

# Evaluation of Technical and Economic Feasibility of Treating Oilfield Produced Water to Create a “New” Water Resource

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## Abstract

A pilot study was conducted to evaluate technical and economic feasibility of treating oilfield produced water for beneficial reuse at the Placerita Canyon Oil Field, Los Angeles County, CA. Beneficial reuse options evaluated included industrial, irrigation and potable water use. The major water quality concerns are: the total dissolved solids (TDS) (~ 5,800 mg/l); temperature (170 °F); ammonia (10 mg/l); boron (16 mg/l); and organics. The produced water contained high levels of silica (255 mg/l), hardness (1,000 mg/l as CaCO<sub>3</sub>), and oil and grease that can potentially foul TDS removal processes such as reverse osmosis (RO).

The pilot units consisted of warm softening, coconut shell filtration, cooling (fin-fan), trickling filter, ion-exchange and reverse osmosis. The warm softening process removed (~95%) hardness from the produced water. Silica levels in the softening effluent were 80 and 20 mg/l at a pH of 8.5 and 9.5, respectively. Silica level decreased to 3 mg/l when 400 mg/l of MgCl<sub>2</sub> were added. More than 95% of TDS was removed by RO. Effective removal of boron (~ 90%) was achieved at a pH of 10.5 or above. Ammonia was removed effectively (80%) at a pH of 8.7 or below. The capital cost of the treatment varied from \$3.4 to 13.2 million. The annual O&M cost varied from 6 to 27 ¢/barrel of water treated.

Sensitivity analyses were performed to evaluate the impact of using waste caustic from refinery operations for the softening process. Analyses indicated that the impact of using waste caustic depended on the proximity of the source to the treatment facility.

# EVALUATION OF TECHNICAL AND ECONOMIC FEASIBILITY OF TREATING OILFIELD PRODUCED WATER TO CREATE A “NEW” WATER RESOURCE

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## Introduction

One of the undesirable by-products of oil production is the generation of produced water. The water-oil ratio (WOR) in some oil wells can be as high as 10 to 20 barrels of water per barrel of oil. Typically, due to the high salinity, boron, ammonia, and dissolved oil, produced water is disposed by Class II deep well injection near oil-production zones. As a field ages, the injection horizons start to “fill” within the oil reservoir, resulting in some degree of recycling of this injected water, loss of thermal efficiency in steam drive enhanced oil recovery operations and higher reservoir pressures which can effect oil production rates. These conditions cause an increase in oil production costs and, finally, result in leaving significant reserves of oil-in-place.

Finding another home for the produced water provides a solution to the above problem facing a significant number of US fields, and especially in California. Kennedy/Jenks Consultants recently managed a project team that performed a pilot study at the Placerita Canyon Oilfield Field, which is located in the County of Los Angeles near the City of Santa Clarita, California. The goal of this project was to evaluate the technical and economic feasibility of converting a currently unusable by-product of oil production, produced water, into a valuable water resource. To accomplish the project goal, the project team built a pilot plant to treat oil field produced water to current and anticipated California potable and reuse water standards. The project was divided into two phases. Under Phase I, a literature-based review of treatment technologies applicable for produced water was performed. Preliminary costs for treatment of produced water using various technologies were developed, and treatment process for pilot study was identified. Under Phase II, pilot testing of various process units were performed.

Based on pilot study results, treatment costs were developed to meet a variety of water quality goals. Sensitivity analyses were performed to evaluate the impact of some key parameters in produced water treatment costs. This paper presents the results of the pilot study and estimated treatment costs for treating Placerita Canyon oil field produced water to meet different water quality goals.

## Produced Water Quality and Evaluation of Treatment Processes

### Produced Water Quality

Produced water requires treatment for a number of water quality constituents depending on the intended water use. In California, there are no current drinking water regulations covering the use of treated produced water. However, there are reclamation standards and design criteria for treatment of domestic wastewater for a direct beneficial use or a controlled use that would not otherwise occur. There are also extensive federal and state regulations for drinking water.

Typical water quality characteristics of Placerita Canyon produced water and the key water quality goals for use through treatment in this project are summarized in Table 1. The major water quality concerns are the removal of Total dissolved salts (TDS) (4,000 - 6,000 mg/l TDS), ammonia (>10 mg/l - N), boron (~18 mg/l B), and organics (TOC ~100+). The presence of silica (~200+ mg/l SiO<sub>2</sub>), hardness (600 - 1,500 mg/l), and oil and grease (up to 50 mg/l) pose well-known problems as potential foulants for TDS removal technologies. In addition, confirmation that residual Total Organic Carbon (TOC) does not present a disinfection by-product formation issue is necessary to meet future drinking water regulations.

