Produced Water Treatment for Reuse in Cyclic Steam Boilers and Crop Irrigation

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ABSTRACT

As water scarcity increases, reuse of the water generated by oil & gas exploration methods is becoming more prevalent. This is especially true in California's Central Valley, where the combination of oil & gas activity and historic drought conditions have pushed reuse to the forefront of many energy companies' efforts. With the main goal to treat produced water for beneficial reuse in their cyclic steam boilers and for agricultural irrigation, a Bakersfield, CA-based exploration and production company has found success with a treatment scheme featuring an electrolysis technology followed by a polymeric ultrafiltration (UF) membrane. Success of this treatment scheme was quantified via field testing in Bakersfield throughout the early part of 2015. The electrolysis technology provided upfront de-oiling and bulk suspended solids removal, while the UF membrane removed any remaining oil and suspended solids to acceptable reuse levels. The raw feed had an average turbidity of 842 NTU and the treatment scheme offered greater than 99.8% removal of turbidity. In addition, the oil levels being fed to the electrocoagulation unit were in the range of 50-150 mg/l, while the UF membrane consistently provided effluent with non-detectable levels of oil. The combination of solids and oil removal demonstrated to the oil producer that this treatment scheme provided effluent appropriate for their reuse purposes.

INTRODUCTION

Industry continues to face new challenges as water becomes increasingly scarce in many regions across the United States. One of the most discussed locations of water scarcity is California. Not only is California currently facing one of its worst droughts in recorded history, but the state is trying to maintain its position as the top agricultural region in the U.S. In 2013 the total value of agricultural cash receipts in California was $46.4 billion, making agriculture an extremely important industry for the state (Tolomeo, 2013). Agriculture is also the largest consumer of water in the state, accounting for 80% of California's water use (Guo, 2015). In facing the ongoing drought however, agriculture is struggling to not only operate as normal but to even keep fields alive as supply from the State Water Project and even Senior Water Rights literally dry up.

Alternatively, another major industry in California, oil & gas, faces the opposite issue, namely an overabundance of produced water that must be handled and managed. Throughout the history of the production of oil and gas, water has been a byproduct pumped out of underground formations along with the hydrocarbons. Oil & gas companies in California annually produce more than 2.5 billion bbl of water from all onshore and offshore production activities (Clark and Veil, 2009). With ever-increasing water demands and historic drought conditions, oil producers and water technology companies are working together to turn California's produced water into a water source.

Produced water poses a unique and complex treatment problem that does not respond well to traditional treatment methods. Not only does it contain high concentrations of various contaminants such as boron and silica, but produced water also contains oil levels in the range of 40-2,000 mg/l, total suspended solids (TSS) up to 1,000 mg/l, and total dissolved solids (TDS) in the range of 1,000-400,000 mg/l (Clark and Veil, 2009). In order to treat this water to acceptable reuse levels, water industry experts are working together with producers to develop innovative treatment techniques.

TREATMENT TECHNOLOGIES: In order to treat produced water for reuse applications, such as crop irrigation, a significant amount of contaminant reduction is required. Successful produced water treatment schemes will involve multiple sequential steps to combat the variety of contaminants present. Current technologies being tested and utilized for produced water treatment include hydrocyclones, induced gas flotation, walnut shell filters, electrolysis technologies, membrane filtration, ion exchange, chemical softening systems and more.

Electrolysis technologies enter this landscape as a promising step in treating brackish oilfield produced water. Electrocoagulation (EC) is an efficient way to de-emulsify influent streams by providing coagulating metal ions to a feed with high TSS and oil content. Electroflotation (EF) further enhances separation in gravity based separators by lowering the density of destabilized materials, which decreases the residence time required for separation and thus system footprint. Electro-oxidation (EO) provides disinfection and can even demineralize certain contaminants down to carbon dioxide (Hurwitz, 2013). All three of these electrolysis technologies require a conductive medium to perform effectively, making the electrolyte-laden produced water a natural fit. The combination of these three electrolysis technologies provides the complete initial pretreatment required for the reuse of most produced waters.

In order to further polish the water to reuse quality standards, another technology is sometimes required following the multi-stage electrolysis process. Ultrafiltration (UF) membranes offer a viable polishing step for produced water. Since UF operates via size exclusion, the large majority of remaining non-dissolved contaminants will be removed. However, traditional polymeric membranes are easily fouled by oil, so a more oil-tolerant membrane is required. The combination of electrolysis technologies as an initial suspended oil and TSS removal step, followed by oil-tolerant UF membranes as a polishing step provides a promising treatment scheme in treating produced water for reuse applications.

