CHEMICAL ENGINEERING TRANSACTIONS
VOL. 43, 2015

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-34-1; **ISSN** 2283-9216

DOI: 10.3303/CET1543384

Membrane Processes for the Treatment of Produced Waters

Vincenzo Piemonte*[a], Marina Prisciandaro[b], Luisa di Paola[a], Diego Barba[a]

[a]University Campus Bio-Medico of Rome, Faculty of Engineering, Via Alvaro del Portillo 21, 00128, Rome, Italy
[b]University of Aquila, Department of Industrial Engineering, Information and Economy, viale Giovanni Gronchi 18, 67100 L'Aquila, Italy.
v.piemonte@unicampus.it

From the oil plants and platforms a large amounts of wastewaters, which are considered a by-product of crude oil extraction, are produced: they are exactly known as “produced waters”, and up to now they have been treated and disposed of in deep wells on the onshore platforms or directly discharged into the sea. Extraction technology and reservoir characteristics affect the amount of produced water generated that sometimes may be tenfold the quantity of produced oil.

The purpose of this paper is to develop a process suitable for the purification of produced waters, by devising a treatment train aimed at industrial and agricultural reuse.

With respect to a municipal wastewaters, produced waters have a very high salinity, that requires specific attention for projecting and managing the specific treatment device. Membranes, commonly used in the production of desalted water, appear to be a suitable technique to overcome the problem; particularly, the vibrating membrane system VSEP (*Vibratory Shear Enhanced Processing*) turned out to be a reliable and good process to be applied to the produced water, since with a single operation gives an effluent with a high purity degree without the addiction of chemicals. Moreover, if the effluent from secondary membrane treatment is further purified with a reverse osmosis as tertiary treatment, with a previous reduction of nutrients, the effluent has all the necessary attributes required by the law for water reuse.

In this paper a process scheme is proposed with a treatment sequence train, in which the a VSEP system is used as secondary treatment, and a Reverse Osmosis process has been implemented as tertiary treatment, simulated with the software IMSDesign Software by Hydranautics. Several case studies have been considered, with waters of different salinity, showing that in all cases a water with very good characteristics is obtained, reusable for different uses.

1. Introduction

A large amount of wastewaters, known as “produced waters”, comes out from oil plants and platforms, considered a by-product of crude oil extraction; currently, they are treated and disposed of in deep wells on the onshore platforms or directly discharged into the sea. Specifically, 65% of this water is re-injected to the well for pressure maintenance, 30% of total is injected to deep well for final disposal in the case of proper aquifer conditions and the rest of the water is discharged to surface water (Çakmakci et al, 2008).

Extraction technology and reservoir characteristics affect the amount of produced waters, up to tenfold the amount of produced oil. Produced waters account for around 70% of total oil production wastewaters volume.

Moreover, leaks and accidental spills occur regularly during all the activities connect to petroleum industry, *e.g.* exploration, production, refining, transport, and storage of petroleum and petroleum products. In 2003, the amount of natural crude oil seepage was estimated to be about $6x10^5$ metric tons. Thus, hydrocarbons release of hydrocarbons into the environment, whether accidentally or due to anthropic activities, is the main source of water pollution (Barba et al., 2006).

Nowadays, as water demand is always increasing, it is essential to recover and reuse water. Thus, many countries with oilfields are generally water-stressed countries, therefore they are increasingly focusing their

Please cite this article as: Piemonte V., Prisciandaro M., Di Paola L., Barba D., 2015, Membrane processes for the treatment of produced waters, Chemical Engineering Transactions, 43, 2299-2304 DOI: 10.3303/CET1543384

efforts to find efficient and cost-effective treatment methods to remove pollutants as a way to supplement their limited fresh water resources (Ahmadun et al., 2009). In addition, it is crucial to find new technologies that aim not only to the environmental sustainability but also comply with the more stringent rules and regulations of the field. The permit limits of O&G for treated produced water according to the United States Environmental Protection Agency regulatory limits are 29 mg L^{-1} for a monthly average and 42 mg L^{-1} for a daily maximum.

