# VOLUME REDUCTION OF PRODUCED WATER GENERATED FROM NATURAL GAS PRODUCTION PROCESS USING MEMBRANE TECHNOLOGY

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## ABSTRACT

This paper presents a case study of a natural gas production site covering various technical issues related to selection of an appropriate Reverse Osmosis (RO) system. The long-term field experience indicates the necessity of the selection of appropriate pretreatment systems for fouling- free RO operational conditions. The produced water has a variety of impurities such as oil and grease, process chemicals used for corrosion and scaling control, and dehydration of natural gas, etc. This situation leads to a complicated and extremely difficult task for a membrane specialist to design RO systems, especially the pre-treatment section.

Here as part of the pretreatment selection, two types of UF membranes modules viz. spiral wound and hollow fibre, with MWCO of 8000 and 50,000 Dalton respectively, were tested in parallel with NF membranes of spiral wound type with MWCO 200 Dalton. The UF permeate is used as feed for RO compatibility testing. Both configurations of UF failed to be compatible, due to irreversible fouling of the RO membrane. The NF membrane, however, showed interesting results, due to membrane stability in terms of cleaning and fouling. The NF plant with 50% capacity gave a recovery of 75% and the RO plant gave a recovery of 60% versus the expected 92-95%. The long-term tests have indicated that the reminder of the membranes could be installed to achieve full capacity of the plant. This study also demonstrates the importance of selection of proper pre-treatment set-up for the RO system design.

## KEYWORDS

Produced Water; Membrane; Pre-treatment; Reverse Osmosis (RO); Nanofiltration (NF); Fouling.

## INTRODUCTION

The terminology “produced water” specifies the wastewater co-produced with oil and gas during exploration of natural oil or gas. However it has to be separated from the oil or gas during the purification process. Though the quantity of produced water generated from a single well is not much, but the total collection of produced water from all wells in an exploration site could be remarkably significant. It is considered as the largest source of wastewater in the oil and gas industry (Tellez *et. al,* 1995).

It contains large sources of waste such as suspended solids, iron, and organic and inorganic contaminants (refer Table 1). In some cases produced water contains radioactive particles that can create severe environmental problems. Since, one of the major contaminants of produced water is dissolved salts, Reverse Osmosis is found to be the best choice among the potential technologies for volume reduction (Lueck, 1995).

Although RO systems permit the rejection of TDS, presence of free oil and the organic_contaminants in the produced water are the major challenging factor in field application of the membrane technology._With the increasing awareness on the environmental pollution and the tightening of regulations with respect to effluent discharge quality, produced water cannot just be discharged to the environment. Thus, its disposal has a significant economic impact on the production process.

At the offshore production facilities often, produced water is discharged into the ocean with little or no treatment. Whereas in the case of onshore production like Deep well injection, land application, spray evaporation, treatment and reuse are deemed to be some of the viable options to dispose the produced water. However reuse of the treated water has been the most widely investigated option in the recent years. In this case the treated water can be used for secondary application, while complying with effluent discharge and reuse regulations.

Table 1. Typical types of pollutants present in the produced water

| | |
|---|---|
| Dissolved Organic | • Fatty Acids<br>• Polar Organic (Ex. Phenol, Aldehyde)<br>• Non Polar Organic (Ex. Aliphatic, Aromatic) |
| Process Chemicals | • Corrosion control, Amide imidazoline compound<br>• Scale control, Phosphate ester/Phosphate compounds<br>• Emulsion breaking, Oxyalkylated resins/Polyglycol ester/ Alkylaryl sulfonates<br>• Dehydration of natural gas, methanol/glycol |
| Heavy Metal and Radioactivity | • Cadmium, chrome, copper, lead, mercury, nickel, silver and zinc |
| Suspended Solids | • Inorganic, geological formation (siliceous and calcareous).<br>• Sparingly soluble inorganic salts, calcium carbonate<br>• Organic, ashphaltenes, parffins, suspended oil, High MW fatty acids<br>• Micro organism, Anaerobes (Ex. Sulfate reducing bacteria) |

Fouling is a serious problem, which is frequently encountered in the process of treating produced water using membrane technology. This problem occurs when the concentration of oil and grease in the produced water is high. Even in a well designed RO, oil precipitates at the membrane surface could cause fouling, and in most cases this is irreversible. It is essential to select a suitable pretreatment system for fouling- free RO operational conditions. Increasing the pH value of the produced water before entering the RO is said to be a solution for this fouling problem (Tao *et al*., 1993). The solubility of oil increases as the pH increases, and the test results reveal that raising the pH to 10.6- 11.0 could control RO membrane fouling. The upper pH-operating limit of most of the membranes is 11. But, on the other hand a higher pH causes scaling in the membrane.