This paper explores the use of electrolysis technologies followed by an oil-tolerant polymeric UF membrane filtration for treatment of produced water at an oil production site in Bakersfield, CA. The oil producer's main treatment goals were to treat the water for the potential reuse in their cyclic steam generators or for crop irrigation.

WATER QUALITY REQUIREMENTS: In order for the oil producer to reuse their produced water, certain water quality requirements had to be met. Internally, their primary motivation for water reuse was as feed to their cyclic steam generators. Prior to their cyclic steam generators was a chemical softening system for hardness removal. The main influent water quality requirements for their softening system were non-detect levels of oil and <5 ppm of TSS. Because the produced water at the site where this study was conducted had salinity levels of less than 1,500 mg/l, only hardness removal, and not complete desalination, was required before being fed to the steam generators. The removal of these non-soluble parameters thus marked the first benchmark for reuse at this site.

The second area of interest for water reuse for the oil producer in Bakersfield was to investigate the feasibility of treating their produced water for crop irrigation. Water quality requirements differ by crop, but there are some general guidelines to follow for irrigation, including salinity control and toxicity control. In terms of produced water, significant oil reduction, TSS reduction, and TDS reduction are required. Table 1 below describes the general acceptable ranges for TDS and various ions in irrigation water. In order to meet acceptable salinity values for reuse as irrigation, an additional membrane desalination step was thus required and investigated for this study.

Table 1: Acceptable salinity ranges for irrigation water

Constituent	Units	Value
TDS	mg/l	0-2000
Calcium	mg/l	0-400
Magnesium	mg/l	0-60
Sodium	mg/l	0-900
Bicarbonate	mg/l	0-600
Sulfate	mg/l	0-1000
Chloride	mg/l	0-1000
Boron	mg/l	0-2
pH	--	6.0-8.5

(Martin, 1993)

METHODS AND MATERIALS

The testing site was at a cyclic steam stimulation heavy oil production site on the east side of Bakersfield, CA. Testing was conducted between February to May 2015. During normal operation at the facility, produced fluid containing low density oil, natural gas, and produced water flows to an upfront three-phase separator, commonly referred to as a gun barrel separator. Following upfront oil-water separation at the gun barrel, the produced water passes through a sequence of high residence time (up to 16 hours per tank) skim tanks before being deep-well injected for disposal.

Feed water for testing was taken from the water leg of the upstream three-phase separator. The influent was first fed to an upfront 25 micron suspended solids self-cleaning filter. Following upfront coarse solids filtration, the electrolysis system was placed to break the influent emulsion and separate out the destabilized oil and suspended solids before being fed to the UF unit for final polishing. Figure 1 shows the process flow diagram for sequential treatment of produced water during testing.