**Table 1.** Typical concentration of constituents in produced water and California MCLs/AIs

<b>Constituent</b>	<b>Produced Water</b>	<b>Treated Water Goal for this Study</b>	<b>Comments</b>
TDS (mg/l)	6,000	500	California primary MCL
Total Hardness	1,500	600	Industrial use goal
TOC	120	1 – 2 mg/l	To minimize THM formation
Ammonia	15	1	To minimize corrosion
pH	7		
Temperature	190	100	
Silica	200	200, 60, 30	Industrial use goal /prevent RO membrane fouling
Boron	20	1	California Action Level
Calcium	240		
Magnesium	70		
Chloride	2,400	500	California Secondary MCL
Sulfate	30	500	California Secondary MCL
Bicarbonate	800		
Oil & Grease	50		Membrane Fouling

### **Review of Treatment Technologies**

Produced water requires treatment for a number of constituents depending on the intended use. Because the produced water is delivered around 160 °F, pathogenic microorganisms are not of concern as with most wastewaters. However, the water temperature must be controlled for some of the processes to be effective. For example, warm precipitative softening, air stripping, and vapor compression desalination can be accomplished at the produced water temperature, while the other processes considered generally perform better at cooler temperatures.

Technology selection for this project was driven by TDS removal and appropriate pre- and post-treatments. The following sections identify potential treatment technologies for the concerns identified in the previous section.

### **Dissolved Salt Removal**

TDS of produced water must be reduced to below 500 mg/l for potable use. Treatment technologies to remove dissolved salt from water include thermal distillation and membrane processes. The most promising treatment technologies considered for removing dissolved salts from produced water are distillation by mechanical vapor compression (MVC) and membrane separation by reverse osmosis (RO). Within the desalination industry, membrane technologies such as RO are generally the technology of choice for brackish water applications.

Both of these proven technologies are capable of removing a large fraction (but not all) of organics and boron under certain pH conditions. Thus, supplemental TOC removal will likely be required. Silica removal, generally achieved by precipitative softening, is required as pretreatment for both processes, although some MVC systems incorporate silica removal as part of the main process, using a seeded silica slurry.

## **Organics**

Treated water TOC goal for this project is in the 1 - 2 mg/l range to satisfy future drinking water regulations and potential California DHS concerns. The removal of organics will be a major challenge because produced water from heavy oil fields are high in low molecular weight aromatic compounds and naphthenic acids. Both fixed-film biological oxidation and granular activated carbon (GAC) are candidate processes for organics removal. Because many of these organics are refractory, pilot tests are necessary to determine the efficacy of these processes.

## **Silica Removal**

Although there is no drinking water standard for silica, low silica concentrations are desirable for steam production and other industrial uses, and a project goal of 30 mg/l was set. Silica removal can be accomplished by precipitative softening. For the Placerita produced water, bench tests indicated this could be most effectively achieved under warm (150 to 170 ° F) conditions at a pH of 9.6 to 10.0, by adding magnesium and sodium hydroxide. Silica can also be removed by anion exchange.

## **Hardness Removal**

Moderate hardness in the range of 80 - 120 mg/l is generally desirable for drinking water, but lower levels may be needed to control scaling in the desalination process. Total hardness, including calcium and magnesium can also be removed concurrently with silica in the warm softening process. In addition, residual hardness remaining in the softened water can be removed by cation exchange. This is important if salinity removal is carried out at high pH.

## **Ammonia Removal**

Ammonia levels needs to be controlled below 1 mg/l to preclude a number of operational problems including increased corrosion in copper and copper alloys, additional chlorine demand, and increased biological activity in potable distribution systems that can lead to nitrification and enhanced biofilm formation. Some of the ammonia may be removed in the biological oxidation process and perhaps the RO process, but the remainder will have to be removed by air stripping. This may be accomplished in the cooling process or in separate strippers at high pH. Ammonia can be removed using ion exchange process also.

## **Boron Removal**

Boron removal is particularly important for water used for irrigation (typical goals of 0.5 - 0.7 mg/l). A treatment goal of 1 - 2 mg/l was set for this project. A large portion of the boron can be removed concurrently with silica in the warm softening process if sufficient magnesium is added. Boron can also be removed by RO at high pH or by ion exchange using special anion exchange resins.

