Report Title:

# DEVELOPING A COST EFFECTIVE ENVIRONMENTAL SOLUTION FOR PRODUCED WATER AND CREATING A "NEW" WATER RESOURCE

| | |
|---|---|
| Report Type: QUARTERLY | Reporting Period Start Date: 01/01/1997 End Date: 03/31/1997 |


Principal Author(s): Glenn Doran
ARCO Western Energy
4550 California Ave.
Bakersfield, CA 93302
(805) 321-4090



| | |
|---|---|
| Report Issue Date: 04/28/1997 | DOE Award No.: DE- FC22 -95MT95008 |



Submitting Organization(s) Name & Address

Glenn Doran
ARCO Western Energy
4550 California Ave.
Bakersfield, CA 93302 (1)


(2)



(3)

(4)

(5)

## DISCLAIMER

## ABSTRACT

This report summarizes the status of this project for the quarter January 1, 1997 to March 31, 1997. Phase II has been started and Task 7, Develop Pilot Scale Test Work Plan has been completed. The operational portion of this phase, Task 8 has been initiated with several pieces of pilot equipment already on-site. The start up of the full process train will not occur until the next quarter. The project is slightly behind schedule. A no cost extension was requested and was granted. The anticipated completion date is December 31, 1997. The project is on budget.

## TABLE OF CONTENTS

**PRODUCED WATER, A "NEW" DRINKING WATER RESOURCE**
**DRAFT QUARTERLY TECHNICAL PROGRESS REPORT**
**FOR THE QUARTER JANUARY 1, 1997 TO MARCH 31, 1997**

## EXECUTIVE SUMMARY


Produced water from the Placertia Oil Field in California will be used for the study. If this project is successful, a commercial scale treatment plant may be built for the Santa Clarita Valley, California. The following was performed in Phase I: analyze current and anticipated state and Federal regulations, perform a detailed literature search of water treatment technologies to meet these regulations, and test at bench scale promising technologies. Phase I has been completed. Phase II involves the following: construct and operate a pilot plant to collect water quality and operational data, and transfer this technology. Phase II started in the first quarter of 1997.

The key produced water quality issues are total dissolved solids (6,000-10,000 mg/L), organics associated with oil (Oil and Grease ~50 mg/L and Total Organic Carbon ~ 120 mg/L), ammonia - N (~15 mg/L), borate (~66 mg/L), water temperature (~170 F), and disinfection byproducts.

The literature review indicated that a membrane based treatment train ( reverse osmosis (RO)) had a lower capital and operating cost than a thermal based technology (mechanical vapor compression (VC)). The planning level estimates for a full scale 42,000 barrel per day product water capacity plant for capital were $11 million and $27 million for the RO and VC, respectively. On an annual cost basis with operations and maintenance the estimated costs were 21-27 and 70 cents per barrel, respectively. VC does not remove ammonia and has a 90 percent removal for organics. The thermal based technology has to have processes to remove these parameters which increased the capital and operational cost.

The bench scale work determined that the hot precipitation process provides no additional advantage over warm precipitation in terms of silica removal. The optimal removal for silica and boron occurred when magnesium was added and the pH was adjustment to 9.5-9.7. Residual silica and boron concentrations at this pH were between 5 and 10 ppm. Residual hardness at these conditions ranged from 100 to 150 ppm total hardness. The bench scale studies indicated that enhanced softening did not remove additional organics.

The tentative pilot process train includes the following:

- Precipitative soften at pH 9.5-10.0 to remove some hardness and boron and most of the silica,
- Heat exchange cooling and pH reduction,
- Fixed film biological oxidation of organics and ammonia removal using a trickling filter,
- Filtration,
- Ion exchange softening to remove residual hardness,
- Reverse osmosis at pH 8.0-11.0,

Water stabilization for internal corrosion control, and disinfection would be required in a full scale system but will not be pilot tested.

The project team is pulling together the necessary equipment to assemble the pilot plant. Pilot scale activities have already begun and will be in full swing by the end of May 1997.

## INTRODUCTION

This quarterly progress report is an update of each task.

## RESULTS AND DISCUSSION

Phase I has been completed and a draft Phase I Summary Annual Technical Report was submitted.  The project is in the early portion of Phase II, Task 8.

### Phase I - Literature review and bench scale studies

#### Task 1A:  Organize a technical review committee.

This task is 100 percent compete and was described in the previous quarterly report.

#### Task 1B:  Manage the Technical Review Panel

This task is 100 percent complete for Phase 1.  A March 6, 1997 meeting was held to obtain verbal comments.  These comments are documented in Appendix A of this quarterly report.

#### Task 2:  Literature Review

This task is 100 percent complete and summarized in the Phase 1 Annual Technical Summary Report.

#### Task 3:  Formulate Alternatives

This task is 100 percent complete.

#### Task 4:  Work Plan for Bench Scale Studies

This task is 100 percent complete.

#### Task 5:  Perform Bench Scale Studies

This task is 100 percent complete.

#### Task 6:  Literature and Bench Scale Report

This task is 100 percent complete.

#### Task 10A:  Technology Transfer

Several abstracts have been submitted for presentations at professional meeting of the Phase I activity and are listed below.

1) Developing a New Water Resource from Oil Field Produced Water
   Water Resources ’97, AWWA Sponsored Specialty Conference
   Seattle, Washington

August 10-13, 1997
Corresponding Author: Darrell Fruth
Status: Accepted for poster presentation

2) Evaluation of Technologies to Treat Oil Field Produced Water to Drinking Water or Reuse Quality
Society of Petroleum Engineers Annual Conference
San Antonio, TX
October 6-8, 1997
Corresponding Author: Glenn Doran
Status: Accepted

3) Simultaneous Removal of Silica and Boron from Produced Water by Chemical Precipitation
1997 International Water Conference, Engineer's Society of Western Pennsylvania
Pittsburgh, PA
November 3-5, 1997
Corresponding Author: Joseph A. Drago
Status: Accepted

**Phase II-Pilot Scale Studies**

**Task 1C: Manage Technical Review Panel**

There was a second meeting of the Technical Review Panel, Technical Review Committee, California Department of Health Services and the California Regional Water Quality Control Board, Los Angeles on 6 March 1997. Ms. Nancy Holt, the contract officer representative (COR) also attended this meeting.

The next activity planned is a review of Task 7 documentation which should be completed in the next quarter. In the fourth quarter of 1997, the above project participants will be reviewing the draft final report.

**Task 7: Develop Pilot Scale Test Work Plan**

The work for this task has been completed. The plan has two components, namely, the work plan presented in Appendix B of this report and the operating plan and water quality sampling plan is presented in Appendix C. The plans identify the treatment processes, the anticipated operating conditions, sampling points, and parameters to be monitored. We are awaiting the review and comments from the Technical Review Committee, Technical Review Panel, California Department of Health Services, and the California EPA, Regional Water Quality Control Board, Los Angeles Region. The process train schematic and appropriate engineering drawings are also included in Appendix B.

**Task 8: Perform Pilot Scale Test Studies**

Three unit processes are currently on-site. The final unit process is scheduled to arrive on-site in May 1997. Final hydraulic testing will take approximately one week and then full pilot studies will begin. The plan calls for 5 months of operations with 3 full months of data collection. This task is on schedule.

**Task 9: Pilot Scale Test Study Summary and Final Report**

This work is scheduled to start in the fourth quarter of 1997. We are currently on schedule with this activity.

**Task 10B: Technology Transfer, Phase II Activities**

This work has started. Abstracts have been submitted and accepted to the meetings listed below. It is anticipated that the presentations could then be turned into an appropriate publishable paper.

