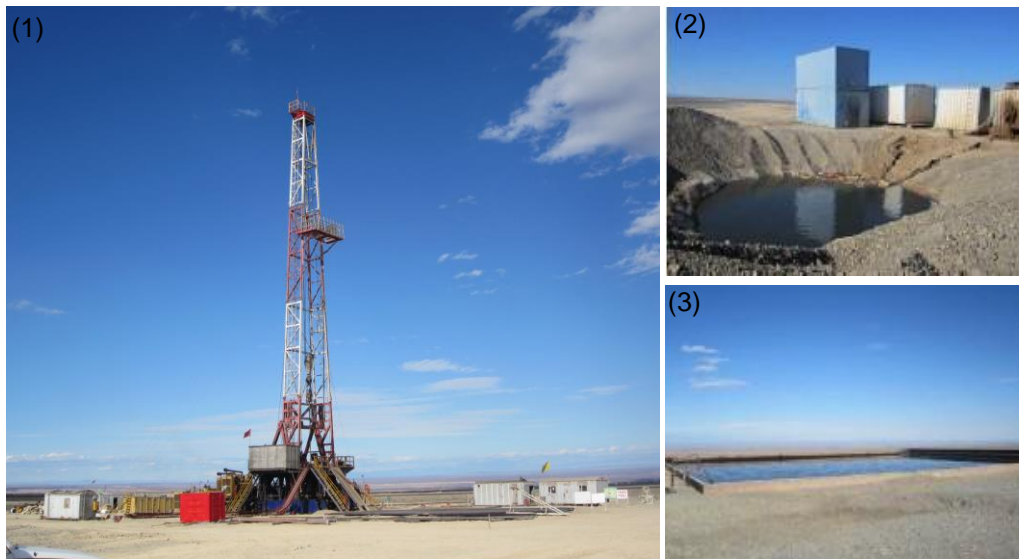
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67 The shale gas resources in many areas had been overlooked because the  
68 production economical feasibility was not attractive enough until the development of  
69 combination of sequenced hydraulic fracture treatments and horizontal well  
70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

83 After a hydraulic fracture treatment and relief of the pumping pressure from  
84 the well, the water-based fracturing fluid, mixed with any natural underground water,  
85 begins to flow back through the well casing to the wellhead. The time for recovering  
86 the majority of fracturing fluid ranges from several hours to a couple of weeks. In  
87 various basins and shale gas plays, the volume of produced water may accounts for  
88 15-40% of the original fracture fluid volume. In some cases, flowback of fracturing  
89 fluid in produced water can continue for several months after gas production has  
90 begun. If not directly treated, the flow back water is stored in a man-made pond  
91 before further treatment or tankering. Figure 25.3 shows a typical site for shale gas  
92 mining in a remote area in the northwest China. Next to the crane, shale gas flowback  
93 water and domestic wastewater were temporarily stored in separate ponds. Both  
94 streams are of different characteristics and remains yet untreated.



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**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.



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**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.

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

109 Table 25.1 listed the constituents of produced water in a Shale play in  
110 Marcellus Shale and the southwest China. The composition varies significantly as  
111 compared to the composition of produced water from Marcellus Shale drilling. The  
112 TDS in the wastewater changes with time as well. Initial TDS of 38500-238000 mg/L  
113 was found in the produced water from wells drilled in Marcellus Shale at 5 days post

114 hydraulic fracturing and was in the range of 3010-261000 mg/L at 14 days of post  
115 drilling. This high TDS makes the treatment of such produced water a great challenge.  
116 In the case of south west China, the saline content appears to be much lower than that  
117 in the US. The difference is a strong reflection of the geological variation from region  
118 to region.

