FINAL REPORT
BENEFICIAL REUSE OF
SAN ARDO PRODUCED WATER

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ABSTRACT

This DOE funded study was performed to evaluate the potential for treatment and beneficial reuse of produced water from the San Ardo oilfield in Monterey County, CA. The potential benefits of a successful full-scale implementation of this project include improvements in oil production efficiency and additional recoverable oil reserves as well as the addition of a new reclaimed water resource. The overall project was conducted in two Phases. Phase I identified and evaluated potential end uses for the treated produced water, established treated water quality objectives, reviewed regulations related to treatment, transport, storage and use of the treated produced water, and investigated various water treatment technology options. Phase II involved the construction and operation of a small-scale water treatment pilot facility to evaluate the process's performance on produced water from the San Ardo oilfield. Cost estimates for a potential full-scale facility were also developed.

Potential end uses identified for the treated water include i) agricultural use near the oilfield, ii) use by Monterey County Water Resources Agency (MCWRA) for the Salinas Valley Water Project or Castroville Seawater Intrusion Project, iii) industrial or power plant use in King City, and iv) use for wetlands creation in the Salinas Basin. All of these uses were found to have major obstacles that prevent full-scale implementation. An additional option for potential reuse of the treated produced water was subsequently identified. That option involves using the treated produced water to recharge groundwater in the vicinity of the oil field. The recharge option may avoid the limitations that the other reuse options face.

The water treatment pilot process utilized: i) warm precipitation softening to remove hardness and silica, ii) evaporative cooling to meet downstream temperature limitations and facilitate removal of ammonia, and iii) reverse osmosis (RO) for removal of dissolved salts, boron, and organics. Pilot study results indicate that produced water from the San Ardo oilfield can be treated to meet project water quality goals. Approximately 600 mg/l of caustic and 100 mg/l magnesium dosing were required to meet the hardness and silica goals in the warm softening unit. Approximately 30% of the ammonia was removed in the cooling tower; additional ammonia could be removed by ion exchange or other methods if necessary. A brackish water reverse osmosis membrane was effective in removing total dissolved solids and organics at all pH levels evaluated; however, the boron treatment objective was only achieved at a pH of 10.5 and above.

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Executive Summary

The goal of this project was to perform a pilot study to evaluate the potential for treatment and beneficial reuses of produced water from an oilfield near San Ardo in Monterey County, CA. The sponsors of this project include Department of Energy (Contract No. DE-FC26-02NT-15463); Aera Energy LLC, (a California Limited Liability Oil Producing company); and Kennedy/Jenks Consultants. The potential benefits of a successful full-scale implementation of this project include:

- Reduction in the volume of oil field produced water reinjected into disposal wells, thereby reducing reservoir pressure and improving steam drive efficiency.
- Reduce the costs associated with the underground disposal of produced water including maintenance, acidizing, drilling new disposal wells, regulatory and administrative activities.
- Lower the energy demand for oil field operations through reduced water production and handling
- Addition of a new water resource to the shrinking number of water resources available in water short California.

This project was divided into two Phases. The tasks performed during Phase I (October 2002 – December 2003) of this project included i) identification of potential end users for the treated produced water at San Ardo, CA, ii) evaluation of regulations related to treatment, transport, storage and use of treated produced waters, and iii) selection of treatment process train for pilot study. The pilot process selected for evaluation included i) warm softening to remove hardness and silica, ii) cooling tower for cooling the water and facilitate ammonia removal, and iii) Reverse Osmosis (RO) unit for dissolved salts (including boron) and organics removal. The pilot study to evaluate treatability of San Ardo produced water (Phase II) was completed in March 2005. Finally, several local and national presentations were made to discuss the findings of this study.

E.1 Evaluation of End Use Options for San Ardo Oilfield Produced Water

Possible end uses considered for the treated water include i) agricultural use in the farms within five mile radius of the oilfield, ii) use by Monterey County Water Resources Agency (MCWRA) for the Salinas Valley Water Project or Castroville Seawater Intrusion Project, iii) industrial or power plant use in King City, iv) use for creation of wetlands in the Salinas Basin,. All of these potential end uses were found to have major obstacles to implementation.

About 3,500 acres of farmland are located within 5 miles from the oilfield, downstream of the Salinas River. The agricultural demand in this area exceeds the amount of water anticipated to be generated from the treatment process. MCWRA has undertaken two major projects (Salinas Valley Project and Castroville Project) to prevent seawater intrusion into the Salinas Valley Basin and protect agricultural water use. A key component of these projects is to identify alternate sources of water for agricultural use in the Salinas Valley Basin. The demand for MCRWA projects also exceeds the treated water production from this project.