## **Brine and Sludge Management**

The production of sludge in the precipitative softening process and brine in the desalination processes may be significant issues in operating the treatment processes. The recovery, or level of concentration in the brine, in part determines the amount of pretreatment necessary to prevent fouling of inorganic constituents, as well as the volume of the waste brine. The composition of the sludge will be important in determining whether the residuals have to be managed as a non hazardous waste. The volumes and compositions of the sludge and brine wastes must be confirmed by pilot studies.

## Treatment Goals

Four potential water use scenarios were developed for the treated water in this study, based on the needs of facilities around Placerita oil fields. They are briefly discussed below:

- Two scenarios pertain to industrial applications for steam flood operation of oil production, and electrical generation by a neighboring facility.
  - ? For the first scenario, the treated water goals are < 600 mg/l total hardness as CaCO<sub>3</sub> and < 200 mg/l of silica (High silica goal)
  - ? For the second scenario, the treated water goals are < 600 mg/l total hardness as CaCO<sub>3</sub> and < 80 mg/l of silica (low silica goal)
- The third scenario is to use the treated water for agricultural use. This involves blending of a portion of the treated water with untreated water. The key goals for this scenario are lower levels of salinity, boron and bicarbonate in the treated water
- The fourth scenario of the treated water is to use for drinking water supply. For this scenario, the treated water must meet all the Title 22 criteria for California Maximum Contaminant Limits and Action Limits