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

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

<b>Chemical constituent or surrogate parameter</b>	<b>Unit</b>	<b>Marcellus Shale at 5 days post hydraulic fracturing</b>	<b>Typical flowback water from southwest China (initial stage)</b>
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 <sub>3</sub> )	mg/L	5100-55000	277
TKN	mg/L as N	38-204	-
NH <sub>3</sub> -N	mg/L as N	29.4-199	-
NO <sub>3</sub> -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

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## 134 2.2 *Water management in shale gas exploitation*

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

- 136 (1) brine volume reduction with the possibility for reuse to future fracturing  
137 purpose  
138 (2) removal of the organic polymeric additives  
139 (3) oil and grease control  
140 (4) removal of suspended solids  
141 (5) microbial control  
142 (6) soluble organics

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

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

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

177 FO systems do not need external hydraulic pressure as the driving force. it has  
178 a high rejection rate of contaminates, and more importantly a lower propensity for  
179 membrane fouling, comparing to pressure driven osmotic processes (Cath and  
180 Bamaga 2011). In case the draw solution is directly reusable without any further

181 post-treatment, the forward osmosis is essentially working at low energy consumption.  
182 Success in the utilization of forward osmosis technology has been reported in  
183 literatures (Hickenbottom et al., 2013). A summary of the technical assessment of the  
184 several membrane technologies are listed in Table 25.4. Forward osmosis was a low  
185 energy and simple process for the reuse of the shale gas flowback water. Therefore,  
186 the following section will mainly focus on the application of forward osmosis for the  
187 reuse of the shale gas wastewater.

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190 **Table 25.2:** Summary of advantages and challenges of the present treatment technologies for  
 191 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

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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 <sub>4</sub> EDTA, HCl, Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> , or H <sub>2</sub> O <sub>2</sub> for cleaning.	Use of NaOH, Na <sub>4</sub> EDTA, HCl, Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> , or H <sub>3</sub> PO <sub>4</sub> for cleaning.	Use of NaOH, Na <sub>4</sub> EDTA 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

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## 196 3 Forward osmosis for treatment of wastewater produced from 197 Shale gas exploitation

### 198 3.1 Overview

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

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

213

### 214 3.2 Membranes

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

226

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

	HTI	CTA <sup>a</sup>	TFC <sup>a</sup>	TFC <sup>b</sup>
Water Permeability A (L/m <sup>2</sup> .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 <sup>-7</sup> m/s)	2.69	3.25	3.16	1.76±0.22
S value (10 <sup>-4</sup> m)	4.12	8.3	7.96	2.66±0.46
Jw (L/m <sup>2</sup> .h)	8.7	6.7	12	N.A.
Js/Jw (g/L)	1.17	1.04	0.3	N.A.

229 <sup>a</sup> Cellulose triacetate and thin-film composite fabricated by our lab ( He et al. 2012)

230 <sup>b</sup> Product developed by Oasys (McGinnis et al. 2013).

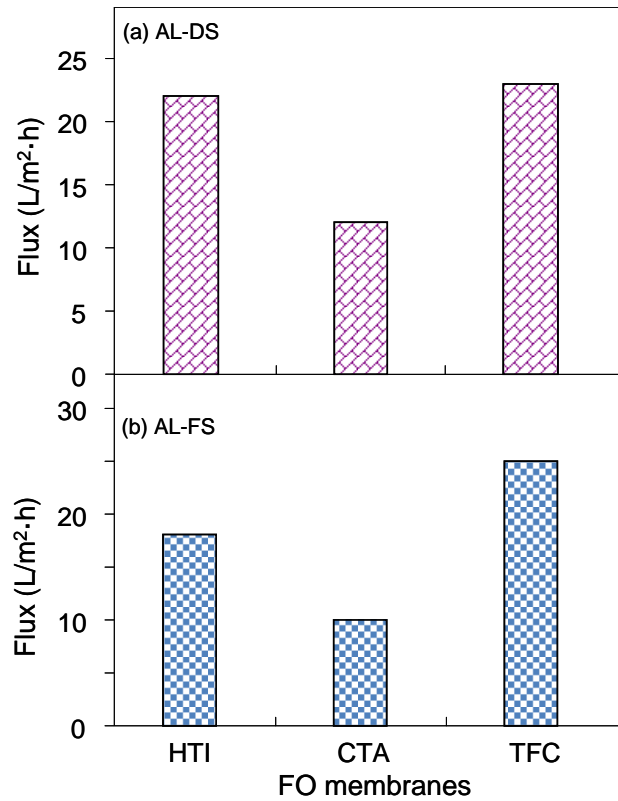
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232 **3.3 Draw solution**