1) Treating Oil Field Produced Water to Drinking Water Standards: Pilot-scale Process Evaluation
   American Water Works Association Water Quality Technology Conference,
   Denver CO,
   November 7-11, 1997
   Corresponding Author: Joseph A. Drago
   Status: Accepted for poster presentation

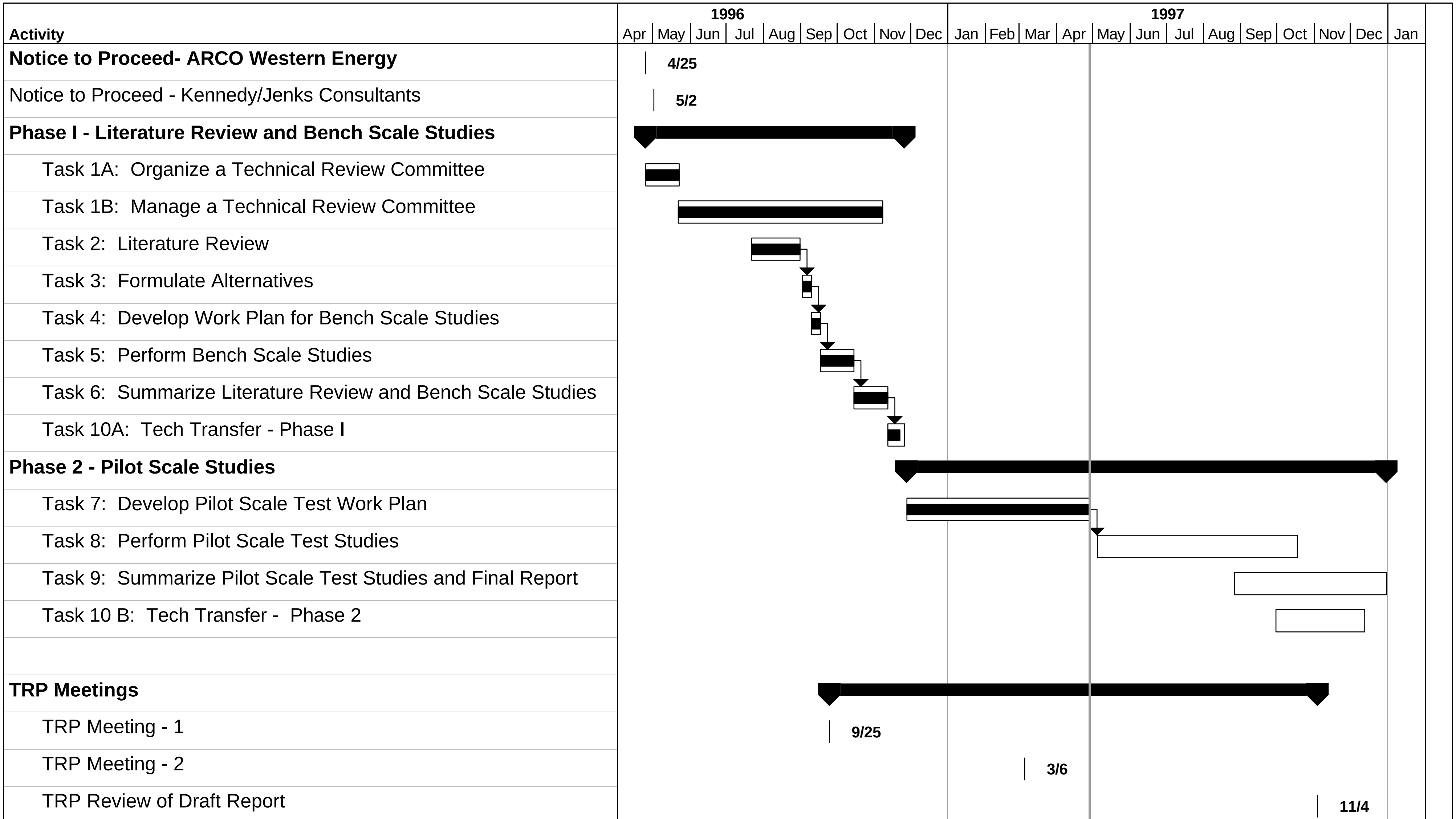
2) Developing a Cost Effective Environmental Solution for Produced Water and Creating a "New" Water Resource
   South-Central Environmental Resource Alliance, University of Tulsa, and DOE
   Fourth Annual International Petroleum Environmental Conference
   San Antonio, TX
   September 9-12, 1997
   Corresponding Author: Darrell Fruth
   Status: Accepted

**SCHEDULE**

A project schedule is attached. It indicates that the estimated project completion in December 1997. The current project completion date is June 24, 1997. A no cost extension was requested for 31 December 1997 and was accepted.

**CONCLUSIONS**

Phase I has been completed and the field portion of the pilot study, Task 8 of Phase II is about to begin. Five abstracts that have been submitted for presentation have been accepted. The project is on schedule. A no cost extension was requested and has been accepted. The anticipated completion date is December 31, 1997. The project is on budget.




ARCO Western Energy and Kennedy/Jenks Consultants
DE-F22-95MT95008
KJ 964634.00

Task
Progress
Milestone
Summary
Rolled Up Task
Rolled Up Milestone
Rolled Up Progress

## APPENDIX A

### Summary of Comments from the 6 March 1997 Meeting with the Technical Review Panel, Technical Review Committee, and Regulatory Agencies

A meeting was held on 6 March 1997 at the pilot plant site from 8:30 to 4:30. The meeting site was at the ARCO Western Energy Placerita Oilfield located at 25121 N. Sierra Hwy, Newhall, CA 91321

### List of Attendees

The list of attendees and respective roles is summarized in Table A.1.

**Table A.1**
**6 March 1997 Meeting Attendees**

| Name | Affiliation | Project Role |
|---|---|---|
| Nancy C. Holt | DOE | Contract Officer Representative |
| Glenn Doran | ARCO Western Energy | Project Manager |
| Ron Hollier | ARCO Western Energy | Reservoir Geologist |
| Kim Williams | ARCO Western Energy | Facilities Engineer |
| Howard Gober | ARCO Western Energy | Placerita Field Manager |
| Larry Leong | Kennedy/Jenks Consultants | Project Manager |
| Joe Drago | Kennedy/Jenks Consultants | Project Engineer |
| Darrell Fruth | Kennedy/Jenks Consultants | Engineer |
| Steve McLean | Castaic Lake Water Agency | Project Manager |
| David Kimbrough | Castaic Lake Water Agency | Laboratory Supervisor |
| Lynn Takaichi | Kennedy/Jenks Consultants | Technical Review Committee |
| Michael Dubrovsky | Chevron R & D Company | Technical Review Committee |
| Lory Larson | Southern California Edison | Technical Review Committee |
| Ammi Amarnath | Electric Power Research Institute | Technical Review Committee |
| Bob Hultquist | California Department of Health Services, Drinking Water Program | Ad Hoc Institutional Reviewer |
| Magdy Baiady | California Regional Water Quality Control Board, Los Angeles | Ad Hoc Institutional Reviewer |
| Ron Linsky | Executive Director, National Water Research Institute | Technical Review Panel (TRP) Administrator |
| Robert Carnahan | University of South Florida | TRP |
| Harvey Collins | DHS, Retired | TRP |
| Stanley Ponce | Bureau of Reclamation | TRP |
| Walter J. Weber, Jr. | University of Michigan | TRP |
| Yosif Kharaka | USGS | TRP |
| Harry Ridgway | Orange County Water District | TRP |
| George Tchobanoglous | UC, Davis | TRP |

**Major Points**

- Boron removal currently drives treatment process. Need to consider other methods, such as blending, to deal with boron rather than brute force.
- Most likely water uses and economics should be examined, especially since mandatory reclamation has leveled the price of reclaimed and potable water in some places
- Regional Water Quality Control Board has non-degradation policy for receiving water bodies. Boron guideline in current basin plan is 1 mg/l
- Understanding the chemistry of boron removal mechanisms is important
- Understanding the behavior of organics is important
  - If organics are not biodegradable, they will not biologically foul the membrane
  - At pH 11.0, expect no biological fouling, and phenols should be rejected
  - Organic acids should be removed well at pH where they are ionized, and do not present a disinfection by-product concern
  - Chevron had disappointing results using fluidized bed to treat produced water biologically, with the exception of benzene removal
- If a majority of TOC is uncharacterized, and assumed to be different than uncharacterized TOC in surface water, then a goal of 2 mg/l is too high. A goal of 1 mg/l may be more appropriate (DHS comment)
- Commercially available membranes should be tested under a variety of operating conditions