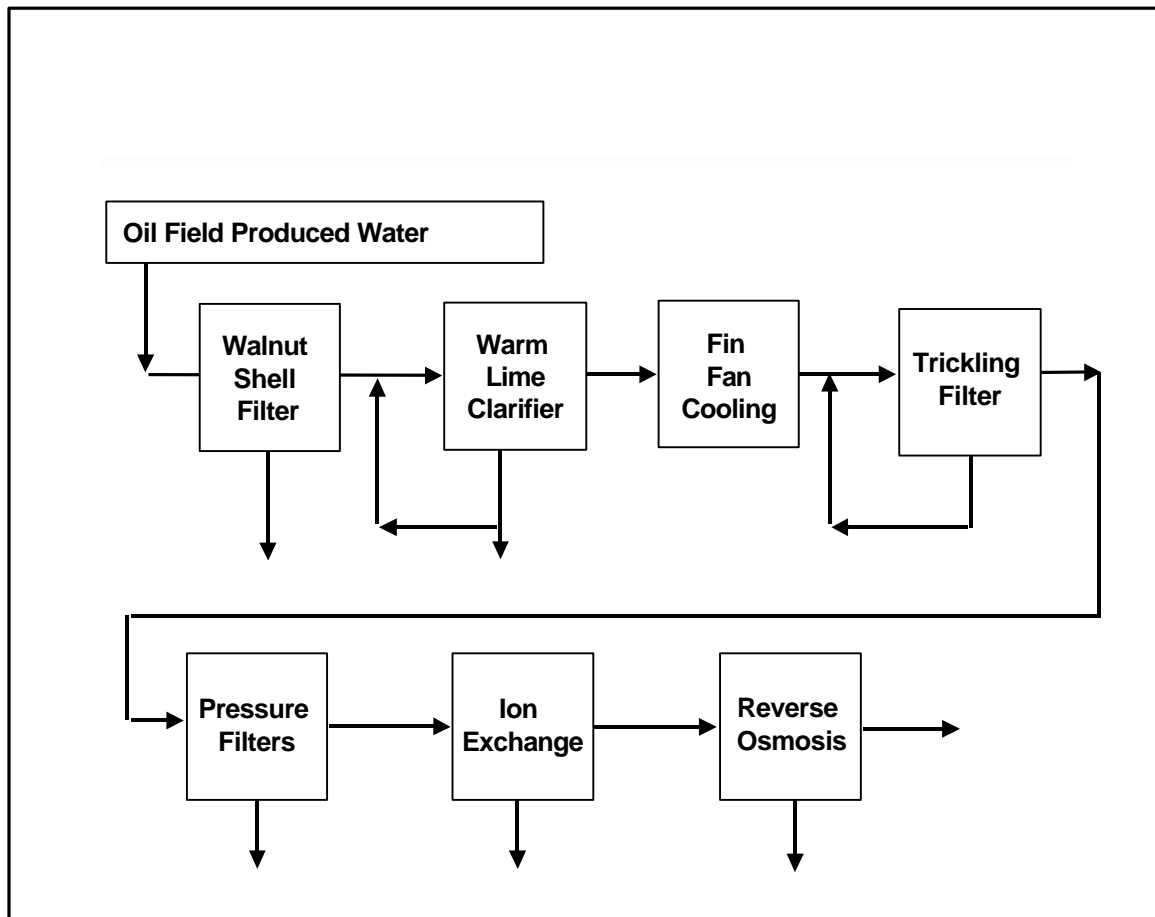
## Pilot Process Description

Figure 1 is a summary schematic of the pilot plant treatment process that was constructed at the Placerita Oil Field. The rationale behind the selection of process is described elsewhere (Leong, et al., 1997). The influent water was passed through a booster pump to achieve the target flow rate through the system and then to the DensaDeg warm precipitative softener. After the DensaDeg, the process water was sent to a 2,000 gallon constant head tank that provided water for the downstream pumps. Excess flow was sent to an overflow line connected to the system drain and was returned to ARCO's water handling system. From the constant head tank, the process water was pumped into a fin-fan type heat exchanger to cool the water from 150+°F to just above ambient air temperature. Such cooling was needed since the units downstream of the DensaDeg were susceptible to damage at temperatures above 100°F. After the heat exchanger, the water proceeded to the trickling filter for biological oxidation of organics. Biological oxidation was followed by a booster pump to increase the system pressure to 80-100 psig and the multi-media filters to remove any biological solids that may have sloughed into the process stream. During most stages of testing, the trickling filter was bypassed to allow the microbes produced to acclimate to the water organics. When bypassing the trickling filter, the water was sent directly from the heat exchanger to the booster pump. The process water was next sent through the pressure filters, then the ion exchange softeners to remove any residual hardness. Subsequently, reverse osmosis unit (RO) was to remove total dissolved solids (TDS), boron and additional organics. The RO permeate was sent to a 2,000 gallon polyethylene tank for storage. The concentrated reject stream was sent to the system drain.

The individual unit processes are further described below:

### Influent

Influent for the pilot plant comes from ARCO Western Energy's WEMCO induced gas flotation cell. The unit's is designed to deliver water with 0-5 ppm oil and grease. Water is taken from a recirculation line with approximately 20 psig of pressure and a temperature of approximately 160 °F.



**Figure 1.** Pilot Plant Schematic

### Warm Softening

Warm precipitative softening for silica and hardness removal was the first step in the treatment process. Sodium hydroxide (caustic soda), magnesium chloride, and an anionic polymer were added at different concentrations to the water to induce precipitation and aid in flocculation. The warm softening is accomplished with a DensaDeg unit provided by Infilco Degremont, Inc. The unit includes a reaction tank and upflow clarifier with lamella separators. Sludge thickening is accomplished as a sludge bed develops in the upflow clarifier. The unit is a 20-100 gpm prototype that can operate at approximately 100 gpm to provide a rise rate of 10 gpm/ft<sup>2</sup> in the clarifier. Sludge was periodically blown-down manually.

### Cooling

The Pilot Study utilized a Fin-Fan type heat exchanger to reduce the temperature of the process water. Cooling was necessary to protect components of treatment processes such as plastic packing media and thin-film composite RO membranes. The highest allowable temperature for these processes is approximately 100 °F, and a design cooled water temperature of 90 °F was used.

## Trickling Filter

Biological oxidation of organics was the next step in the full treatment train. A trickling filter was selected to evaluate biological organic oxidation at a range of loading rates. The goals for organics removal were 80 to 90 percent removal of soluble BOD to lessen organic fouling of membranes and achieve an RO permeate with less than 2 mg/L TOC.

The trickling filter was 5 feet in diameter with 20 feet of Q-PAC from Lantec Products, Inc. Q-PAC is made of polypropylene and has a nominal diameter of seven inches. There was approximately 400 cubic feet of packing material in the trickling filter. For this study the trickling filter was operated at a hydraulic loading rate of 2.5 gpm/ft<sup>2</sup> and an organic loading rate of 20 lbs/1000 ft<sup>3</sup> of media per day. In the initial phases, this unit process was bypassed to acclimate the bacteria to the produced water substrate. During this phase, the unit was operated separately in a semi-batch mode. Effluent from the warm precipitative softener was fed to the unit in a separate slipstream on a daily basis. Subsequently the unit was operated in a continuous flow through mode.