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

244 Hickenbottom et al (Hickenbottom et al. 2013) employed sodium chloride  
245 solution (NaCl, 4.5mol/L) as draw solution in FO process for concentration of drilling  
246 mud and fracturing wastewater from oil and gas operations. Moreover, McGinnis et al  
247 (McGinnis et al. 2013) used ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) as draw solution in  
248 desalination of high salinity (>70,000 ppm TDS) produced waters from shale gas  
249 exploration in order to produce clear water. This product water generated in the  
250 process was found to meet surface water discharge quality criteria (<500 mg/L TDS,  
251 <250 mg/L chlorides, <10 mg/L barium, <10 mg/L strontium) for the Site of  
252 Pennsylvania. However, ammonium bicarbonate is alkaline in nature, may deteriorate  
253 membrane.

254 Sodium chloride, magnesium chloride (MgCl<sub>2</sub>) and disodium  
255 ethylenediaminetetraacetate (EDTA) were compared as draw solutes in concentration  
256 of shale gas wastewater (SGW) using different FO membranes (HTI, CTA and TFC)  
257 (He et al. 2012). CTA and TFC FO membranes were tailor-made (Li, G. et al. 2013).  
258 Both in AL-DS and AL-FS test mode (Figure 25.4), TFC FO membrane showed better  
259 performance in the process of SGW concentration than that of HTI and CTA FO  
260 membranes using sodium chloride draw solution (3.26 mol/L).



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**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)

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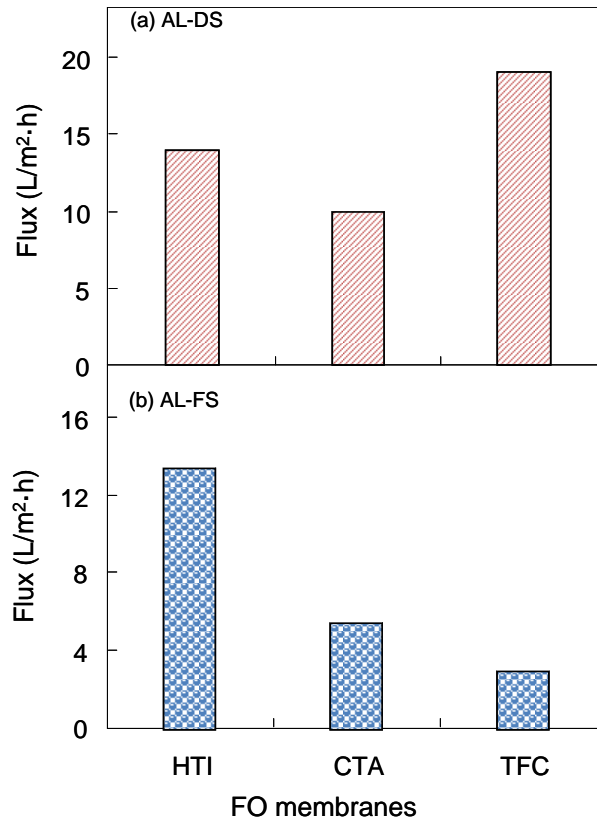
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However, when  $MgCl_2$  draw solution (1.74 mol/L) was used, the FO fluxes of three different FO membranes differed quite much in the order of  $J_{w-TFC} > J_{w-HTI} > J_{w-CTA}$  in the AL-DS mode and  $J_{w-HTI} > J_{w-CTA} > J_{w-TFC}$  in AL-FS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