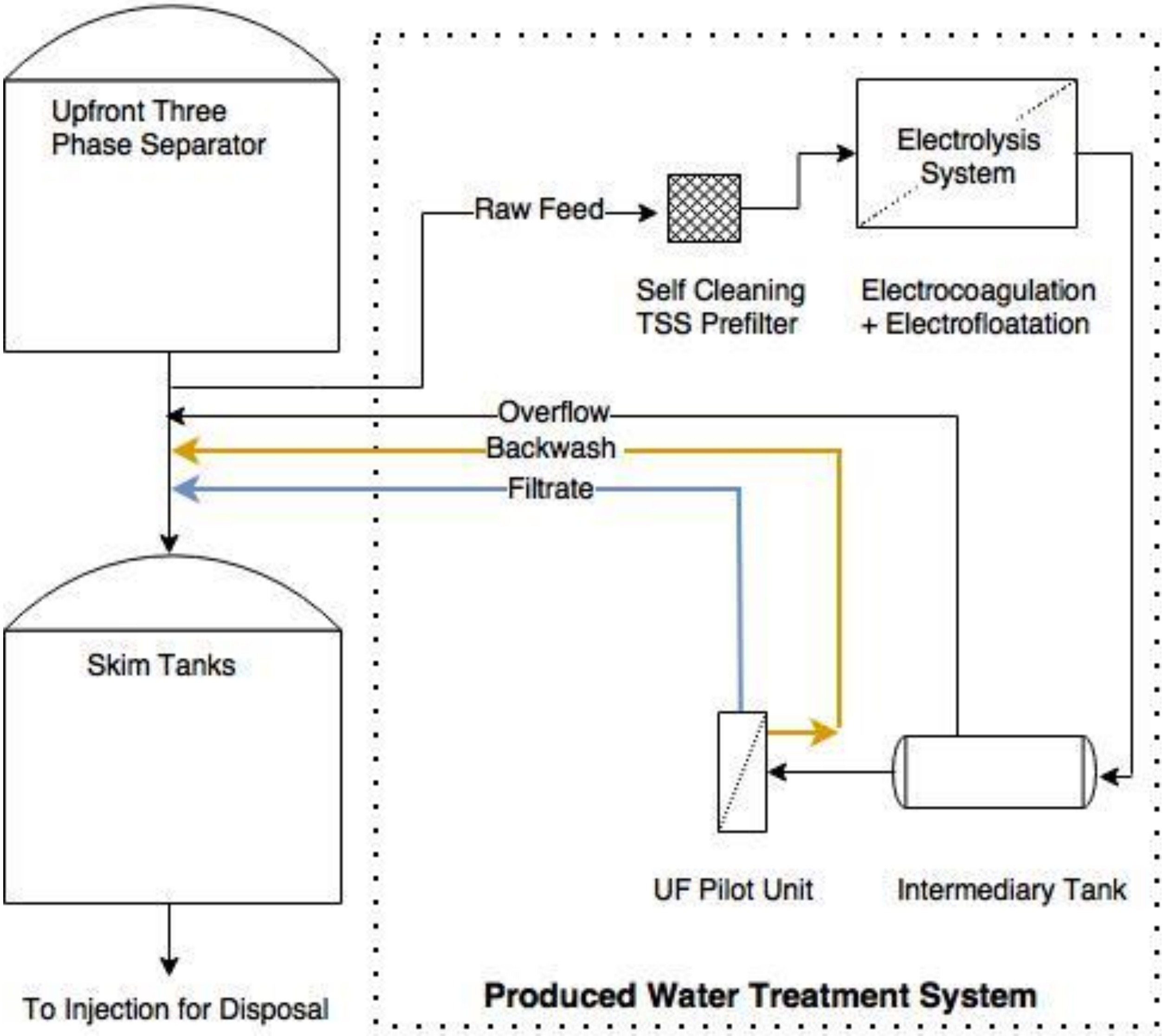

Figure 1: Process flow diagram for testing

The electrolysis unit operated in this study was the Electro Water Separation, *EWS©*, system provided by OriginClear. The system was comprised of three stages of electro-chemistry within the singular footprint: 1) electro-coagulation, 2) electro-floatation and 3) electro-oxidation.

The electrolysis system was designed to remove up to 95% of non-soluble contaminants and provide an initial dose of disinfection. The unit is controlled by a programmable logic controller (PLC), which operates the system at set treatment capacitates and maintains fluid levels within the separation chambers automatically. Floated destabilized material was collected in an oil sludge trough, which would automatically purge during operation. Settled solids removed in the system were collected in multiple solid collection points and purged periodically during operation. After pretreatment by the electrolysis system, the effluent was fed downstream for UF polishing.

The UF unit features an *i*Sep™500-PVDF module, a permeate (vacuum) pump, permeate tank, backwash pump, chemical metering pumps, blower, automated valves, and other instrumentation. The UF module contains a proprietary 0.03 micron pore size polyvinylidene fluoride (PVDF) membrane that has significantly greater oil tolerance (up to 300 mg/l oil) than traditional polymeric UF membranes. The module itself is a spiral-wound, submerged-style (vacuum-operated) module with air-scouring and backwashing capabilities. The UF unit contains a touch-screen HMI for control and automation, and all process sequences, including production, backwash, and chemically-enhanced backwash. The HMI also displays appropriate operating conditions, such as feed flow, trans-membrane pressure (TMP), and temperature.

During normal operation, the intermediary tank was purged to the downstream skim tank separators and refilled every 20 minutes by the electrolysis unit. Water from the intermediate tank was then fed to the UF unit. The UF unit was programmed for automatic backwashes every 15 minutes using permeate from its on-skid permeate tank. UF backwashes, permeate, and reject all recirculated back to the intermediary tank.