**Specific Actions Suggested for Pilot Study**

- Characterize biodegradability of produced water
  - Conduct more BOD tests
  - Send samples to Orange County Water District (OCWD) for membrane biofouling tests
  - Continue our bench scale biodegradation tests
- Prepare trickling filter as soon as possible to allow time for acclimation
  - Obtain acclimated seed, possibly several seeds including, thermophilic bacteria and bacteria from OCWD brine nitrification study
- Look at high-energy gradient mixing in our pilot study
- Select appropriate membrane elements and array
  - Solicit input from membrane manufacturers and obtain their process models
  - Research case studies
  - Consider 3x2x1 array at 15 gpm
  - Look into boron removal of specific membranes
- Test more than one membrane
  - Install single element test stand in parallel to array
  - Have membrane manufacturers test elements before selecting membrane for pilot
  - Consider use of EPRI membrane test trailer
- Develop detailed operating plan
  - Develop protocol for identifying steady-state conditions
  - Use data loggers to record pressure and flow measurements for RO
  - Test membranes without trickling filter while the filter acclimates
  - Test membranes without ion exchange softening, but carefully control precipitative softening to remove calcium and carbonate alkalinity
  - Clean membranes after a 15 percent reduction in flux
  - Mineral rejection more critical, do not focus on fouling

- Develop detailed sampling plan
  - Test for Mg and Ca
  - Test for solids disposal
  - Use UV-visible for organics surrogate
  - Test occasionally for coliforms in process
  - Do Ames test on effluent

**Specific Actions Suggested for Pilot Design**
- Design for parallel flow around trickling filter, not just a by-pass
- Design sample ports with velocities similar to pipe flow
- Collect large samples to fill smaller sample bottles
- Use “quills” to sample before bends
- Consider using PVC pipe
- Design so that we have quick mixing

**Specific Actions Suggested for Phase I Report**
- Modify graphical presentation of bench-scale data
  - Present results in 4-3 as pC vs. C
  - Remove or revise contour plots from graphs 4-4 through 4-6
- Conduct further experiments to understand boron removal mechanisms
  - Obtain computer models from USGS to model precipitation reactions
  - Send Yousif sludge samples for spectral and crystal analysis
- Change TOC in report to 5 mg/l to be consistent with ammonia concentration (but it depends on how much TOC is refractory)
- Increase annual operating cost estimates for RO so that $/AF ~ $1,000
- Consider ion exchange with clinoptolite for ammonia removal after RO
- Clarify potential re-uses of water
  - Expand sections about options other than flange-to-flange potable goal
  - Consider blending to meet boron removal goals
  - Make reclamation terms consistent with Title 22

**Leads Suggested**
- April 17th USBR National Centers Conference at OCWD Water Factory 21 for talking to membrane manufacturers and consulting engineers
- EPRI membrane research trailer
- On-line TOC analyzer being tested in San Diego
- Submit abstract to IPEC by 3-14-97 (DOE suggested)
- Consider blending on-site to control boron; allow boron to bleed through RO at pH where organics are removed
- Investigate nanofiltration as alternative to ion exchange

**Questions Posed**
- Why are we in a hurry to start the pilot testing?
- Are we ready to pilot?
- Why are we testing only one treatment train?
- How do we expect to remove bacteria < 2 μm before RO?
- Did we try high energy gradient mixing?

## APPENDIX B
## PILOT SCALE TEST WORK PLAN

### INTRODUCTION

This document outlines the train of treatment processes that are recommended for pilot scale testing to reclaim produced water from the ARCO Placerita oil field. The goal of the four or five month pilot study is to demonstrate the feasibility of converting produced water into a reusable water resource and generate 3 months of operating data.

Technology selection was driven by the need to remove boron and dissolved solids. High-pH reverse osmosis (RO) was chosen to accomplish these goals. Pretreatment requirements identified for RO operated with pH between 8 and 11 include:

- walnut shell filtration to remove suspended oil and grease
- warm precipitative softening to remove silica and hardness that would scale in RO
- cooling to protect RO membrane and promote biological oxidation of organics
- biological oxidation of organics to reduce TOC of treated water and prevent organic fouling
- multimedia filtration to remove particles, including sloughed particles from biological process
- cation exchange to remove residual hardness that would scale in RO

Figure FD-1045 presents a schematic of the planned pilot plant. All processes will be operated in series with enough capacity to provide approximately 10 gpm of continuous flow to the RO unit. Table B.1 lists anticipated concentration levels for constituents of concern throughout the process. Table B.2 lists design parameters for the pilot units to be tested. The following paragraphs explain the treatment processes.

V-1 WALNUT SHELL FILTER SKID 3'-0" DIA. x ___ FT. HIGH

T-4 CLARIFIER SLUDGE BIN ___ FT. x ___FT. x ___ FT. HIGH 20 CUBIC YARDS

P-2 HEAD TANK PUMP 1 1/2" x 1 1/4" x 5 0.5 HP

V-3 TRICKLE FILTER 5'-0" DIA. x 25'-0" HIGH

V-6A PRESSURE FILTER SKID -

T-9 TREATED WATER STORAGE 3'-9" DIA. x 7'-0" HIGH 1000 GAL.

P-12 FILTER BACKWASH PUMP 1 1/4"x1" 4 HP

P-1 WATER CHARGE PUMP ST 1 1/2"x1" - 6AA

V-2 DENSADEG CLARIFIER SKID

T-5 HEAD TANK 7'-0" DIA. x 8'-0" HIGH 1000 GAL.