Produced waters are characterized by a high content of salts and oil, which makes mandatory to draw a specifically purposed treatment train, different, for example, from those commonly used for municipal wastewaters treatment. Typically, produced water contains high concentrations of aromatic hydrocarbons *e.g* BTEX (benzene, toluene, ethylbenzene, xylene), NPD (naphthalene, phenanthrene e dibenzotiophene) and PAH (polycyclic aromatic compounds) (OGP, 2002), minerals, radioactive substances, dissolved gases, scale products, waxes, microorganisms and dissolved oxygen (IgunnuandChen, 2012). The salt concentration may range from a few mg $L^{-1}$to 300,000 mg L^{-1}; the total organic carbon (TOC) concentrations are between 0 and 1,500 mg $L^{-1}$and oil and gas (O&G) concentrations between 2 and 565 mg L^{-1} (Pendashteh et al., 2010).

Biological, physical and chemical methods are available to specifically remove hydrocarbons from produced water,. In offshore extraction facilities, due to space constraints, compact physical and chemical treatment technologies are preferred (Ahmadun et al., 2009) (photo-electrocatalytic processes, hydrocyclones, coagulation and flocculation). Most of these techniques are only suitable for pretreatment of wastewater for in situ reuse, e.g. reinjection to enhance oil recovery yield (Pendashteh et al., 2010).

On the other hand, membrane technology may be successfully used to remove hydrocarbons from oil-contaminated wastewater, also in the presence of a high salinity. Membrane processes offer several advantages over conventional treatments, such as compact module, lower energy consumption, environmental friendliness and high quality product, independently on fluctuations in feed quality. Moreover, membrane equipments have a smaller footprint, energy costs are often lower and the plant can be highly automated. For these reasons, microfiltration (MF) and ultrafiltration (UF) membrane processes have been increasingly used in potable water production and wastewater treatments as an alternative technology to conventional treatments, getting rid of the coagulation, flocculation and sedimentation steps, aimed at removing particles, turbidity, microorganisms and natural organic matter (NOM) (Di Zio et al., 2005).

Moreover, process based on water separation from saline solution by reverse osmosis membrane processes (R.O.) are widely industrially spread, usually applied not only to sea waters with high salinity, but also to brackish waters and low salinity waters, which are characterized by different compositions, thus needing specific pre-treatments (Prisciandaro et al., 2008).

Because of the presence of dissolved and suspended oil in untreated produced water, the membrane equipment may become fouled, thus increasing operation costs. On the other hand, the problem of membrane fouling is a key issue, which frequently limits the widespread of such an effective technique, thus being a hot topic for research purposed at finding ways to overcome or limit it (Prisciandaro et al., 2008).

On this respect, the vibrating membrane process VSEP® (*Vibratory Shear Enhances Process)* limits membrane fouling, removing the main contaminants from wastewater without the addition of antiscalant chemical substances; thanks to the design characteristics, the fouling common to all membrane processes is greatly reduced (Shi and Benjamin, 2008). The pressure vessel moves in a vigorous vibratory motion, tangential to membrane surface, thus creating shear waves, which prevent membrane fouling (Petala and Zouboulis, 2006). The volume of retentate sent to disposal is about one third of the feed and power duties, and corresponding costs, are very low (Petala and Zouboulis, 2008).

The aim of the present paper is to analyse the possibility of adapting membrane processes, e.g.VSPE and R.O., by using as feed produced water, properly pretreated, to provide water of high quality, reusable as process water and/or in agriculture. We devise a treatment train comprising a two steps membrane filtration stage (VSEP followed by R.O.).

We analyse the process in terms of mass balances of the whole scheme; we assumed the removal efficiencies from literature and we performed the R.O. process simulation by the software IMS Design Software by Hydranautics™ (2012). Results show that in all cases under analysis (at different salinity of the feed stream) the treatment results into stream purification so that the pollutant concentrations lie within the limits for reuse; thus, an ultra-pure water is obtained, proper for multipurpose reuse (industrial or agricultural).

2. Process simulation

The real composition of produced water variesconsiderablydepending on the geographiclocation of the reservoir, the geologicalstructure of the soil, the characteristics of the extractedhydrocarbons, the productionprocessand the exploitationdegree of the well.