PERFORMANCE CHARACTERIZATION: For onsite characterization into the removal of non-soluble contaminants, such as oil & grease and TSS, a Hach 2100Q was used to manually record turbidity values. Periodically, sampling was performed and provided to third party analytical labs to analyze total recoverable petroleum hydrocarbons by the hexane extraction method (TRPH-HEM), biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS) and total petroleum hydrocarbons by GC/FID.

For investigation in the feasibility of complete desalination, UF permeate was collected for use in laboratory cell tests utilizing two separate polyamide reverse osmosis (RO) membranes. This type of flat sheet testing is a critical tool to assess the treatability of certain waters and gives a good indication of a membrane's removal capabilities for a specific application. The final desalinated permeate from the RO cell testing was tested for TDS, sodium adsorption ratio, boron, and TPH by GC/FID by an independent third party analytical lab.

RESULTS

MEMBRANE OPERATION: The UF unit was initially operated at a nominal module flux of 25 gallons/ft^2/day (gfd). Following successful initial operation, the flux was increased to a nominal 30 gfd. Since the UF continued to receive high quality water from the electrolysis system, 30 gfd was maintained for the remainder of testing. TMP and permeability remained fairly steady throughout operation, as shown in Figure 2. This shows that the UF did not experience prohibitive fouling, despite the presence of oil in the feed.

Backwashes were performed using permeate stored in the on-skid UF permeate tank and were conducted every 15 minutes for a period of 60 seconds. The backwash flow rate was set at a flow rate equal to two times that of the production flow. No chemical enhancements were employed during backwash.

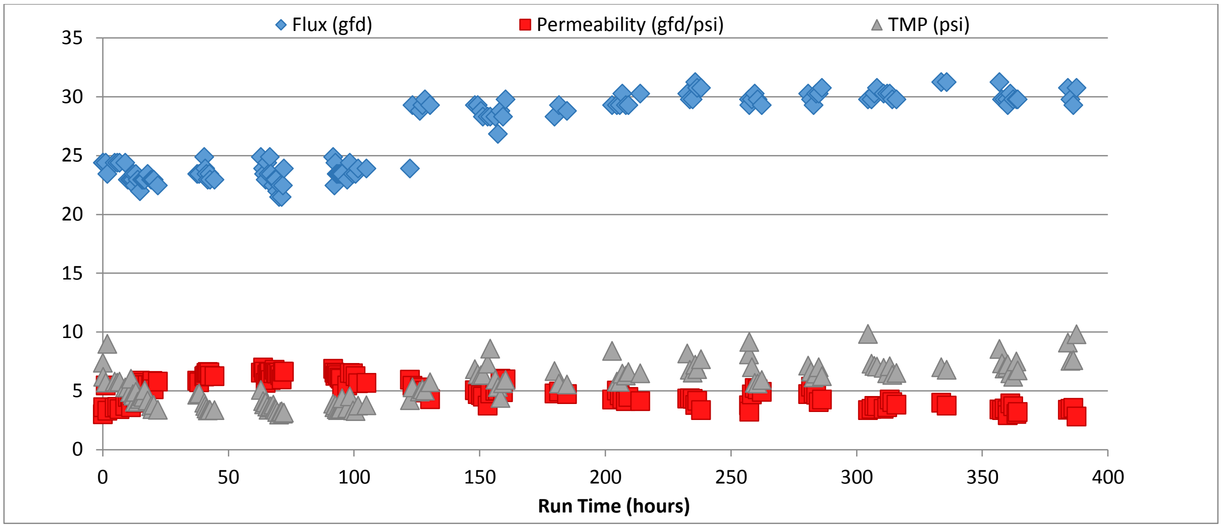

Figure 2: Flux, permeability, and TMP of the UF throughout operation

TSS / OIL REMOVAL: During testing, turbidity was used as a quantitative indicator of oil & grease and TSS removal, and was employed onsite in lieu of more time and equipment intensive analytical testing. Influent and UF pilot effluent turbidity values are summarized in Figure 3. The data shows consistent final water clarity over the complete operating time. The average turbidity reduction for the entirety of operation was found to be 99.8%.