## Pressure Filtration

Two multimedia pressure filters were operated in parallel. The filters are 22 inches in diameter and have approximately 4 feet of multimedia filter material consisting of anthracite, sand, and garnet. The hydraulic loading rate for the filters is approximately 2.5 gpm/ft<sup>2</sup>. The filters were backwashed with RO permeate manually with down stream units (ion exchange and RO) off line.

## Ion Exchange

Two cation exchange columns in parallel were used to remove divalent cations that might cause scaling in high-pH RO for half of the testing period. Each column contained approximately 5 ft<sup>3</sup> of Ionac C-249 resin with a rated capacity approximately 25-30 kilo-grains per ft<sup>3</sup>. Regeneration is performed using a RO permeate for washing and making up the brine solution. For a half of the test period the hardness from the DensaDeg was low enough (<15 mg/L CaCO<sub>3</sub> Total Hardness) that the ion exchange units were bypassed.

## Reverse Osmosis

Reverse osmosis (RO) was the final unit in the treatment process as shown in Figure 1. It consisted of the following components: twelve 4" x 40" brackish water spiral wound membrane elements housed in 4 pressure vessels that were arranged in a 3-stage (2 x 1 x 1) array; two interchangeable banks of 5-micron filters that preceded the membrane elements; a high pressure pump; and a recycle line that returned a portion of the reject stream to the incoming feed. The membranes were Fluid Systems XR "extra-high rejection" polyamide elements. The flow configuration was set and maintained at a permeate recovery of 75 percent. The unit typically operated at feed pressures from 380 to 450 psig, but experienced feed pressures as high as 600 psig.

During its operation, the RO was tested at several feed water pH conditions ranging from pH 8.2 up to pH 10.8. The elevated pH range was intended to examine the rejection of boron that was reported by Dyke *et al* (1992). The low pH range was intended to examine the membranes' ability to reject organics. Adjustment of the pH was accomplished through the addition of caustic or sulfuric acid as required.

## PILOT TESTING RESULTS

The results from the pilot study are summarized in this section. This section is organized to discuss the fate of individual constituents of concern in various process units.

### Removal of TDS From Produced Water

The main unit process that addresses TDS removal is the RO. The DensaDeg unit increased the TDS slightly and depending on the pH adjustments, the TDS was not substantially changed until the RO unit. The TDS removal is summarized in Table 2. The average TDS of the water after treatment with all the pilot plant unit processes was 143 mg/L. The TDS would increase slightly in the conceptual design when stabilizing the water with respect to corrosion control and final disinfection.

**Table 2.** Average Removal of TDS by RO

Unit Process	Samples	Average TDS Concentration (mg/L)
Raw Water	5	5428
RO Feed	24	5,825
RO Product	45	143
RO Concentrate	41	24,447

### Hardness Removal

Hardness was primarily removed in the warm softening process. On some occasions ion-exchange was used to polish residual hardness of the DensaDeg effluent prior to RO treatment. Table 3 summarizes the hardness of the treated water at different pH levels. For an industrial water that only has a hardness water quality goal of 600 mg/L as CaCO<sub>3</sub>, the operational pH would be ~ 7.7. However, to meet the other water quality goals of this study, which have lower silica limits, the DensaDeg unit may have to be operated at elevated pH levels. Silica removal is discussed in the next sub-section. The total hardness from the DensaDeg spikes that occur as indicated by the high maximum values is primarily due to the floc carryover.

**Table 3.** Residual Total Hardness as CaCO<sub>3</sub> at Varying Operational pH of DensaDeg or Ion Exchange Softening

Operational pH of DensaDeg	7.5-8.5	8.5-9.0	9.1-8-9.5	9.6-10.0	>10	Ion Exchange
Average	221	112	64	15	6.1	15
Max	242	172	260	35	6.1	41
Min	200	37	10	8	6.1	3
Samples	2	7	24	14	1	7

### Silica Removal

Significant amount of silica was removed in the warm softening and RO processes (Table 4). The influent to DensaDeg unit had an average silica level of about 255 mg/l. When only 30 mg/l of magnesium chloride was added, approximately 90% of the silica was removed during softening at a pH of about 9.5. When the magnesium chloride concentration was increased (400 to 800 mg/l) nearly 98% of the silica was removed.

For the RO effluent, as the operational pH increased, the silica in the effluent increased. At the higher pH of 10.8 one would expect the opposite since more of the silica would be ionized. Perhaps, the membranes “leak” more molecules due to the higher pH.