Thus we adopted a model solution bysimulating real produced water. The averagemainproperties of the produced water forthiswork are reported in Table 1 (Ahmadun et al., 2009).

Table 1: Simulated produced water composition

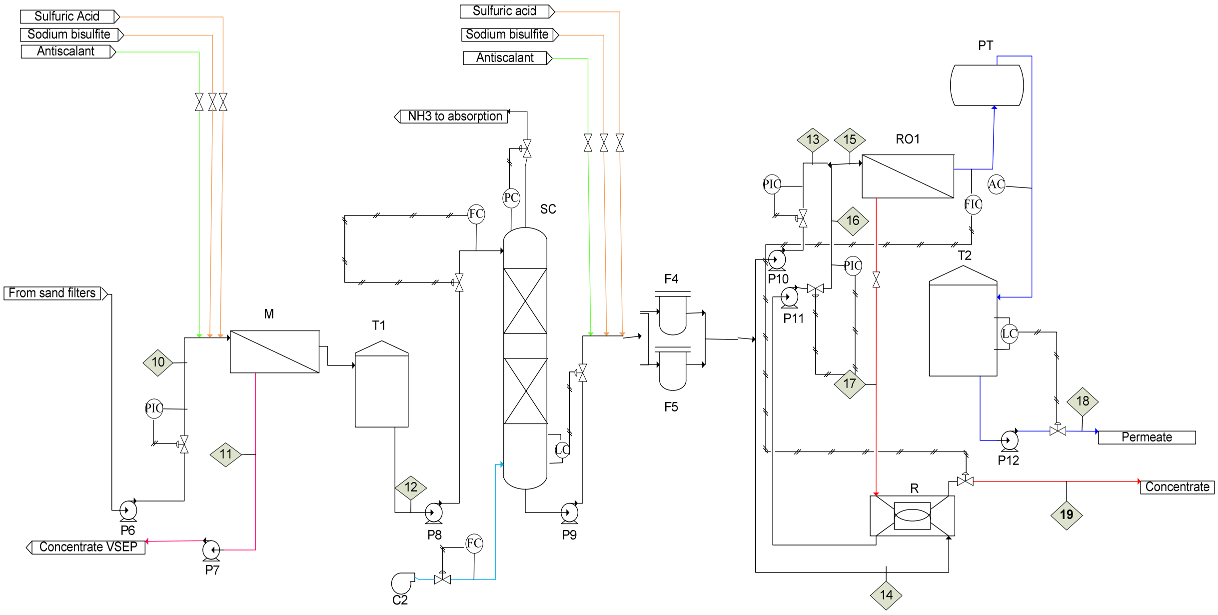
PARAMETER	***VALUE [mg/L]***
Oil andGrease	565
Total Suspended Solid	1000
Chemical OxygenDemand	3000
BiochemicalOxygenDemand	1500
Total Organic Carbon	1500
Ammonia NH_4^+	200
BTEX	2.0
Total Dissolved Solid	37500

.

The process scheme used in the simulation runs is reported in Figure 1. Produced water (stream 10), coming from primary treatments, aimed at removing the largest part of contaminants (suspended particles, inorganic compounds and heavy metals) is sent through a high-pressure pump to the VSEP membranes system. At this stage, the retentate water stream (11), still rich in pollutants, is disposed of, while the permeate (stream 12) is sent to a stripping column to remove ammonia. To avoid solids to be drawn from the stripping column, this is equipped with a cartridge filter (microfiltration up to 5 microns).

To prevent precipitation of low soluble salts on the membrane surface, antiscalant and chemicals are added to water in the upstream of reverse osmosis stage. The permeate is then pressurized and sent to the reverse osmosis stage (stream 16). The process scheme includes also an energy recovery device (ERI-PX) and a booster pump. Part of the produced water coming from the pre-treatment is pressurized by a high pressure pump, while the other part is put under pressure by the energy recovery system operating in series with the booster (stream 14). The retentate from the reverse osmosis stage (stream 19) is sent to disposal, while the permeate (stream 18) is conveyed to a storage tank, ready to use.