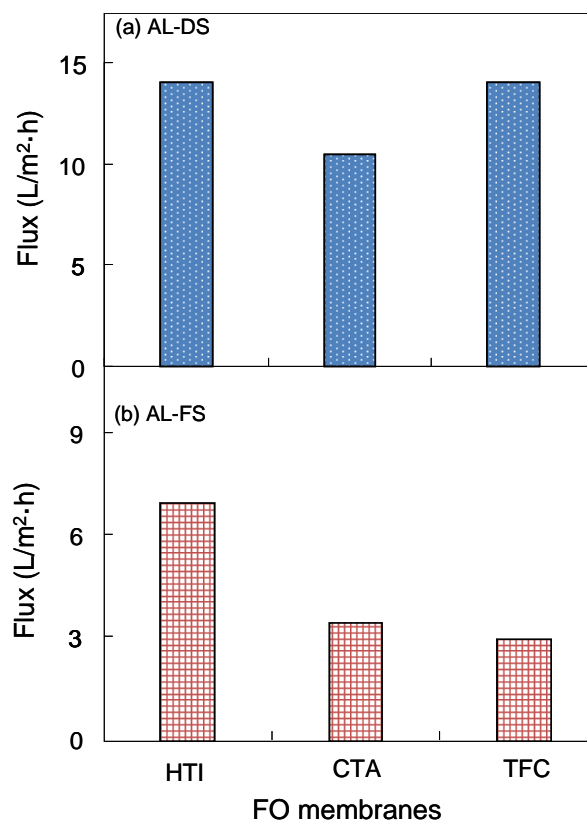
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**Figure 25.5:** The water fluxes of three different membranes used in SG wastewater treatment by FO process. (1.74M MgCl<sub>2</sub> as the draw solution and SG waste water as the feed, (a) Water flux under AL-DS mode; (b) Water flux under AL-FS mode)

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).



279

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

283

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

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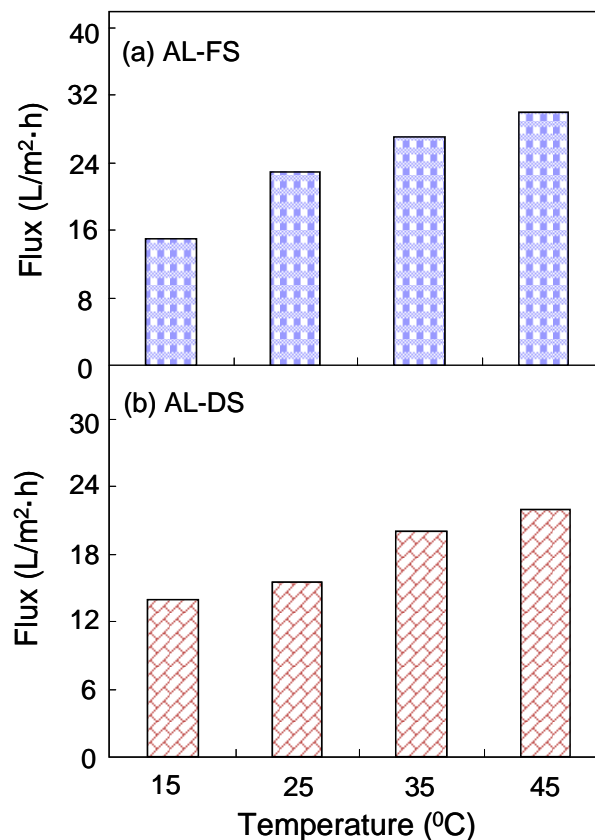
### 293 3.4 *Operating conditions*

#### 294 3.4.1 Feed and draw solution temperatures

295 Several studies have investigated the effect of temperature on water flux and  
 296 salts permeation (You et al. 2012; Phuntsho et al. 2012; Zhao and Zou 2011) in the FO  
 297 process. Generally, it was concluded that water flux and salt permeation increased  
 298 with increasing temperature in the FO process (McCutcheon and Elimelech 2006;  
 299 Nayak and Rastogi 2010; Phuntsho et al. 2012; Zhao and Zou 2011). Recent studies  
 300 have also focused on the impact of the temperature difference between the feed and  
 301 draw solutions on water and draw solute permeation across FO membranes. Phuntsho  
 302 et al. (Phuntsho et al. 2012) examined the water flux change with feed and draw  
 303 solutions of different temperature and found that water flux increased significantly by  
 304 increasing draw solution temperature. You et al. (You et al. 2012) proposed that the  
 305 heat flux generated by the temperature difference between the feed and draw solutions

306 could enhance the water flux due to the decrease in feed solution viscosity and the  
307 increase in water diffusivity.