All of these uses, however, have several limitations that must be addressed prior to implementation of a full-scale treatment process. For example, these possible uses must satisfy stringent regulatory, economic, user-perception, and long-term reliability criteria prior to actual implementation. Furthermore, depending on the type of use, implementation may also require complex water trade arrangements with one or more water agencies. Finally, large storage facilities (hundreds of million gallons capacity) would be needed if there is a large seasonal variation in water demand for the identified end use. Such limitations may increase the overall costs of the project significantly and render the use non-viable.

An additional option for potential reuse of the treated produced water was subsequently identified. That option involves using the treated produced water to recharge groundwater in the vicinity of the oil field. The recharge option may avoid the limitations that the other reuse options face.

E.2 Regulations for Treatment, Storage, Delivery and Use of Treated Produced Water

Full-scale treatment and offsite use of the produced water may require permits from several regulatory agencies. The Central Coast Regional Water Quality Board (CCRWQCB) is responsible for most of the water quality related issues. A Monterey County Air Pollution Control Board (MCAPCB) permit may be required for potential volatile organic compounds (VOC) and ammonia emissions during treatment. The California Water Resources Control Board (CWRCB) may be involved if treated water is transported via the Salinas River. The California Department of Water Resources – Division of Dam Safety, Army Corps of Engineers, and the Monterey County Planning Department may be involved in building and storage permits, depending on the type of construction. The mode of treated water delivery (e.g. direct delivery by hard pipe, delivery through river) will also impact the permitting process. For example, for delivery of treated water to agricultural land by hard pipe, the treated water quality must meet crop water quality and basin plan water quality requirements. Waste Discharge Requirements (WDRs) order must be obtained from the CCRWQCB. For delivering water via the river the following would be required:

- The released water must facilitate agricultural or wildlife restoration requirements.
- The water quality must be in compliance with National Pollution Discharge Elimination System (NPDES), National Toxics Rule (NTR), California Toxics Rule (CTR) and anti-degradation requirements.
- A permit from the CWRCB must be obtained for water appropriation.
- Approval from the California Department of Fish and Game (CDFG) may be required for the appropriation of water to verify that the loss of water will not have an adverse effect on fish and wildlife resources.

Finally, storage of water during periods of low demand may involve regulations from the California Department of Water Resources - Division of Safety and Dams (DSD), Monterey County Environmental Health & Planning Department, and the CCRWQCB depending on storage location and water quality.

E.3 Pilot Results

E.3.1 Pilot Process

Central to the pilot process is an RO unit for Total Dissolved Salts (TDS) removal. An upstream warm softening unit removed hardness and silica to minimize scaling of the membranes. Caustic was added to remove hardness, and magnesium was added to precipitate silica from the produced water. A cooling tower was used to cool the softened water and facilitate ammonia removal prior to RO. Most of the RO operations were performed using a brackish water membrane. In these studies the RO was operated at alkaline (9.5 – 11) pH levels to remove boron. Several additional studies were performed to evaluate treatment cost reduction including i) investigation of RO membrane fouling characteristics to optimize the Clean-in-Place (CIP) process and membrane replacement frequency, and ii) evaluation of special boron rejection seawater membrane at pH 9.5 to minimize chemical and operational cost associated high pH (>10.5) operations using conventional membranes.

E.3.2 Summary of Pilot Results

Pilot study results indicated that San Ardo produced water can be treated to meet project water quality goals. Approximately 600 mg/l of caustic and 100 mg/l magnesium dosing was required to meet the hardness and silica goals in the warm softening unit. In addition to cooling, approximately 30% of the ammonia was removed in the cooling tower. The brackish water membrane was effective in removing TDS to below the treatment goal at all the pH evaluated. However, boron treatment goals were achieved only at pH above 10.5 using this membrane. Evaluation of trans-membrane pressure relief as well as analyses of low pH (for inorganic removal) and high pH (organic removal) solutions used for CIP indicated that most of the membrane fouling was caused by inorganic scaling (Mg, silica) rather than organic fouling. Preliminary studies using a special boron rejection seawater membrane yielded boron levels of 1 mg/l at an operating pH of 9.5 in a 1X0 array mode. However, this membrane appeared to be more prone to scaling than the brackish water membrane. Approximately 200 % higher silica and 400 % more magnesium were measured in the low pH CIP solution after 50 hours of operation. Based on the operational data it was estimated that the specific flux (gfd/psi) of the boron rejection membrane was approximately 14 % lower, and the energy use was about 20% higher than those of the brackish water membrane.