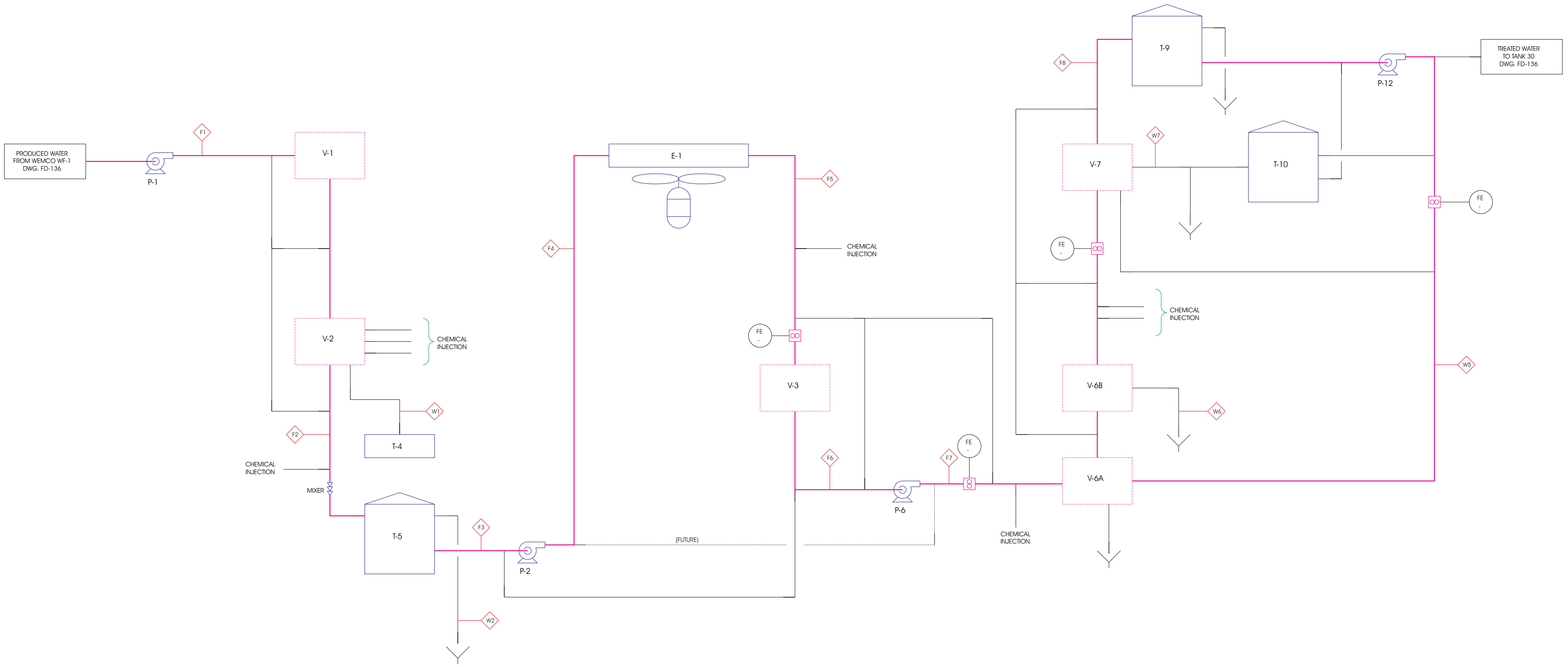
E-1 AIR COOLED EXCHANGER 2 STAGE 20 HP

P-6 TRICKLE FILTER EFFLUENT PUMP 1 1/4" x 1" 2.5 HP

V-6B ION-EXCHANGE SOFTENER SKID -

V-7 REVERSE OSMOSIS SKID -

T-10 R.O. CLEANING TANK 9'-6" DIA. x 4'-0" HIGH 500 GAL.




STEAM FLOW SUMMARIES

| STREAM No. / DESCRIPTION | F1 PRODUCED WATER | F2 CLARIFIER EFFLUENT | W1 CLARIFIER BLOWDOWN | F3 ACIDIFIED WATER | W2 WASTE WATER | F4 PUMPED WATER | F5 COOLED WATER | W3 | W4 | F6 CLARIFIER EFFLUENT | F7 R.O. PRETREAT | W5 FILTER BACKWASH | W6 SPENT REGENERANT | W7 R.O. CON-CENTRATE | F8 R.O. PERMEATE | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MAX. FLOW (GPM) | 100 | 100 | 20 | 50 | 90 | 50 | 50 | | | 15 | 15 | 40 | 2 | 5 | 10 | | | | | |
| AVERAGE FLOW (GPM) | 50 | 50 | 0 | 10 | 40 | 10 | 10 | | | 10 | 10 | 40 | 2 | 3 | 7 | | | | | |
| TEMPERATURE ( °F) | 160 | 160 | 160 | 150 | 160 | 150 | 90 | | | 90 | 90 | 90 | 90 | 90 | 90 | | | | | |
| PRESSURE (PSIG) | 45 | 10 | 10 | 10 | 10 | 25 | 25 | | | 5 | 70 | 5 | 5 | 5 | 5 | | | | | |
| pH | 7.0-8.0 | 9.5-10.0 | 9.5-10.0 | 8.0-9.5 | 9.5-10.0 | 8.0-9.5 | 8.0-9.5 | | | 8.0-9.5 | 8.0-9.6 | 8.0-11.0 | 8.0-9.5 | 9.0-11.0 | 8.0-11.0 | | | | | |

PROCESS FLOW DIAGRAM

# D.O.E. PILOT PLANT
# PRODUCED WATER RECLAMATION SYSTEM

PLACERITA CANYON PRODUCTION FACILITY
LOS ANGELES COUNTY, CALIFORNIA

ARCO Western Energy

| Rev | Date | Description | By | App'd |
|---|---|---|---|---|
| 1 | 4/14/97 | ISSUED FOR FINAL APPROVAL AND CONSTRUCTION | TR | |
| 0 | 3/26/97 | ISSUED FOR FINAL APPROVAL AND CONSTRUCTION | TR | |

| | | |
|---|---|---|
| Drawn By | TAR | 3/3/97 |
| Check | | |
| Approved | | |
| Engineer | GFD | 3/3/97 |

| | | |
|---|---|---|
| Design | KENNEDY/JENKS | 2/10/97 |
| Cad No. | FD-1045 | D |
| Scale | NONE | |
| Dwg. No. | FD-1045 | |

**Table B.1**

**Concentrations of Constituents of Concern**

**Anticipated in Planned Pilot Plant**

| Process | Temp (°F) | pH | NH3-N (mg/L) | TOC (mg/L) | Tot Hardness (mg/L $CaCO_3$) | TDS (mg/L) | Silica (mg/L $SiO_2$) | B (mg/L B) |
|---|---|---|---|---|---|---|---|---|
| **Influent** | 160 | 7.0 | 15 | 120 | 1,500 | 6,000 | 200 | 20 |
| **Walnut Shell Filter** | 160 | 7.0 | 15 | 115 | 1,500 | 6,000 | 200 | 20 |
| **Warm Precipitative Softening** | 150 | 9.7 | 15 | 110 | 100 | 5,500 | 10 | 10 |
| **pH and flow Control** | 150 | 8.0 - 9.5 | 15 | 110 | 100 | 5,500 | 10 | 10 |
| **Cooling** | 90 | 8.0 - 9.5 | 15 | 110 | 100 | 5,500 | 10 | 10 |
| **Fixed-Film Organic Removal** | 85 | 8.0 - 9.5 | 2 | 30 | 100 | 5,500 | 10 | 10 |
| **Sand Filtration*** | 85 | 8.0 - 9.5 | 2 | 20 | 100 | 5,500 | 10 | 10 |
| **Ion Exchange Softening** | 85 | 8.0 - 9.5 | 2 | 20 | 10 | 5,500 | 10 | 10 |
| **Reverse Osmosis (including pH control)** | 85 | 8.0 - 11.0 | 2 | < 2 | 0 | 300 | < 1 | < 0.5 |
| **Full-scale Effluent (pilot scale tests will not include post-treatment such as disinfection or stabilization)** | 80 | 7.5 | < 1 | < 2 | 70 | 350 | < 1 | < 0.5 |

**Table B.2**

**Design Parameters for Pilot Scale Treatment Technologies**

| Technology | Design Parameters |
|---|---|
| Walnut Shell Filter | 3 ft diameter (approx. area of 7 $ft^2$)<br>Max Hydr. loading = 15 gpm/ $ft^2$ |
| Warm Precipitative Softening | pH between 9.5 and 10 with caustic soda<br>NaOH dosage 700 - 1000 mg/L<br>$MgCl_2$ dosage 40 - 400 mg/L |
| Heat Exchange | Fin-fan exchangers |
| Trickling Filter | 5 ft diameter (approx. area of 20 $ft^2$),<br>20 ft of 7-inch random packed media (30 $ft^2/ft^3$)<br>Media volume approx. 400 $ft^3$<br><br>Hydr. loading 0.5 - 2.5 gpm/ $ft^2$ (10 - 50 gpm including recycle)<br>BOD loading = 60 - 300 lbs/day / 1000 $ft^3$ media<br>or 2 - 10 lbs/day / 1000 $ft^2$ of media surface area,<br>(assumes 200 mg/L BOD at 10 - 50 gpm not including recycle) |
| Sand Filtration | Average hydraulic loading rate = 2.5 gpm/$ft^2$<br>Max. hydraulic loading rate = 5 gpm/$ft^2$ |
| Cation Exchange | EBCT = 6 min<br>Effective resin capacity approx. 20 kilo-grains / $ft^3$ |
| RO | (12) 4” x 40” TFC brackish RO elements<br>6 pressure vessels, 2 elements each, in (3 x 2 x 1 array)<br>pH 8.0 - 11.0 |

**INFLUENT**
Influent for the pilot plant will come from ARCO Western Energy's (AWE's) Air Floatation cell WF-2. The elevation from the unit will provide head for the initial treatment steps in the pilot plant. The temperature of the influent water will be approximately 170 °F.