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



318

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

322

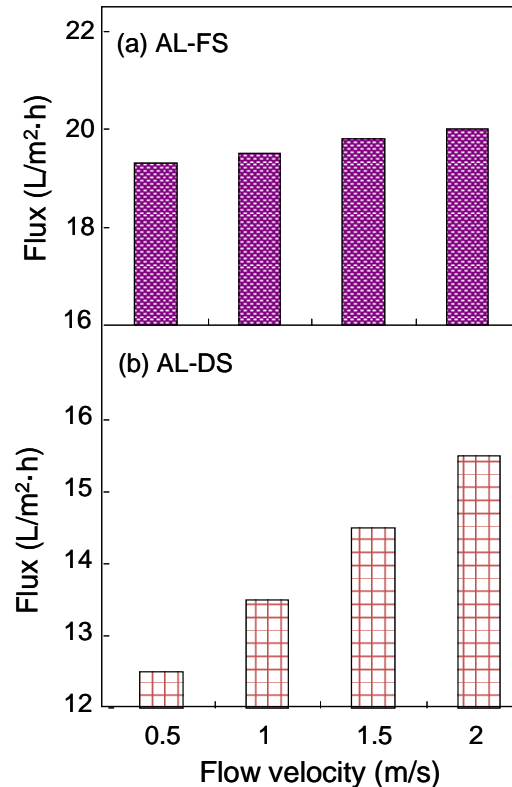
### 323 3.4.2 Flow velocity

324 The flow velocity affects the hydraulic status of the FO system, which is very  
325 important for the determination of the scale of the FO plant as well as the cost.  
326 Recently, He (He 2013) reported the effect of the flow rate on the FO flux in  
327 concentrating shale gas wastewater in the AL-FS mode (Figure 25.8). It was found  
328 that the FO flux did not change with the flow velocity, but in AL-DS mode, an  
329 obvious increase of FO flux was observed. This phenomenon is most probably  
330 ascribed to the internal concentration polarization in the AL-FS mode where the  
331 porous support layer is facing the DS. Moreover, the flux in AL-FS mode was higher



332 than that in AL-DS mode. Literature has shown that AL-FS mode has shown much  
333 steady performance than in the AL-DS mode for feed solutions of complicated  
334 compositions especially those tend to foul the membranes, thus, for shale gas  
335 produced water treatment, the AL-FS mode should be the primary choice.

336



337

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

341

### 342 3.5 Membrane fouling

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

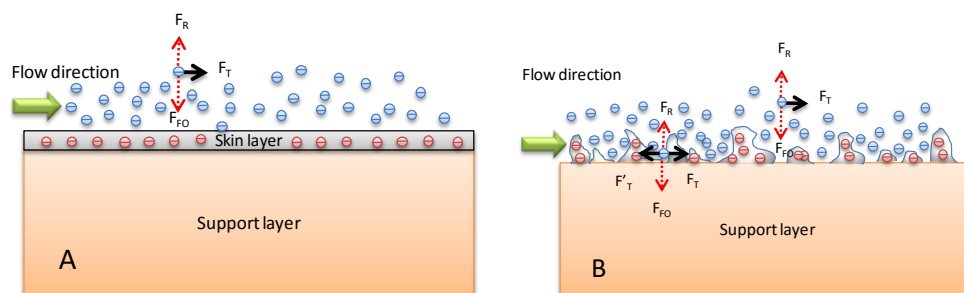
347 (1) Surface roughness may affect the fouling behavior; A rough top surface tends  
348 to trap micro or submicro-size pollutants, especially the particulate aggregates or  
349 foulants of potential to form a particulates, but not a smooth surface (Hashina et al.  
350 2011). Moreover, once trapped, they are difficult to be washed away by the tangential  
351 flow. For a smooth surface, the possibility for the trapping of the particles is lower  
352 than the rough surface, thus less aggregation of the foulant to the membrane surface.  
353 It is thus probable that the HTI CTA membranes of a smooth surface is less accessible  
354 to the foulants in the SGW wastewater; However, for a rough membrane surface as  
355 TFC membranes, it is most likely to form a fouling layer during the FO process for  
356 the concentration of the SGW wastewater.