Figure 1: Process simulation scheme



3. Results and discussion

In the following, we discuss three case studies for the desalination process of produced waters with three salinitylevels (35,546; 71,127 and 106,670 ppm). The sizing of the reverse osmosis process was performed using the programIMSDesign Software by Hydranautics™ (2012).
The membranes for reverse osmosis are the SWC4 Max and SWC5 Max by Hydranautics™ Nitto Group Company, both allowing a salt rejection of 99.8%. Membrane geometry (spiral wound) ensures less membrane fouling, because of the tangential water flux to membrane surface, which allows high velocities and turbulent flow regimes.
Each membrane has a length of 1 m and an active area of 40.8 m^2; the composite membrane comprises an active layer of polyamide (providing the membrane selectivity) and a porous layer of structural support (polyethersulfone, PES), with a low resistance to water flow. These membranes are chemically and physically stable; they don't hydrolyze water, tolerate pH values in the range of 3-11 and are virtually immune towards biological degradation (Crittenden et al., 2012).

Case study A

In this case study, we considered one reverse osmosis stage in order to meet the water quality required by the decree no. 152/2006, related to "water for irrigation purposes" (no food applications). The salts concentration of the produced water is reduced from 37,500 ppm to 35,546 ppm by upstream pre-treatments, which are here not discussed here. The ionic composition of produced water at T = 25 °C and pH = 8.1 is shown in Table 2, while Table 3 reports the operative membrane parameters.

Case study B

The ionic composition of produced water analysed in the case is reported in Table 4. Also in this case it has been considered only one stage of reverse osmosis. The operative membrane parameters are reported in Table 5.

Case study C

The ionic composition of produced water in this case study is reported in Table 6. In this case, because of the high water salinity, we consider a double reverse osmosis stage, where the permeate, coming out from the first stage, enters into the second stage with a larger recovery factor (35%). The features of the two membrane stages are reported in Table 7: to meet the requirements for this case study, the feed pressure to the first stage must be reduced , by recirculating 0.4 m^3/h of the retentate flow from the second stage, thus the feed pressure to the first stage drops to 89.3 bar.For comparison, Table 8 reports the collective results, in terms of final TDS content of produced water, for all case studies: the processed produced water always meets the requirements by law for the reuse (TDS from 400 to 2000 ppm).

Table 2: Ionic composition of produced water for case study A (see Fig. 1, stream 12)

Cations	***Value [ppm]***	***Anions***	***Value [ppm]***
Ca^{2+}	410	HCO_3^-	152
Mg^{2+}	1310	SO_4^{2-}	2000
Na^+	10987.9	Cl^-	20260.2
K^+	390	F^-	1.4
NH_4^+	0	NO_3^-	0.6
Ba^{2+}	0.050	B^{3+}	4
Sr^{2+}	13	SiO_2^{2-}	0.5
Total TDS = 35546 ppm			

Table 3: operative membrane parameters - case study A.

Stage Number	1	Feed flowrate (m^3/h)	3.8
Vessel Number	1	Permeateflowrate (m^3/h)	1.70
Elements Number	3	Retentateflowrate (m^3/h)	2.1
Total active area (m^2)	122.4	Recovery (%)	45
TDS Feed (ppm)	35546	Feed Pressure (bar)	57

Table 4: Ionic composition of produced water for case study B

Cations	***Value [ppm]***	***Anions***	***Value [ppm]***
Ca^{2+}	820	HCO_3^-	304
Mg^{2+}	2620	SO_4^{2-}	4000
Na^+	21975.8	Cl^-	40520.4
K^+	780	F^-	2.8
NH_4^+	0	NO_3^-	1.2
Ba^{2+}	0.1	B^{3+}	8
Sr^{2+}	26	SiO_2^{2-}	1
Total TDS = 71127 ppm			

Table 5: operative membrane parameters - case study B

Stage Number	1	Feed flowrate (m^3/h)	91.2
Vessel Number	1	Permeateflowrate (m^3/h)	22.80
Elements Number	3	Retentateflowrate (m^3/h)	68.4
Total active area (m^2)	122.4	Recovery (%)	25
TDS Feed (ppm)	71127	Feed Pressure (bar)	80.4