**OIL REMOVAL**
The first treatment process is oil removal utilizing a Hydromation walnut shell filter. The goal of the process is to reduce suspended oil and grease (O&G) concentrations from influent values of 2 to 50 mg/L to less than 1 mg/l. AWE DAF Wemco unit plant upsets will be simulated to evaluate how effectively the filters can handle slugs of oil.

The 3-foot diameter test unit has 7 $ft^2$ of surface area that can filter 106 gpm at a maximum loading rate of 15 gpm/ $ft^2$ . The filter will be operated at approximately 100 gpm to provide adequate flow for the warm softener.

**WARM SOFTENING**
Warm precipitative softening for silica and hardness removal is the second step in the treatment process. Sodium hydroxide (caustic soda), magnesium chloride, and polymer will be added to the water to induce precipitation and aid in flocculation. Based on bench-scale tests, the operating pH for softening will be controlled between 9.5 and 10 where silica and boron removal are highest.

The warm softening will be 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 75-100 gpm prototype that will be operated at approximately 100 gpm to provide a rise rate of 10 gpm/$ft^2$ in the clarifier. Sludge will be periodically blown-down manually.

**PH CONTROL**
A chemical feed pump will provide the ability to add concentrated acid to lower the pH of the process water if required. Since the RO process will operate at high pH values, no acid will be added unless it is required to prevent continued precipitation from the softening process or to improve the biological oxidation of organics.

**FLOW CONTROL THROUGH HEAD TANK**
The flow required for the remainder of the pilot plant will be approximately 10 to 12 gpm, with occasional demands of up to 50 gpm for the trickling filter. The flow will be regulated by pumping against a constant back-pressure provided by a water reservoir with a fixed-elevation weir approximately 15-20 feet above grade. Overflow from the weir will fall into a second tank and be directed to the waste header.

**WASTE HEADER**
Excess softened water and wastes from filter backwash, clarifier blow-down, and ion exchange regeneration will all be routed to a common waste header that will be pumped to drain with a sump pump.

**COOLING**

Cooling is necessary to protect components of treatment processes such as plastic packing media and thin-film composite RO membranes. The highest allowable temperatures for these processes is approximately 100 °F, and a design cooled water temperature of 90 °F will be used. In a full-scale plant, cooling will likely be accomplished by a cooling tower.

The pilot study will utilize fin-fan heat exchangers. These devices route the process water though a series of pipes which have fins protruding to increase pipe surface area. Air is blown across the fins to transfer heat from the water to the air. The cooled water temperature of this process is limited by air temperature, which often exceeds 90 °F during summer afternoons. Additional cooling during summer days will be provided by surrounding the process pipe with water that is cooled by adding ice bags as necessary.

**TRICKLING FILTER**

Biological oxidation of organics is the next step in the treatment train. The bio-chemical oxygen demand (BOD) of the produced water is estimated at approximately 200 mg/L based on total organic carbon (TOC) measurements of approximately 120 mg/L and chemical oxygen demand (COD) measurements of 350-450 mg/L. Measurements of BOD during bench-scale tests yielded BOD values of approximately 15-25 mg/L.

A trickling filter was selected to evaluate biological organic oxidation at a range of loading rates. The goal for organics removal is 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 fixed-film approach of a trickling allows for a wide variety of cell ages to adapt to the particular constituents of produced water. For example, bacteria that use organic acids as an energy source may colonize near the top of the filter while bacteria that use ammonia or relatively recalcitrant organics may colonize the bottom of the filter.

The trickling filter will be 5 feet in diameter with 20 feet of media depth. This design provides approximately 20 $ft^2$ of filter area with a media volume of approximately 400 $ft^3$. Hydraulic and organic loadings can be controlled between 0.5 - 2.5 $gpm/ft^2$ and 60 to 300 lbs/1000 $ft^3$ of media by adjusting the flow rates of the independent influent and recycle pumps between to yield a combined flow of 10 to 50 gpm.

**PRESSURE FILTRATION**

Particles will be removed through filtration prior to ion exchange and reverse osmosis. Two multimedia pressure filters will be operated in parallel, with each filter capable of filtering the entire flow while the other backwashes. The filters are 22 inches in diameter and have approximately 4 feet of media. The type of media have not been selected. With approximately 2.5 $ft^2$ of area per filter, the hydraulic loading rate for the filters will be approximately 2.5 $gpm/ft^2$ during parallel operation and 5 $gpm/ft^2$ through the active filter while the other backwashes.

The filters will be backwashed with RO permeate and controlled by timer.

**ION EXCHANGE**
Two cation exchange columns in series will be used to remove divalent cations that might cause scaling in high-pH RO. Each column will contain approximately 5 $ft^3$ of resin with a rated capacity approximately 25-30 kilo-grains per $ft^3$. The high TDS of the water is expected to reduce the capacity of the resins by approximately 20 percent, so the expected capacity is approximately 20 kilo-grains per $ft^3$. Regeneration will be controlled by timer. Concentrate from the RO may be tested as a regenerate for the ion exchange resin.

**REVERSE OSMOSIS**
A reverse osmosis skid will test 12- 4" x 40" brackish water elements, housed in 6 pressure vessels that are arranged in a 3-stage (3 x 2 x 1) array. The three stages and a concentrate recycle line facilitate tests at water recovery rates above 70 percent. A 7.5 hp pump will be used to conduct tests at pressures as high as 600 psi.

A single type of thin-film composite membranes, with high resistance to elevated pH and organic attack, will be tested. Membranes will be selected with input from membrane manufacturers based on characteristics such as the membrane hydro-phobicity or hydro-philicity. Before installing a full set of 12 new membranes, tests will be conducted with either a full set of used membranes or a single pressure vessel filled with new membranes and brine recycle. These early experiments will evaluate whether pre-treatment is sufficient to prevent rapid, irreversible damage to the membranes.

Once the full set of elements are installed, the pH of the influent water will be controlled between 8.0 and 11.0 to evaluate the effectiveness of boron and organics removal at a variety of pH values. During the optimized tests, the membranes will be operated under a constant pH for a number of weeks to obtain data about scaling and fouling.

The following information will be collected to evaluate membrane performance. These parameters were adopted from the ICR membrane pilot test requirements.

**Pressure with liquid-filled in-line instruments**
Influent for each stage
Permeate for stage
System permeate
System concentrate

**Flow Rate by in-line flow meters**
Permeate from each stage
System permeate
System concentrate
Concentrate recycle

**Flow Rate by time volumetric displacement (bucket calibration)**
System permeate
System concentrate

**TDS (conductivity)**
Influent to each stage

Permeate from each stage
System concentrate
System permeate

**pH**
System influent
System permeate

**POST-TREATMENT**
The pilot tests will not include post-treatments such as disinfection and stabilization that would be necessary in full-scale treatment.  Test will be conducted to evaluate the formation potential of disinfection by-products on treated water.

## APPENDIX C
## PILOT SCALE OPERATING AND DATA COLLECTION PLAN

### SUMMARY

A pilot facility will test the performance and feasibility of treatment alternatives to treat produced water from the Placerita Oil Field to current and anticipated California potable and reclaimed water requirements. The goal of the pilot plant is to provide the equivalent of 3 continuos months of experimental data..

Experiments will be performed by adjusting the following pretreatment components to the reverse osmosis system: dosage of magnesium and caustic soda in 170 °F clarifier, pH of RO influent, the use of zeolite ion exchange softeners for hardness removal and trickling filter for organics removal. Data collection will be phased to help assist startup, characterize and optimize process performance, and document treatment efficiencies as a proof of concept.