Treating produced water without scaling or fouling is the key for the successful RO operation. This pilot scale study was aimed at developing suitable pre-treatment systems for adopting a RO system for the treatment of produced water in a natural gas production unit in Thailand. Based on the nine months experience, appropriate pre-treatment and final membrane selection criteria were discussed in detail.

## CURRENT SITUATION OF THE PRODUCED WATER MANAGEMENT:

The natural gas production facility under study generates approximately $30m^3$ of produced water per day with an average TDS concentration 6,000mg/L (range of 5,000 – 20,000 mg/L) and oil and grease 0 – 25 mg/L. The high concentration of oil and grease is mainly attributed to the discharge from condensate tower. Meanwhile some new wells generate produce water with TDS as high as 20,000 mg/L. The original produced water treatment scheme consisted of simple free oil separation system, followed by a gravity sand filter. The filtered wastewater, collected in a large pond, is pumped to the evaporation pit equipped with spray system. Although this original design of spray evaporation system worked well in terms of concentrating the effluent, it did create additional problems such as organic vapor odor problem and corrosion of pipe and instrument on the gas well, in addition to being restricted in capacity during rainy season. Meanwhile, with the increasing quantity of produced water from new and existing wells, the treatment system needed to be modified, with volume reduction as the major objective.

Since TDS is the major contaminant in the produced water, RO was selected as the most appropriate technique, as it has the advantage of simultaneous volume reduction and salt concentration. The relatively smaller quantity of reject stream with high salt concentration could be treated in the existing treatment systems. Whereas, the permeate would be compatible with the discharge regulation and/or may be used for general proposes such as irrigation.

**Pre-treatment Options:**

The estimated amount of produced water generation from the facility under study is approximately 50 $m^3$/day with the characteristics listed in Table 1. Pretreatment for the removal of oil and grease, organics and other contaminants is an essential pre-requisites of the RO process, as they would otherwise adversely affect the membrane. Hence, in order to effectively use the RO system to produce a permeate water of potable quality, three different options were selected for investigation, namely:

1. Multimedia Gravity Filter + Microfiltration + RO
2. Multimedia Gravity Filter + Ultrafiltration + RO
3. Multimedia Gravity Filter + Nanofiltration + RO

## RESULTS AND DISCUSSIONS

### 1. Multimedia Gravity Filter + Micro-filtration + RO

Here the multimedia filter (anthracite and sand) followed by 20 μm and 1 μm filter bags were used as part of the pre-treatment system to the RO. The experimental runs demonstrated that, soon after the operation, RO flux reduced significantly. It was found that the proposed pre-treatment system was unable to remove up to 25 mg/L free oil occasionally found in the feed water. Attempts to clean the membrane turned out to be unsuccessful and membrane autopsies confirmed that the fouling was irreversible.

### 2. Multimedia Gravity Filter + Ultra-filtration + RO

The previous experimental run revealed, that produced water not only contains the free oil, but also a significant amount of dissolved oils, which could not be retained by the multimedia gravity filter and microfiltration pre-treatment combination. Therefore, it was suggested to replace the microfiltrtion with ultrafiltration, which normally, will able to retain the dissolved portion of the oil components (Tansel *et al*, 1995, Bodzek. and Konieczny. 1992). Here the following two types of membranes were tested as part of the pre-treatment system:

a. Hallow fiber UF membrane with a MWCO 50,000 Dalton (Koch)
b. Spiral wound UF membrane with a MWCO 3,500 Dalton (Desal G-20)

These two types of membranes generally are used in the effluent treatment applications for both free and dissolved oil removals. However, in this study both these UF pre-treatment systems failed leading to rapid