**Table 4.** Summary of Silica as SiO<sub>2</sub> by Warm Softening and RO Treatment

Unit Process	Condition	Average Silica Concentration (mg/L)
Influent	NA	255
DensaDeg	pH 8.5-9.0	40
DensaDeg	pH 9.5-9.8	20
DensaDeg	Mg, 400-800 mg/L	3.8
RO Effluent	Influent pH 8.7	0.8
RO Effluent	Influent, pH 9.5	1.7
RO Effluent	Influent, pH 10	2.6
RO Effluent	Influent, pH 10.8	5.7

**Boron Removal**

Boron removal was evaluated using different approaches. The first approach involved varying the magnesium dose to the DensaDeg to facilitate removal by precipitation or sorption to the magnesium floc. The second approach was to change the pH ahead of the RO to change boron to ionic form for rejection by the membrane.

The effluent boron concentration from the warm softening unit was about 13.2 mg/l (20% removal) when 30 mg/l of magnesium chloride was added (Table 5). It decreased to 7.4 mg/l when the magnesium chloride concentration was increased to 400 to 800 mg/l.

Boron removal in the RO unit increased with increase in pH (Table 5). As the pH increases a larger fraction of the boron becomes ionized and rejected by the RO membrane. At pH 10.8 the residual boron concentration reduced to 1.9 mg/l. To meet the California action level of 1 mg/l, the pH may have to be elevated to above 11, which is beyond the long-term operational criterion of most polymeric membrane.

**Table 5.** Summary of Boron Removal by Warm Softening and RO Treatment

Unit Process	Condition	Samples	Average Boron Concentration (mg/L)	Cumulative Removal (%)
Influent	NA	59	16.5	NA
DensaDeg	Mg, 30 mg/L	72	13.2	20
DensaDeg	Mg, 400-800 mg/L	4	7.4	55
RO Effluent	Influent pH 8.7	16	6.1	63
RO Effluent	Influent, pH 9.5	12	4.8	71
RO Effluent	Influent, pH 10	6	3.9	76
RO Effluent	Influent, pH 10.8	7	1.9	88

### Ammonia Removal

Table 6 is a summary of the behavior of ammonia through the pilot treatment process. The pKa for ammonia at 30 C is approximately 9.2. As pH increases to near pH 11, more than 90 percent of the ammonia is un-ionized and not removed by the RO membrane. At pH 8.7 approximately 30 percent of the ammonia is un-ionized. The RO membrane removed approximately 80% of the ammonia at pH 8.7.

**Table 6.** Summary of Ammonia Removal by Pilot Treatment Units

Unit Process	Condition	Samples	Average Ammonia Concentration (mg/L)	Cumulative Removal (%)
Influent	NA	45	9.3	NA
DensaDeg	pH 9.5-9.8	47	8.6	7.5
Trickling Filter	pH 9.5	8	7.7	20
RO Effluent	Influent pH 8.7	16	1.8	81
RO Effluent	Influent, pH 9.5	16	5.7	39
RO Effluent	Influent, pH 10	8	5.2	44
RO Effluent	Influent, pH 10.8	7	11	118

### TOC Removal by Unit Processes

The DensaDeg removed very little of the TOC. It appears that most of the organics are soluble and smaller than the larger disinfection byproduct (DBP) precursors such as humic and fulvic fractions that have been reported to be removed by enhanced softening. The combined precipitative softening and trickling filter removed about 12 percent. The RO process removed majority of the organics (Table 7). Pretreatment using trickling filter slightly enhanced TOC removal at the RO.

**Table 7.** Summary of TOC Removal by Pilot Unit Processes

Unit Process	Condition	Samples	Average TOC Concentration (mg/L)	Cumulative Removal (%)
Influent	NA	60	107	NA
DensaDeg	Mg, 30 mg/L	50	97	9.3
RO Effluent	Influent pH 8.7	13	2.1	98
RO Effluent	Influent, pH 9.5	12	2.1	98
RO Effluent	Influent, pH 10	7	3.7	96.5
RO Effluent	Influent, pH 10.8	7	2.8	97.4
RO Effluent with Trickling Filter	Influent pH 8.9-9.9	8	1.8	98.3

### Warm Softening Sludge

It was observed that the volume of sludge production as a percentage of flow decreases with increasing flow rate and when operating with the high magnesium dose (Table 8). The sludge production with the high magnesium dose was expected and was due to the poor settleability of the magnesium floc.