The plant is designed to operate unattended for most of the time. A few hours per day of operator oversight will be required throughout the test for routine maintenance operations and collect performance data. Additional time will be required for trouble shooting during shakedown and for sampling during proof of concept testing.

The following sections outline the pilot testing, sampling and data collection procedures.

### GOALS

The objective of this project is to demonstrate a treatment train that treats excess produced water and converts the water to a potable water resource for use by the public. A pilot facility will test the performance and feasibility of treatment alternatives to treat produced water from the Placerita Oil Field to current and anticipated California potable and reclaimed water requirements.

In California, the Department of Health Services (DHS) or Regional Water Quality Control Board must consent to a water's use or reuse. This project is structured to obtain agency approval to establish guidelines and design criteria that are applicable throughout California. If the project is successful, the results of the pilot study will be used to assess the feasibility of constructing a 2 mgd facility.

The pilot study is designed to be a proof of concept rather than a complete pre-design study. Three months of test data should provide adequate information to evaluate strategies to maximize water quality and minimize costs.

The specific goals of the pilot study include:

- Demonstrate the feasibility of treating produced water to drinking water standards
- Evaluate organics removal with fixed-film oxidation and reverse osmosis
- Optimize boron removal with warm precipitative softening and reverse osmosis
- Estimate treatment costs based on chemical usage and labor requirements

## EXPERIMENT DESIGN

To accomplish the project goals, pretreatment for the reverse osmosis system will be tested to optimize the system for water quality and cost effectiveness. From a cost standpoint, the dosage of magnesium and caustic soda in warm clarifier, and the associated volumes of sludge represent the largest target for cost control. Additional pretreatment parameters that will be tested include the pH of RO influent, the use of zeolite ion exchange softeners for hardness removal, and the use of a trickling filter for organics removal.

### Schedule of Experiments

Experiments are scheduled to first, optimize water quality and demonstrate proof of concept and then, evaluate treatment alternatives to lower costs by adjusting pretreatment elements and changing chemical dosages. Figure 1 presents the schedule for renting equipment and conducting experiments. Experiment will be conducted in series. The duration of experiments will be decided based on data collected during the experiment. On the schedule, testing duration were assumed to be approximately 3 weeks. The experiments are designed to start with the most conservative approach and gradually become more aggressive. If one experiment indicates that an operating condition will not work, then future experiments designed to test this condition in conjunction with other conditions will be canceled, unless the other condition favor a better outcome. For example, if operating the membranes without zeolite softening is not successful without using the trickling filter, then future tests with the trickling filter will include the softeners. The following sections describe the experiments.

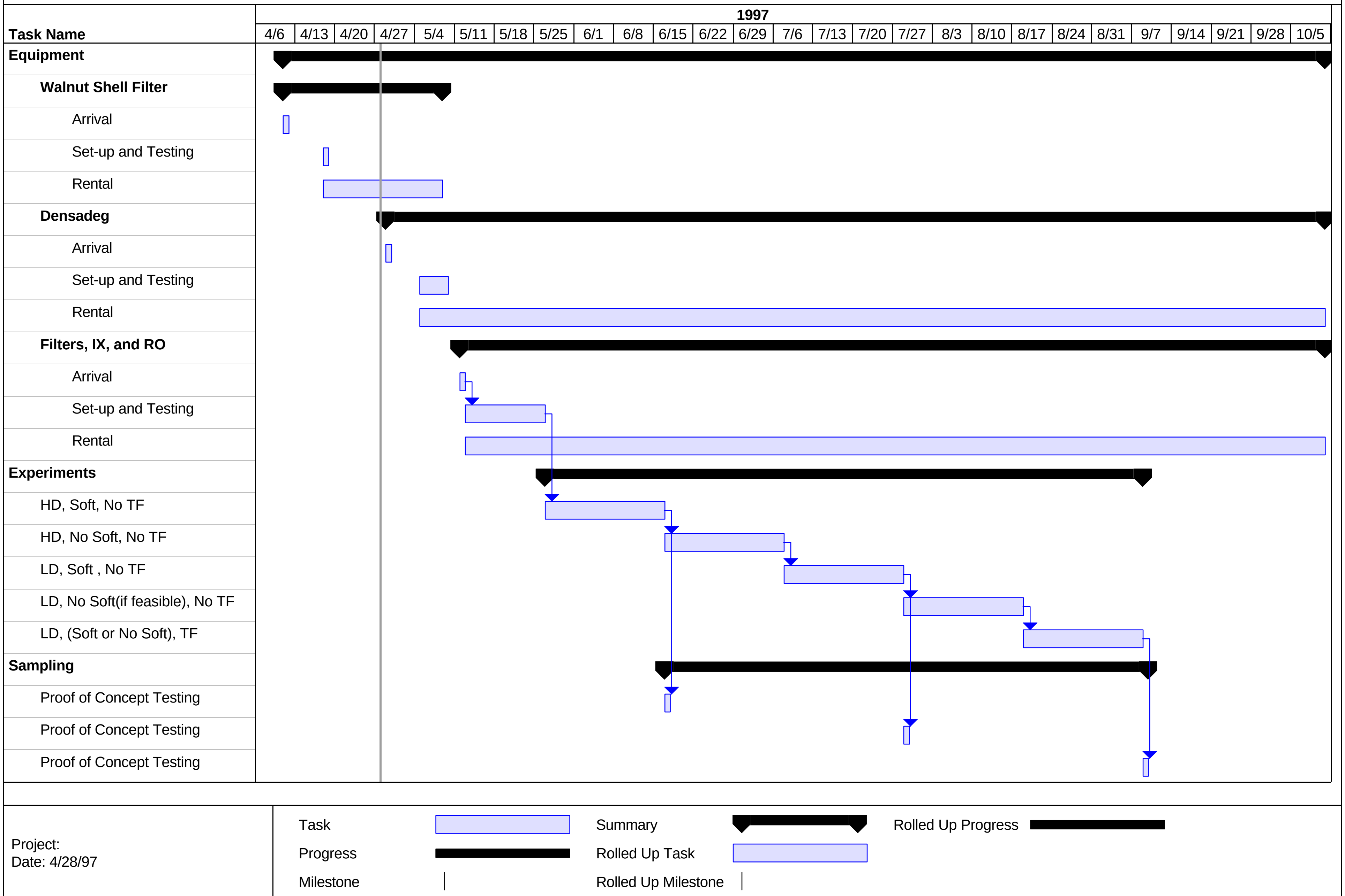
<u>Shakedown</u>
Before any experiments are conducted, the system will be tested to determine appropriate chemical dosages, loading rates and operating pressures for each of the processes. These tests will rely on measurements of flow rate, pressure, pH.

<u>Optimize Water Quality for Proof of Concept</u>
The pilot plant will first be operated to provide the highest water quality. Chemical dosages will be selected to optimize boron removal based on jar tests experiments conducted in Phase I of this study. Pressure filtration and ion exchange softening will be utilized. The trickling filter will be by-passed for these initial experiments though water will be directed to it to develop biomass. Intensive sampling for proof of concept will commence when operating parameters indicate that the process are optimized for boron and TOC removal.

<u>Reduce Treatment Costs by Removing Zeolite Softeners</u>
In the second experiment, the process will be operated without the zeolite softener. Chemical dosages for boron optimization will be adjusted to also minimize calcium concentrations. Calcium concentrations will be carefully controlled in the warm clarifier, and the use of anti-scalant will be maximized to prevent mineral scaling. The success of the experiment will be evaluated based on the scaling tendency of the water in the RO system. If the RO feedwater requires adjustment downward to prevent scaling, then the residual concentration of boron will also be an important measure of success.