RO flux decline, with O& G rejection less than 40 %. This indicates that, the molecular weight of oil is less than 50,000 Dalton, which could be the reason for the failures of hollow fiber system. In the case of Desal G-20 system unit a MWCO 3,500, the RO flux reduction was less than those of hallow fiber system, but with a O&G rejection more than 85%. However, after few days of operation, the RO system flux declined significantly indicating the irreversible membrane fouling. These results indicated the irreversible fouling caused not only by the oil molecules but also by other organic compounds present in produced water (Refer Table 1). Thus, it is important to eliminate not only the oil but also these low molecular weight organic compounds as a part of the treatment process. The COD analysis indicates only 5- 10 % rejection by the UF membranes. Therefore in the next stage a NF membrane system was studied.

## 3. Multimedia Gravity Filter + Nanofiltration + RO

In the earlier pre-treatment option, it was found that although the ultrafiltation systems could remove a significant portion of the O&G, they are not capable of removing the low-molecular dissolved organic substances. Nanofiltrtion(NF) membranes have very low pore size ( 1 nanometer), with low MWCO. This often helps to sieve and arrest low molecular weight compounds. NF membranes are used for removal of dissolved organic matters and micro-pollutants in water treatment ( Anselme et al, 1993), and in large no of industrial wastewater treatment (Geraldes & de Pinho,1995, Meadow *et al*, 1992).

Here, as part of NF membrane selection, various membranes available in the market were tested. The initial test runs revealed that Film Tech NF membrane, which is polypiperazine based one, performed well to handle specially the oil fouling. This initial bench scale module runs demonstrated that NF 45 membrane was very stable with respect to fouling and cleanability. Based on these results, a full scale NF and RO membrane unit was constructed, and tested continuously for three months. Detail schematic diagram of the unit is presented in Figure 1.