**Table 8.** Summary of Sludge Production from the DensaDeg

Flow Rate	MgCl <sub>2</sub> Addition (mg/L)	Average Sludge Volume (% of Flow)	Average Percent Solids
40 gpm	100	1	6
27 gpm	100	2	8
19 gpm	100	4	3.5*
19 gpm,	400-800	12	2.4

\*Based on one trial.

An analysis of the DensaDeg solids indicates that the sludge is primarily a calcium carbonate, magnesium hydroxide, and magnesium silicate sludge. There were high concentrations of sodium and boron, which may restrict the beneficial use of the sludge as a soil amendment. Boron and sodium can potentially leach out causing problems for plant or soils with high clay content.

All testing for the sludge (California EPA rules as described in the California Code of Regulations, Title 22, Article 2, and Section 66261.24(a)(2)) indicated that it would not be considered a hazardous waste.

### RO Concentrate

The concentrate consisted of approximately 25 percent of the treated flow. The average TDS of 24,447 mg/l (Table 9) is approximately four times the TDS of the currently injected produced water. Comparison of the dissolved ions in the RO concentrate with that of the produced water currently injected indicated that the higher pH of the RO concentrate may be the only potential problem in disposing the concentrate. The pH of the concentrate can be appropriately adjusted by acid prior to disposal by deep well injection.

**Table 9.** Summary of Water Quality Parameter for the RO Concentrate

Parameter	Average	Max	Min
pH, units	9.0	10.2	7.65
Turbidity, NTU	0.65	0.9	0.4
Conductivity, $\mu\text{mhos}/\text{cm}^2$	36,370	42,600	16,000
TDS, mg/L	24,447	28,700	21,800
Sodium, mg/L	10,068	11,200	8,960
Magnesium, mg/L	40	207	2.5
Calcium, mg/L	14	47	2.5
Silica, mg/L	28	88	0.8
Iron, mg/L	0.43	3.65	<0.01

## Treatment cost for various water use scenarios

Table 10 shows the process units and capital, O&M and total treatment costs for different treated water goals. Capital cost estimates include both the actual construction (“bid”) costs and the indirect costs associated with implementing the project. The capital cost estimates are conceptual level estimates and assume a level site and have an accuracy of approximately -15 to +30 percent. The treatment cost was developed for a 44,000 barrel per day (bpd) produced water reclamation facility. Annual cost includes operations and maintenance costs and amortized capital costs. O&M cost includes chemicals, energy (electric power), labor, maintenance materials, and residuals disposal. In addition, a 10 percent contingency was added for administrative and unforeseen maintenance costs.

The treated water cost varied from \$0.09 /bbl (industrial use) to \$0.41/bbl for drinking water use. Chemical (caustic), electricity, replacement of membranes and disposal of RO concentrate are among the major factors impacting the cost of treating the produced water.

The cost for caustic is a major factor influencing the treatment cost of produced water. For the drinking water scenario, the cost of caustic is about 25% of the overall annual O&M cost. Any variation in the cost of caustic will significantly impact the overall cost for the treatment of produced water. Hence sensitivity analyses were performed for the use of an alternate source of caustic for warm precipitation in this project. This involved the use of spent caustic generated in petroleum refinery processes. Refineries use caustic for various process needs. For example, caustic scrubbers are used to scrub HCl gas from LPG streams. Also, they use caustic to scrub CO<sub>2</sub> gas from liquid butane stream. The HCl streams typically do not contain impurities and the spent caustic is relatively clean. In typical HCL scrubbing operations, the initial strength of the caustic is about 10% and it dilutes to about 2 to 3 % prior to disposal. The spent caustic from the CO<sub>2</sub> scrubber contains about 10 to 12% Na<sub>2</sub>CO<sub>3</sub>. The spent caustic from the HCl scrubbing is further neutralized and sent for offsite disposal. The sensitivity analyses for this study assumed that the spent caustic will be obtained from a refinery by paying only the transportation cost for hauling the spent caustic to the treatment site. The transportation cost varies with the distance and the mode of transport (truck vs. rail) and the quantity of caustic transported. Equivalent cost of caustic of hauling spent caustic (10%) 200 miles in a 90 barrel truck is about \$0.11/lb. The cost will decrease if caustic is transported by train and to a shorter distance. Sensitivity analyses were performed at equivalent caustic costs of \$0.025/lb, \$0.050/lb and \$.10/lb. The variation in O&M cost and the overall treated water costs are shown in Table 11.