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

360 certain time duration before significant reduction in flux is visualized.

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

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



386

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

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

401 et al. 2009; Holloway et al. 2007; Sagiv et al. 2010).

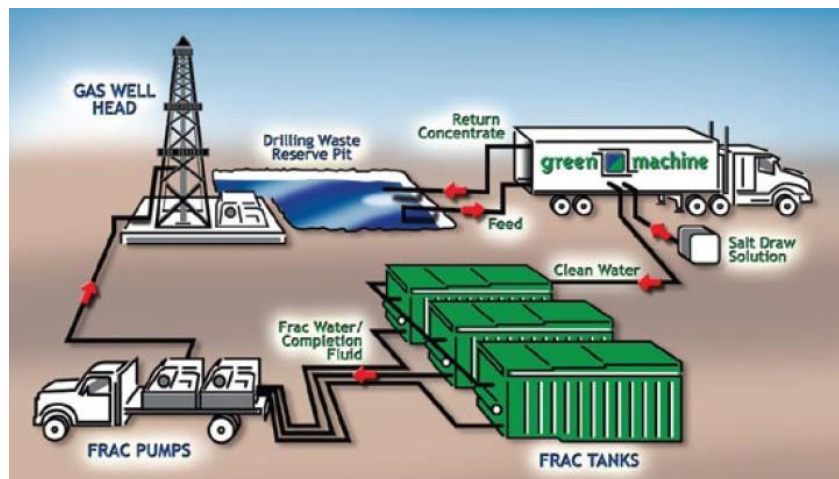
402

## 403 4 Application cases

### 404 4.1 Osmotic dilution

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

418



419

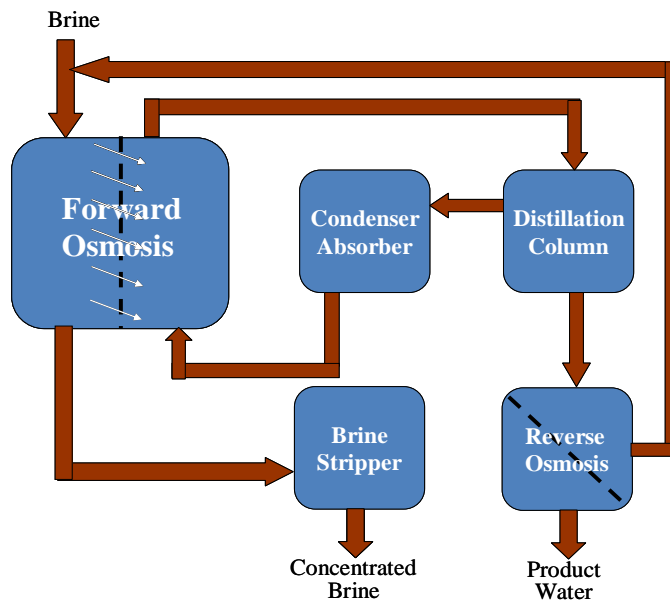
420

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

423

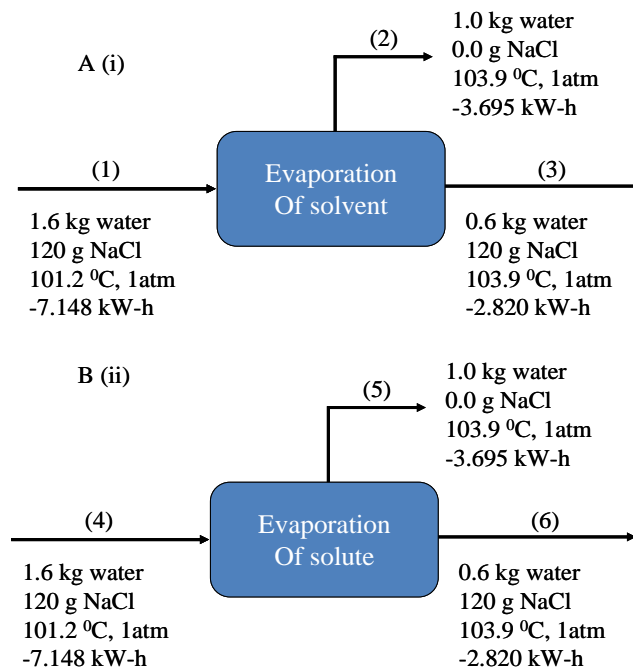
### 424 4.2 FO-Distillation Process

425 Although osmotic dilution can reduce the water demand in the hydraulic  
426 fracturing process, it does not generate fresh water that meets the discharge standards.  
427 Moreover, because of the operation principle, solely an individual FO membrane  
428 process can never produce water that meets discharge standards (Cath et al. 2006). To  
429 purify the flowback wastewater from shale gas wastewater, a hybrid FO-MD process  
430 was investigated by McGinnis et al (McGinnis et al. 2013). They demonstrated a pilot  
431 scale integral FO-MD concentrator (shown in Figure 25.11) to desalinate fracturing  
432 flowback and produced waters from natural gas extraction operations in the Marcellus  
433 shale region. Compared to initial concentration of wastewater with TDS of  