<u>Reduce Treatment Costs by Reducing Chemical Usage</u>
The goal of the third experiment is to reduce chemical usage in the warm clarifier to reduce chemical and sludge costs. The measure of success will be residual boron in the RO

**Figure C.1**
**Produced Water Pilot Plant  Equipment Rentals and Experimentation**




HD/LD = High/Low Dosage MgCl2 and NaOH, Soft = IX Softeners, TF = Trickling Filter permeate. Calcium removal in the warm clarifier will likely decrease when chemical dosages are lowered, zeolite softeners will likely be used.

<u>Reduce TOC by Incorporating Trickling Filter for Biological Organic Oxidation</u>
Throughout the first three tests, the trickling filter will be operated to develop biomass, but no trickling filter effluent will be treated with reverse osmosis. During the initial experiments, the feasibility of operating the trickling filter without adjusting the pH after clarification will be evaluated. The criteria for successful operation of the trickling filter is a reduction in soluble organic carbon. Bench-scale experiments and paper estimates predict that a 20 percent reduction of TOC is feasible.

After the first three experiments are conducted, the trickling filter will become part of the pretreatment for the reverse osmosis. Experiments that were successful without the trickling filter will then be tested with the trickling filter. The success of these new tests will be measured by the TOC content of the RO permeate, and by the microbial fouling tendency of the membranes.

## SAMPLING AND DATA COLLECTION

Sampling and data collection will be tailored to provide adequate information for each phase of testing. During shakedown basic hydraulic data and pH readings will be collected to establish operating parameters. During process characterization and optimization, additional water quality data will be collected to optimize silica, boron, and organics removal. During testing for the proof of concept phase and regulatory compliance, additional sampling will be conducted to determine whether treated water meets drinking water standards. This additional sampling will occur periodically, throughout the pilot tests, when process characterizations indicate that the system is optimized. Table C.1 lists the duration and typical sampling parameters for the three phases, and the following list provides specific goals and sampling required. A detailed sampling plan and schematic indicating sample points are included as Table C.2 and Figure C.2, respectively.

**Table C.1**

**Three Phases of Operation for Produced Water Pilot Study**

| Type of Sampling | Duration | Typical Sampling Parameters |
|---|---|---|
| Startup | 2 weeks | Temperature, pH, pressure |
| Process Characterization and Optimization | 8 weeks | Above parameters plus Silica, Boron, oil and grease, Tot. Hardness, $UV_{254}$ adsorbence, TOC, conductivity, and TDS |
| Proof of Concept and Reliability Testing | 4 weeks | Above parameters plus Title 22 screening, Ames Test, Disinfection Byproducts, Metals in Residuals |

### Startup

Goals

- Determine pumping required to maintain hydraulic conditions
- Determine chemical requirements for pH control
- Determine backwash frequencies and sequences
- Verify adequate pretreatment for Reverse Osmosis, including softening

Testing

- Flow rates, pressures, pH values throughout process
- Oil and grease in walnut-shell filter influent and effluent
- Turbidity and Silt Density Index (SDI) values in RO influent

**Process Characterization and Optimization**

Goals

- Optimize silica and boron removal in warm lime clarifier at two different chemical dosage schemes: high dosages of caustic soda and magnesium for maximum boron removal, and low dosages for minimum cost
- Determine pH range for trickling filter (start at 9.7 and decrease if necessary)
- Determine TOC reduction verse loading rates (few weeks per rate)
- Optimize boron and organics removal in RO

Testing

- TSS, TOC, COD, BOD, and UV/visible from trickling filter
- Silica, boron, hardness, alkalinity, calcium, oil and grease, iron, ammonia, turbidity, and TOC in influent and effluent of warm lime softener and ion exchanger
- Boron, TOC, conductivity, and TDS in influent and effluent of RO

**Proof of Concept and Reliability Testing**

Goals

- Determine if treated water meets California Title 22 Requirements, including Maximum Contaminant Levels (MCLs)
- Develop cumulative distribution plots of process performance
- Evaluate reliability of treatment system in simulated plant upset

Testing

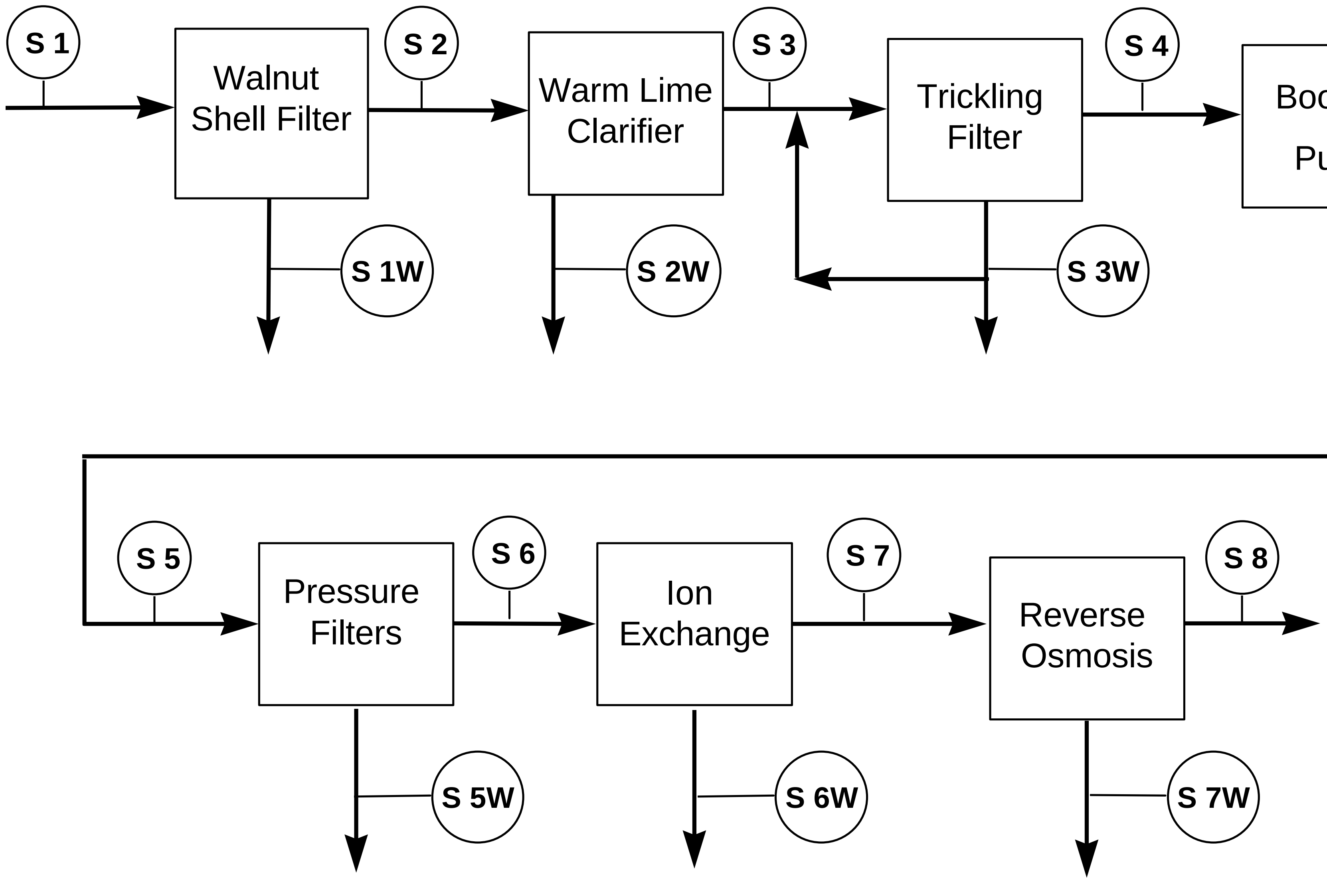
- Title 22 Maximum Contaminant Levels (MCLs)
- Iodine, bromide
- Radioactivity
- Metals in residual streams
- Simulate plant upsets by by-passing trickling filter or walnut shell filter