**Table 10.** Process conditions and treatment cost of treating produced water for various water use scenarios

Use Scenario	Treatment Processes			Capital Cost (Million \$)	O&M Cost (Million \$)	Total Treatment Cost (\$/AF)	Treated Water Cost (\$/bbl)
	Unit Process	pH	Temperature				
Industrial (High Silica)	Warm Softening Equalization Storage pH Adjustment Sludge Handling	7.7	160 ° F	3.45	1.35		\$0.09
Industrial (Low Silica)	Warm Softening Equalization Storage pH Adjustment Sludge Handling	8.6	160 ° F	3.60	1.65		\$0.10
Agricultural	Warm Softening Cooling Equalization Storage Pressure Filtration Cartridge Filtration Reverse Osmosis Disinfection Sludge Handling Reject Disposal	9.5±     9.5±	160 ° F 105 ° F    105 ° F	11.80	4.90		\$0.41
Drinking Water	Warm Softening Cooling Equalization Storage Pressure Filtration Cartridge Filtration Reverse Osmosis pH Adjustment Ion-Exchange for Ammonia Disinfection Sludge Handling Reject Disposal	9.5 ±     10.8±  7.7	160 ° F 105 ° F    105 ° F  Ambient	13.20	4.20		\$0.41

**Table 11.** Impact of using spent caustic for warm precipitative softening

<b>Equivalent Caustic cost for hauling spent caustic (\$/lb)</b>	<b>Annual O&amp;M Cost for a 44,000 bpd treatment</b>	<b>Total Cost of treated water (\$/bbl)</b>
0.025	250,000	0.32
0.05	270,000	0.33
0.075	290,000	0.35
0.1	315,000	0.38

## Summary

The pilot study evaluated the technical and economical feasibility of treating oil-field produced water for use as a new source of water. TDS removal and appropriate pre and post treatment requirements dictated the selection of treatment processes for pilot study. Reverse Osmosis was the treatment of choice for TDS removal. Warm precipitative softening (DensaDeg process) was the pretreatment to remove hardness and silica to prevent membrane fouling. Fin-fan cooling, trickling filter, filtration units were also evaluated. In addition to TDS, hardness, silica, boron, TOC and ammonia removal were evaluated for some use scenarios.

Warm precipitative softening removed more than 90% of hardness at pH 9 or above. Optimum silica removal (90 %) was observed at about pH 9.8 during warm precipitation. Addition of magnesium chloride (400 to 800 mg/l) enhanced silica removal to 98 %. Some boron (20%) removal was observed in the DensaDeg unit. Addition of magnesium chloride (400 to 800 mg/l) enhanced boron removal to about 55%. The RO process effectively removed TDS over a range of pH (7.5 to 10.8). Boron was effectively removed (permeate concentration 1.9 mg/l) at a pH of about 10.8. Approximately 80% ammonia was removed at a pH of about 8.7 in the RO unit. Efficiency of ammonia removal decreased with increase in pH.

For treated water use scenarios (two industrial, agriculture and drinking water) were evaluated in this study. Results indicated that, the treated water quality goals for two industrial use scenarios could be achieved by warm precipitative softening. The treated water quality goals for the agricultural and drinking water scenarios can be achieved by warm softening followed by RO process.

The planning level cost of treating the produced water to meet the industrial water use was about \$0.12/bbl. The cost of treating the water to meet the agricultural or drinking water goals was about \$0.50/bbl. The cost of disposal of produced water by deep well injection is about \$0.010/bbl and the cost of potable water from state water project water is about \$0.10/bbl. While the cost of treating produced water is higher than the potable water from other sources, there are additional benefits to treating produced water. Treatment and use of produced water eliminates the need for injecting the produced water in oil production zones. This eliminates dilution of oil and build up of high pressure resulting in enhanced production of oil. A complete cost benefit analyzes needs to be performed to evaluate the economic viability of treating oil field produced water.

## References

1. Leong, L.Y.C., D. Fruth, J. Drago, G. Doran. 1997. Developing a Cost Effective Environmental Solution for Produced Water and Creating a "New" Water Resource. The 4<sup>th</sup> International Petroleum Environmental Conference, San Antonia, Texas (September).
2. Dyke, C.A., F.T. Tao, S. Curtice, D. Tuohey, R.D. Hobbs, J.L. Sides, J.D. Wieser. Removal of Salt, Oil, and Boron from Oil Field Wastewater by High pH Reverse Osmosis Processing, in the proceedings of the AIChE Annual Meeting, Miami Beach, Florida (November).