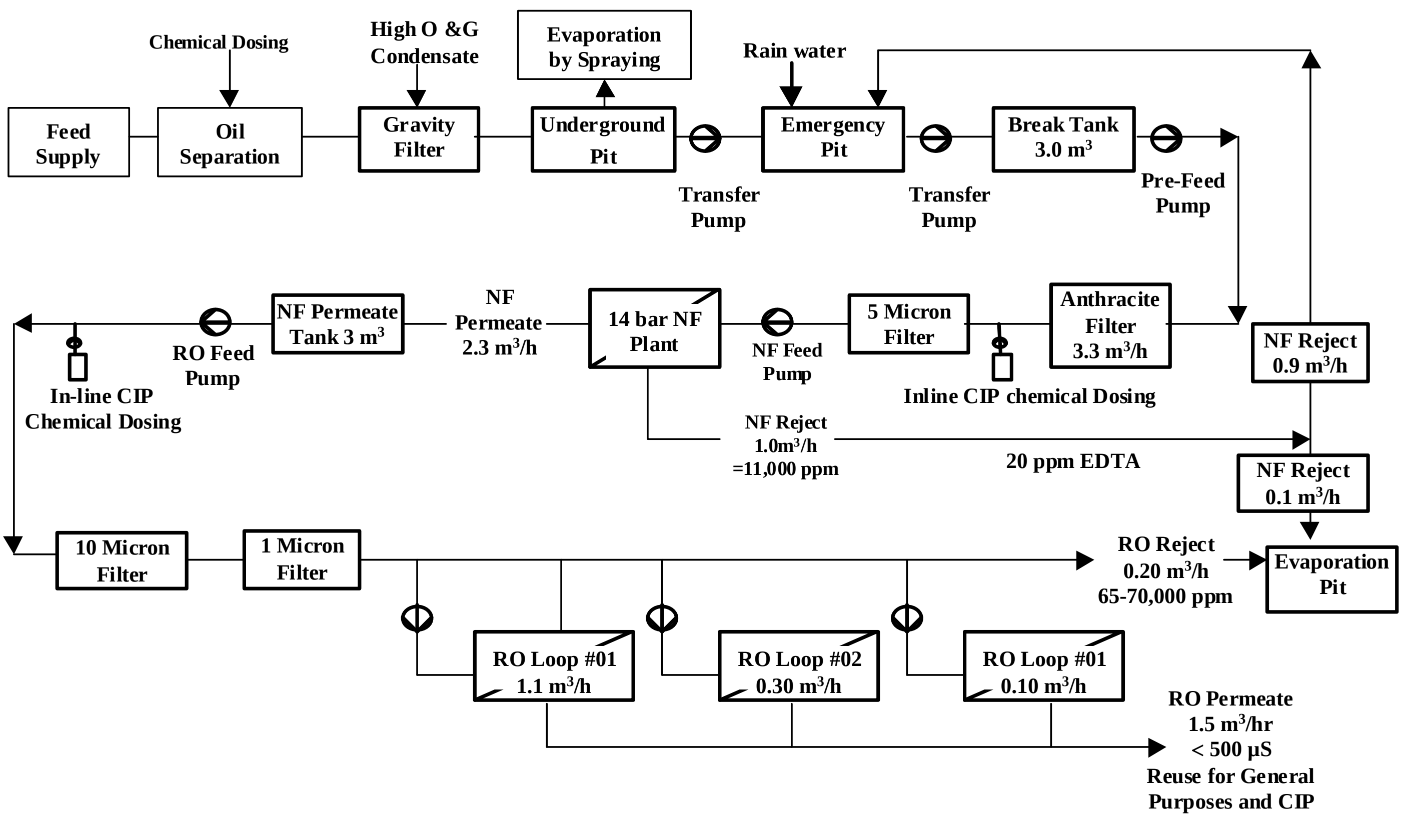


**Fig. 1. System Balance for Volume Reduction of Wastewater from Gas Exploration**

These test runs indicated that RO membranes showed little sign of fouling, and which could be cleaned easily. During these test runs a mixture of 20 mg/L of EDTA and 20 mg/L NaOH was dosed into the test streams of both NF and RO systems. This practice resulted in a reduction of membrane cleaning frequency by half.

Table 2 represents the characteristics of the permeates from the Reverse Osmosis system integrated with the NF Pre-treatment arrangement. From the table it can be seen that the substantial amount of pollutants are removed by NF. The design parameters of this membrane unit is summarized in Table 3.

Table 2. Characteristics of the permeates from the Reverse Osmosis system.

| | Raw wastewater | NF permeate | RO feed | RO reject | RO permeate |
|---|---|---|---|---|---|
| pH | 7.03 | 7.08 | 6.81 | 6.53 | 6.04 |
| Conductivity (μS /cm) (values*1000) | 11,720 | 7,660 | 7,540 | 44,600 | 510 |
| TDS (g/L) | 9.88 | 3.83 | 3.77 | 22.3 | 0.26 |
| M- Alkalinity (mg/L as $CaCO_3$) | 245 | 140 | 87 | 205 | 18 |
| Total Hardness (mg/L as $CaCO_3$) | 4,990 | 1,680 | 1,978 | 11,800 | 60 |
| $Cl^-$ (mg/L) | 5,630 | 2,677 | 2,667 | 18,480 | 161 |
| $Fe^{2+}$ (mg/L) | 640 | 0.59 | 0.37 | 0.70 | 0.01 |
| Mn (mg/L) | 6.5 | 0.10 | 0.10 | 5.1 | - |
| COD | 10,296 | 4,720 | 3,960 | 46,728 | 792 |
| O&G (mg/L) | 393.3 | 3.3 | 1.7 | 16.7 | 0.7 |
| TOC (mg/L) | 3,133 | 2,050 | 1,980 | 14,320 | 226 |
| SS(mg/L) | 310 | - | - | - | - |

Table 3. Design Characteristic of NF & RO membrane units.