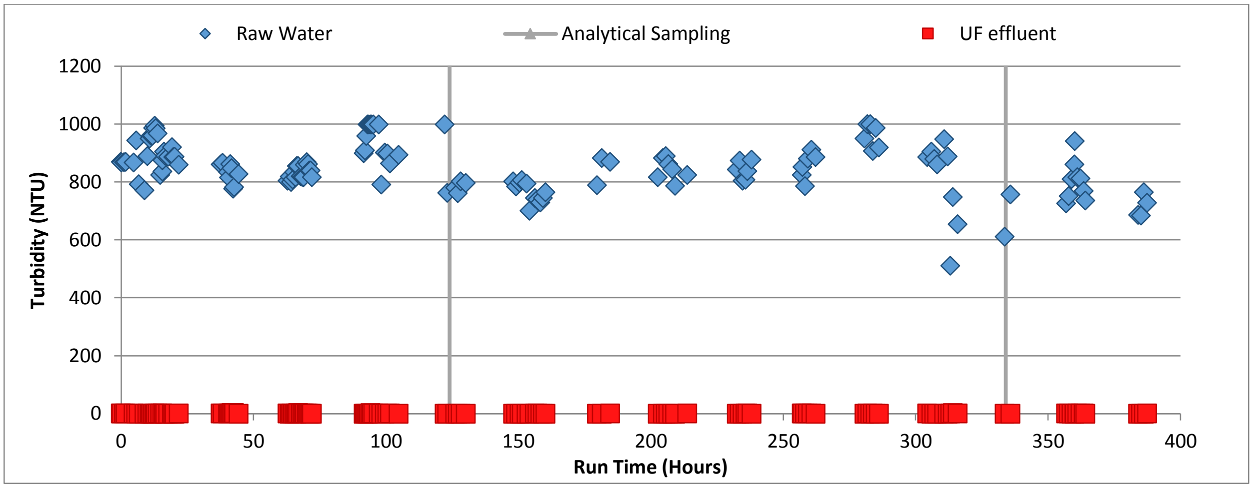

Figure 3: Influent and effluent turbidity over full operating duration

EFFLUENT CHARACTERIZATION: Further analytical testing was performed by a 3rd party lab on two occasions as shown in Figure 3. The results were averaged and summarized in Table 2. Results showing comparative values are representative of the limit of quantification. In these circumstances, the minimum detection limit was used in calculating the mean and removal efficiency.

Table 2: Analytical testing values during regular operation (mg/l)

Constituent	**Influent**	**Process Effluent**	**Reduction**
BOD	17.5	4.3	75.7%
COD	385	32.5	91.6%
TSS	101	3.0	97.0%
TRPH	63	<5.0	>92.0%
GAS RANGE	0.261	<0.057	>78.1%
DIESEL RANGE	131	1.50	98.9%
MOTOR OIL RANGE	147	<0.59	>99.6%

DESALINATION TESTING: The complete process effluent from this site was sampled and used as feed for two polyamide RO membrane cell tests. Two types of RO membrane were used to further validate the potential to use RO, with membrane Type 1 being a low-fouling brackish water RO membrane, and Type 2 being a standard brackish water RO membrane. The permeate produced from the bench top membrane tests was then analyzed for an agricultural ion composition assessment and TPH by GC/FID. These results are summarized in Table 3.

Table 3: Polyamide membrane performance data (values in mg/l unless specified)

Constituent	**UF**	**Type 1**	**Type 2**
Conductivity (mmhos/cm @ 25 C)	1.6	0.014	0.012
Calcium	44	0.96	0.96
Magnesium	5.4	0.17	0.17
Sodium	250	<7	<7
Potassium	9.6	1	0.99
Bicarbonate Alkalinity	700	6.1	4.6
Chloride	71	<2	<2
Sulfate	33	<0.5	<0.5
Nitrate	<2	<2	<2
Boron	3.1	1.3	1.2
Sodium Adsorption Ratio	9.9	0.7	0.6
Gypsum Requirement (lb/ac-ft)	541	1978	1927
Gas Range	<0.050	<0.050	<0.050
Diesel Range	1.4	<0.050	<0.050
Motor Oil Range	<0.15	<0.15	<0.15

ENERGY CONSUMPTION: During initial operation, the average specific energy consumption for the complete electrolysis and UF treatment process was found to be 0.12 kWhr/bbl. After preliminary operation the electrolysis system was modified to provide an increased electrocoagulation dose and the new specific energy consumption was 0.22 kWhr/bbl.

DISCUSSION

TREATED WATER QUALITY: The final effluent water quality results of the electrolysis and UF treatment scheme, as summarized in Table 2, show high removal efficiency in both TSS and oil & grease constituents.