434  $73,000 \pm 4200$  mg/L, the salt concentration of the product was  $300 \pm 115$  mg/L TDS that  
435 meet surface water discharge quality criteria for the State of Pennsylvania.



436  
437 **Figure 25.11:** Block flow diagram of the FO membrane brine concentrator setup  
438 (McGinnis et al. 2013)  
439

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



449  
450 **Figure 25.12:** Mass and enthalpy balance diagrams based on thermophysical  
451 modeling. (A) Case (i), production of 1 kg of pure water through evaporation of the

452 solvent (water) from a saline source. (B) Case (ii), production of 1 kg of water  
 453 through evaporation of the solute (shown here as molar flows of C and N, which are  
 454 equivalent to molar flows of CO<sub>2</sub> and NH<sub>3</sub> in stream (5)) from a draw solution diluted  
 455 by permeate from an FO membrane process

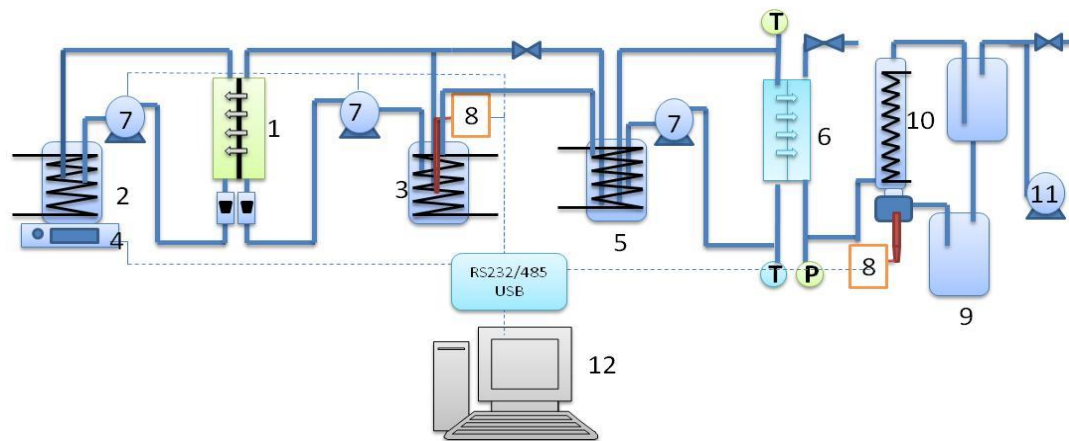
456

### 457 4.3 Forward osmosis-vacuum membrane distillation

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

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

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



476

477

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

480

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

	Potable water in Shanghai	FO-MD permeate
Conductivity ( $\mu\text{s}/\text{cm}$ )	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

483

## 484 5 Conclusions

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

499

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