**NF membrane**

| | |
|---|---|
| Type: | Film Tec (Polypiperazine Thin film Composite NF 45 – 8040) |
| Configuration: | Spiral Wound |
| Av. Operating Pressure: | 12 bar |
| Average Recovery: | 65- 70% |
| Average Rejection: | 35% |
| Flux | 0.95 L/m$^2$.h at 30$^0$C. |

**RO Membrane**

| | Loop I | Loop II | Loop III |
|---|---|---|---|
| Type: | Film Tech BW 30-4040 (Thin film Composite) | Film Tech SW30-2540-2 (Thin film Composite) | Film Tech SW30-2540-2 (Thin film Composite)) |
| Configuration: | Spiral Wound | Spiral wound | Spiral wound |
| Av. Operating Pressure: | 18 Bar | 60 Bar | 62 Bar |
| Flux: | 0.89 L/m$^2$.h at 30$^0$C. | 0.5 L/m$^2$.h at 30$^0$C. | 0.14 L/m$^2$.h at 30$^0$C. |
| Total Recovery: | 89% | | |
| Average Concentration Degree (CD) | 9 | | |

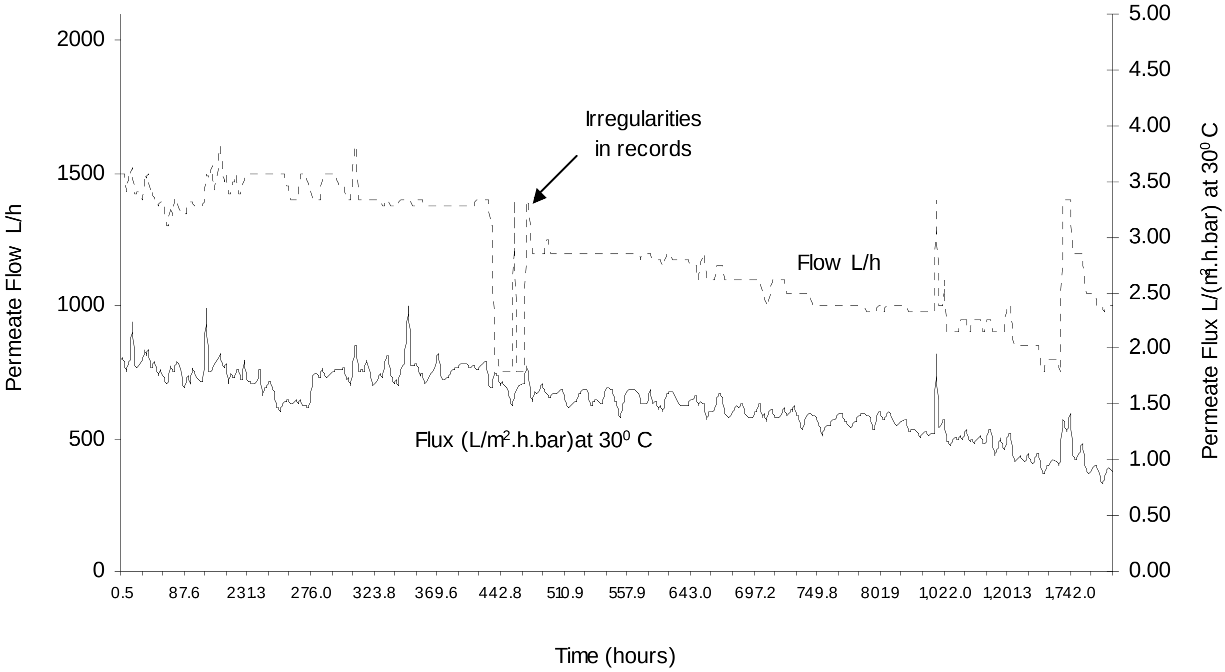


Figure 2. The permeate flux and flow variation as function of time in the NF Pilot Unit.