While detection limits of the analytical tests used prevent an exact determination of percent reduction for TRPH, gas range, and motor oil range constituents, overall high percent reductions are implied by the data. For TRPH, the EPA 1664 hexane extraction method has a minimum detection limit of 5 mg/l. With a value of 63 mg/l in the raw feed, this implies greater than a 92.0% reduction in TRPH. Even higher percent reduction is shown by the diesel range constituents at 98.9%. Finally, motor oil range constituents in the final effluent were below the detection limit of 0.59 mg/l, implying greater than 99.6% reduction. In addition, high TSS removal was shown with a 97.0% reduction.

The aforementioned percent reduction values demonstrate the electrolysis and UF treatment scheme's high efficacy at removing suspended oil and solids from water.

REUSE AS BOILER FEED: The oil and suspended solids content of the treated effluent was effectively reduced to below or near the detection limit, indicating near complete reduction of the non-soluble parameters present. The quality achieved met the influent parameters for onsite reuse as feed to the chemical softening system and confirmed the feasibility of reusing treated produced water for additional oil and gas production processes.

REUSE FOR IRRIGATION: As shown earlier in Table 1, the reuse of produced water for irrigation requires TDS removal, such as by RO. Polyamide RO membranes require extremely low levels of TSS and oil & grease for successful operation, which are provided by this electrolysis and UF treatment scheme. In addition, the relatively low TDS, (between 900 and 1,500 mg/l) found in east Bakersfield produced waters allows for standard RO desalination as long as there is adequate pretreatment. The analytical results from the RO cell testing, as shown in Table 3 above, meet the acceptable salinity ranges for irrigation water in Table 1. As a result, the electrolysis and UF treatment scheme followed by RO offers acceptable treatment for general crop irrigation.

ECONOMIC ANALYSIS: The economic analysis for this electrolysis and UF process is based off of the total operating costs of the process. Based on the specific energy consumption for the entire process, the energy cost was $0.018/bbl of water to $0.033/bbl at $0.15/kwh. Adding the consumable and maintenance cost to the energy cost, the total operating cost without labor was about $0.14/bbl or $1,086/acre-ft.

The market for water in Central California, where this pilot test was performed, ranges based on the quality and availability for a local fresh water source. Based on those factors, fresh water can sell for \$100 – \$200 \$/ac-ft for parties with water rights and available supply, while on the open market in areas of short supply it can demand a price up to \$1,500 – \$2000 \$/ac-ft (Krieger, 2014). Thus, the \$1,086/acre-ft water cost given by the electrolysis and UF treatment scheme makes economic sense for regions where water is in short supply.

FURTHER REUSE POTENTIAL: To increase the reusability of the water produced by this treatment scheme, further removal of boron is required. The flat sheet testing conducted for the RO desalination feasibility test was done at the produced water's ambient pH of 7.6. At neutral pHs boron is more commonly in the form of boric acid, and thus has a lower rejection with RO membranes. However, as pH is increased the boron is converted into borate, which an RO membrane can better reject. For this study the implementation of pH modification upstream and downstream was not investigated. However, for future applications of this treatment scheme, pH modification of the stream before RO offers a method to further reduce boron.

CONCLUSION

The produced water treatment scheme employed at the oil producer's site in east Bakersfield, CA met their reuse requirements. The treatment scheme involved an electrolysis system for initial oil and solids removal followed by a UF membrane system for further polishing. The two main areas of interest for reuse for this oil producer are: 1) for their cyclic steam generation system, and 2) for crop irrigation. Sufficient TSS and oil removal by the electrolysis and UF treatment scheme made produced water reuse feasible for the cyclic steam generation system. Similarly, the electrolysis and UF treatment scheme effectively prepared the produced water for RO. The RO permeate from further testing meets general water quality requirements for reuse in crop irrigation. Most importantly, the oil producer was satisfied with the results given by the treatment scheme for reuse potential.

While these exact results only apply to this specific site, the implications of these results can apply to many other sites in California and beyond. Further research and development will help to make the described treatment scheme a viable solution. Since produced water can vary in quality from well to well and even day to day, further testing at other sites would help qualify the electrolysis and UF process for reuse applications even further. In addition, research and development on the regulatory landscape surrounding water reuse will help this treatment scheme become a commercial reality.

Overall, this site testing represents only a small part of the complex water issues in California, but the promising results generated merit further research and development. As water quality regulations become increasingly stricter and water becomes increasingly scarce, unique treatment schemes such as the one described in this paper will become extremely valuable.

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