Table 6: Ionic composition of produced water for case study C

Cations	***Value [ppm]***	***Anions***	***Value [ppm]***
Ca^{2+}	1230	HCO_3^-	456
Mg^{2+}	3930	SO_4^{2-}	6000
Na^+	32977.4	Cl^-	60781.4
K^+	1170	F^-	4.2
NH_4^+	0	NO_3^-	1.8
Ba^{2+}	0.15	B^{3+}	12
Sr^{2+}	39	SiO_2^{2-}	1.5
Total TDS = 106670 ppm			

Table 7: Operative membrane parameters - case study C

	First Stage	***Second Stage***
Membrane type	SWC4 Max	SWC5 Max
Stage number	1	1
Vessel number	1	1
Membrane number per vessel	6	3
Total active surface (m^2)	244.8	22.3
Feed flowrate (m^3/d)	91.2	13.7
Permeate flowrate (m^3/d)	13.68	4.79
Retentate flowrate (m^3/d)	77.5	8.9
Recovery factor (%)	15	35
Feed pressure (bar)	115	3

Table 8: TDS for the three case studies.

	Case study A (one stage)	**Case study B (one stage)**	**Case study C (double stage)**
TDS Permeate [ppm]	160.2	449.5	55.1

4. Conclusions

The reuse of water is a hot topic in the industrial practice; the produced waters in oil extraction and production represent a good water source for reuse, when properly treated.

We demonstrated the reliability and feasibility, on an economical ground too, of membrane processes, embedded in a treatment train.

The analysis of three case studies allows a comprehensive survey of possible applications even for brackish waters, showing the costs may be cut when simpler processes are applied for non-food water reuse purposes.

This approach provides encouraging perspectives in the application of innovative membrane devices (VESP) coupled with traditional reverse osmosis modules, which by reducing fouling allows to get very good performance of the treatment processes.

References

Ahmadun F.R., Pendashteh A., Abdullah L.C., Biaka D.R.A., Madaeni S.S., Abidin Z.Z., 2009, Review of technologies for oil and gas produced water treatment, J. Haz. Mat. 170, 530–551.

Barba D, Prisciandaro M., De Maio A., Analysis of desalination processes aimed at industrial wastewater reuse, First Mediterranean Congress Chemical Engineering for Environment, Venice San Servolo, October 4–6, 2006.

Çakmakci M., Kayaalp N., Koyuncu L., 2008, Desalination of produced water from oil production fields by membrane processes, Desal., 222, 176-186.

Crittenden J.C., Trussell R.R., Hand D.W., Howe K.J., Tchobanoglous G., 2012, MWH's Water Treatment: Principles and Design, 3rd Edition, Wiley.

Di Zio A., Prisciandaro M., Barba D., 2005 Disinfection of surface waters using UF membrane, Desalination, 179, 297-305.

Hydranautics IMS Design Software Software, v. 2012, Nitto Group Company.

OGP - International Association of Oil&Gas Producers 2002, 2002, “Aromatics in produced water: occurrence, fate and effect, and treatment” Report No. I.20/324.

Pendashteh A.R., Fakhru’l-Razi A., Chuah T.G., Dayang Radiah A.D., Madaeni S.S., Zurina Z.A., 2010, Biological treatment of produced water in a sequencing batch reactor by a consortium of isolated halophilic microorganisms, Environ. Tech. 31, 1229–1239.

Petala M.D.,Zouboulis A.I., 2006, Vibratory shear enhanced processing membrane filtration applied for the removal of natural organic matter from surface waters, J. Mem. Science 269, 1–14.

Petala M.D.,Zouboulis A.I., 2008, Performance of VSEP vibratory membrane filtration system during the treatment of landfill leachates, Desalination 222, 1–3.

Prisciandaro M., Salladini A., Barba D., 2008, Membrane filtration of surface water for the removal of humic substances, Chem. Eng. Trans. 14 , 437-442.

Shi W., Benjamin M.M., 2008, Membrane interactions with NOM and an adsorbent in a vibratory shear enhanced filtration process (VSEP) system, J. Mem. Science 312, 23–33.