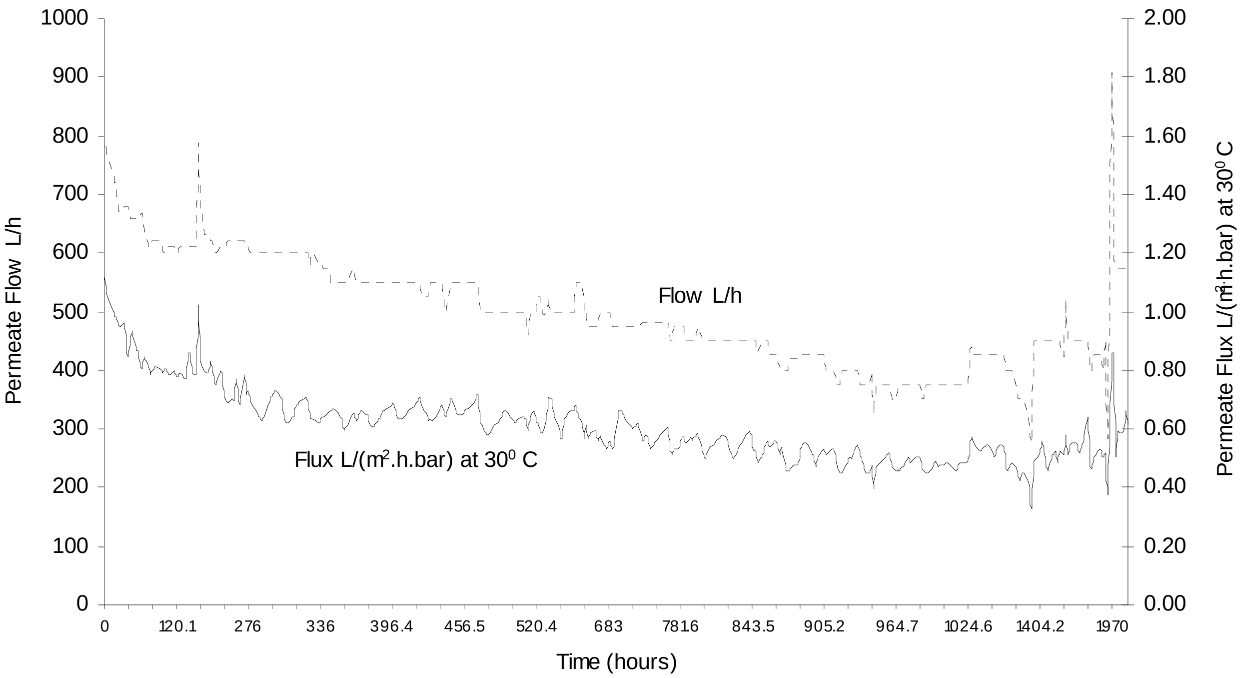


Figure 3. The permeate flux and flow variation as function of time in the RO Pilot Unit.

Figure 2 and 3 present the NF and RO filtration flux data recorded during the long term pilot runs. From these figures, it can be noted that the proposed pilot unit could be used for volume reduction of produced water, without any significant reduction in the permeate flux. The application of non-conventional approach of continuous addition of 20 mg/L of EDTA and 20 mg/L of NaOH prior to NF and RO modules reduces the membrane surface fouling. Here, one can note that both NF and RO flux has a similar trend, both decreasing slowly with time.

In spite of irregular spike in the pollutant concentration in the raw water, it did not affect the filtration much. Periodic chemical cleaning (once in every two weeks) of membranes was conducted as recommended by the membrane manufacturers to avoid continuous reduction in filtration flux. The final effluent quality of the RO permeate as indicated in Table 2, meets the required design quality. Based on this initial long-term pilot run, the pretreatment and membrane system operational parameters have been optimized, and a full scale plant is currently under operation.

## CONCLUSIONS

The treatment of produced waters is one of the major waste management problem the oil and gas industries are currently facing. The high volume of the produced water, and its high TDS concentration and associated variety of dissolved organic compounds, makes its treatment more complicated. As the conventional biological or physico -chemical treatment systems do not allow this waste stream treatment, there is a need to explore new advanced treatment options.

The pilot scale runs demonstrate that, RO system can be adopted for volume reduction of produced water. However, successful application of RO depends on various factors. The basic factor for the usefulness of RO system is dependent on appropriate pre-treatment matrix. Characteristics and concentration of pollutant present in the produced water is another factor, which controls the duration of successful application of RO system. Membranes should be cleaned regularly based on the initial produced water characteristics, which is responsible for effective run of membrane frequency. Since the quality of produced water does not remain constant all the time, it is essential to determine the produced water characteristic, which determines the pre-treatment process efficiency. The variation of feed water quality is the most important parameter, directly affecting the RO system efficiency and its effective run for long duration. Since the reject from the RO system contains various chemicals with high COD, it should be disposed safely or treated accordingly. Finally, it is essential to have an additional pretreatment unit with RO system to control fouling problem, which is obvious in membrane system when more concentrated waste is treated directly through the membrane.

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