# Table C.2
# Sampling Plan for Process Characterization and Optimization

| Sample | | Field Readings | | | | Parameters Analyzed in Field | | | | | | | | | | | | | Parameters Analyzed in Lab | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Location** | **Description** | Flow | Pres. | Temp | | pH | Cond | Turb | SDI | Alk | TH | Ca | UV | SiO2 | B | O&G | | Fe | TOC | NH3 | TSS | TDS | Settleability | Solids |
| S1 | Influent | | D | | | D | D | D | | D | D | | D | D | D | D | | D | D | D | | | | |
| S2 | Walnut Shell Effluent | | | D | | | | | | | D | | D | D | D | D | | | D | | | | | |
| S3 | Warm Lime Effluent | D | | D | | D | | D | | D | D | D | D | D | D | | | D | D | D | D | | | |
| S4 | Trickling Filter Effluent | D | | | | D | | | | | | | D | | | | | | D | D | | | | |
| S5 | Booster Pump Effluent | D | D | | | D | | | | | | | | | | | | | | | | | | |
| S6 | Pressure Filter Effluent | | D | | | D | D | D | D | D | D | | D | | | D | | | | | | | | |
| S7 | Ion Exchange Effluent | | D | D | | D | D | | D | D | D | D | | | | | | | 3XW | | | 3XW | | |
| S8-cf | Cartridge Filter Effluent | D | D | | | | | | | | | | | | | | | | | | | | | |
| S8-i | RO Influent (after CF) | | D | | | D | D | | D | | | | | | | | | | | | | | | |
| S8-1p | Stage 1 Permeate | D | D | | | | D | | | | | | | | | | | | | | | | | |
| S8-2p | Stage 2 Permeate | D | D | | | | D | | | | | | | | | | | | | | | | | |
| S8-3p | Stage 3 Permeate | D | D | | | | D | | | | | | | | | | | | | | | | | |
| S8-sp | System Permeate | D | D | | | D | D | | | | | | | D | D | | | | 3XW | | | 3XW | | |
| S8-sc | System Concentrate | | D | | | | D | | | | | | | | | | | | | | | | | |
| S8-wc | Waste Concentrate | D | | | | | | | | | | | | | | | | | | | | | | |
| S8-rc | Recycle Concentrate | D | | | | | | | | | | | | | | | | | | | | | | |
| | **Residuals** | | | | | | | | | | | | | | | | | | | | | | | |
| S1W | Walnut Shell | | | | | | | | | | | | | | | W | | | | | | | | W |
| S2W | Warm Lime | | | | | | | | | | | | | | W | W | | | | | | | | W |
| S3W | Trickling Filter | | | | | | | | | | | | | | | | | | | | | | W | W |
| S5W | Filtration | | | | | | | | | | | | | | | | | | | | | | | |
| S6W | Ion Exchange | | | | | W | W | | | | | | | | | | | | | | | | | W |
| S7W | RO | | | | | | W | | | | | | | | | | | | | | | | | W |

Notes
D= Daily
W= Weekly
3XW = 3 times per week

# Figure C.2
# Sampling Locations for Water Quality Plan



## OPERATING PLAN

The pilot plant is designed to run continuously with regular periodic operator attention. Specific operating strategies for each of the technologies are described below.

### Operating Strategies for the Treatment Technologies

Walnut Shell Filter
The walnut shell filter will be backwashed with 2 bed-volumes of influent produced water once daily. While the filter is backwashing, influent water will not receive oil removal. Backwashing will be initiated manually. No produced water will be directed to the warm clarifier for the few minutes that the walnut shell filter is backwashed. The walnut shell filter will be evaluated during the first few weeks of testing, before the other technologies are brought on-line.

Warm Softening Clarifier
The warm softening clarifier will operate continuously between 50 and 100 gpm. Flow rate will be controlled by manually adjusting the raw water feed pump and a throttling valve. Chemical feed rates for caustic soda, magnesium chloride, and anionic polymer will be set manually at the chemical feed pump to maintain pH near 9.7.

Sludge will be blown-down from the clarifier every few hours based on a timer control. The solids content of the “densafied” sludge is estimated at approximately 20 percent. The sludge will flow by gravity into a 20 cubic yard bin for storage. Excess water will be decanted off the top of the bin with a vacuum truck every few days. The sludge will be hauled to Castaic Lake Water Agency Earl Schmidt Plant.

pH Control
A chemical feed pump will provide the ability to add dilute sulfuric acid to lower the pH of the process water if required. Since the RO process will operate at high pH values, no acid will be added unless it is required to prevent continued precipitation from the softening process or to improve the biological oxidation of organics. The output of the chemical feed pump will be controlled manually.

Flow Control Through Head Tank
The flow required for the remainder of the pilot plant will be approximately 10 to 12 gpm, with occasional demands of up to 50 gpm for the trickling filter. A pump and throttling valve will be used to change the flow-rate of the water. The flow will be regulated by pumping with a constant back-pressure provided by a water reservoir with a fixed-elevation overflow approximately 5 feet above grade. Overflow will be directed to the waste header.

Waste Header
Excess softened water and wastes from filter backwash, and ion exchange regeneration will all be routed to a common waste header that will be pumped to drain with a sump pump. The drain will return the flow to the head of Arco Western Energy’s (AWE’s) treatment works.

Cooling

The pilot study will utilize fin-fan heat exchangers that require little or no operator attention. Additional cooling during summer days will be provided by surrounding the process pipe with water that is cooled by adding ice bags as necessary, or by spraying water into the fans of the exchanger to promote evaporative cooling.

Trickling Filter

Biological oxidation of organics is the next step in the treatment train. Hydraulic and organic loadings will be controlled between 0.5 - 2.5 gpm/$ft^2$ and 60 to 300 lbs/1000 $ft^3$ of media by adjusting the flow rates of the independent influent and recycle pumps to yield a combined flow of 10 to 50 gpm.

Re-Pumping

Water will be pumped from the sump of the trickling filter through pressure filters, ion exchange, and to the RO unit. A Y-strainer will remove particles prior to pumping with a multi-stage centrifugal pump.

Pressure Filtration

Particles will be removed through filtration prior to ion exchange and reverse osmosis. The filter valves will switch to backwash mode on a timer and a pump will be electronically activated to pump RO permeate for backwash water.

Ion Exchange

Two cation exchange columns in series will be used to remove divalent cations that might cause scaling in high-pH RO.

Reverse Osmosis

The pH of the influent water will be controlled between 8.0 and 11.0 to evaluate the effectiveness of boron and organics removal at a variety of pH values. During the tests, the membranes will be operated under a constant pH for a number of weeks to obtain data about scaling and fouling. Chemical dosing to maintain a constant pH will be controlled by manually setting the feed rate on a chemical feed pump.

The elements will be chemically cleaned when the normalized flux rate drops 15 percent or more. Several cleaning solutions will be employed to remove organics and inorganic scale.

**Safety**

Each individual must sign-in at the production office before coming onsite. Workers are to follow procedures outlined in the ARCO Oil and Gas Company *Safety and Health Manual* that is available at the production office. ARCO Western Energy and Kennedy/Jenks Consultants have developed independent Health and Safety Plans for work at the site. The most basic requirements of these plans include hard-hats, safety glasses, leather boots, and no beards.

**Operations**

The tasks required for operations include (sampling will only be done during work days):

*Daily*

Backwash walnut shell filter (first few weeks) unit if necessary

Backwash pressure filters if necessary

Change cartridge filters if necessary

Record operating parameters such as flow rate and pressure from in-line gauges

Measure conductivity (10 places) and pH (5 places) with probe after drawing samples

Collect samples from each unit process for field and laboratory analysis

Analyze samples in field

Send samples to laboratory

Enter data into computer database and upload information for analysis

*Weekly*

Dispose of sludge

Load salt or brine for ion exchange softener

Collect samples from residuals of unit processes

*Monthly*

Receive chemicals

Chemically clean RO unit