E.4 Full-scale Capital and O&M Costs

Capital and O&M cost estimate was developed for a conceptual 70,000 bpd full-scale treatment facility. The recommended treatment process includes warm precipitative softening at pH 9.5, cooling, equalization storage, booster pumping, multi-media filtration, upward pH adjustment (to 10.5), cartridge (automatic bag) filtration, reverse osmosis, pH adjustment and ammonium selective ion exchange. This process would reclaim approximately 50,000 bpd (2,360 acre ft/yr) of water. The preliminary cost estimates assume a level site and have an accuracy of approximately -15 to +30 percent. The total project capital cost includes a 38 percent indirect capital cost that includes such expenses as engineering design and construction management, financial, legal, and administrative services, interest during construction, utility connection fees, environmental impact reports, and permits. The estimated "bid" construction cost is $12.5 million with an indirect capital cost of $4.8 million adding up a total project capital cost of $17.3 million. The unit construction and total capital costs are $179/bpd and $247/bpd produced water treated, respectively. Note the capital cost estimates given above are only for the treatment facility as described above; additional capital required for equipment upstream and downstream of the treatment facility is not included. Significant additional capital expenditures for trace oil removal and filtration upstream of the treatment process as well as expenditures for post-treatment storage and handling of the treated water are excluded from these figures.

Total annual O&M cost is estimated to be $6.5 million/yr which is equivalent to 26 ¢/bbl of produced water treated. The itemized O&M cost for the flange-to-flange option consists of $2.6 million/yr (10¢/bbl) for chemicals, $0.98 million/yr (4¢/bbl) for energy, $0.65 million/yr (3¢/bbl) for labor, $0.3 million/yr (1¢/bbl) for maintenance materials, $1.4 million/yr (6¢/bbl) for residuals management, and $0.57 million/yr (2¢/bbl) for contingencies. The maintenance material costs include $0.25 million/yr for replacing two-thirds of the RO membrane elements (24 month life assumed).

If the treated water were to be used for an offsite use, Water Utilities often evaluate the total treatment cost which is the sum of the annual O&M cost and amortized capital cost per acre-foot of water treated. Accordingly, amortized capital cost for this project was estimated using a 20 year loan period, at an annual interest rate of 7 percent, which is a typical scenario for municipal projects that are financed through bonds. The total annual cost thus estimated for the 70,000 bpd (3 MGD) facility is $8.15 Million. The unit treatment cost estimate is approximately 46 ¢/bbl ($3,600/acre-ft) of water reclaimed.

E.5 Tech Transfer Activities

The findings of the study were presented in several local and national meetings for discussion. This included presentations in several Society of Petroleum Engineers Section meetings, International Petroleum Environment Conference, Annual Water Reuse Symposium and Water Environment Federation Annual Conference.

Section 1: Introduction

1.1 Background

Oil production generates a significant by-product, commonly known as "produced water". As the oil is produced from an oil field, produced water can reach 90 percent or more of the fluids pumped from an oil well. In fact, heavy oil fields in California produce 10 to 15 barrels (420 to 630 gallons) of water for every barrel of oil. It is estimated that, in 2002 approximately 14 billion barrels (1.8 million acre-feet) of produced water was generated in the United States from on-shore oil production alone (Veil et al., 2004). This represents a significant potential reclaimed water source in water-short areas such as California. However, the feasibility of water reclamation is highly dependent on the chemical composition of the produced water, which is typically highly saline. The salinity can range from about 3,000 to more than 350,000 mg/l total dissolved solids (TDS), with sodium and chloride generally comprising 70 - 90 percent of the ions and concentrations of calcium, iron, manganese, boron, and dissolved organics generally high (USGS, 2002).

The most prevalent method of handling oil field produced water is through underground injection. Over 65 percent of the produced water from onshore sources is currently re-injected into producing zones for enhanced oil recovery (water and steam flooding and subsidence control) and another 30 percent is injected into deep wells. Such in-field injection may increase the produced water to oil ratio and cause higher pressure in steamfloods, leading to heat losses and, perhaps, lower recovery. Reducing Class II Injection through beneficial reuse of treated produced water can optimize oil production and increase recoverable reserves in an oilfield.

The Clean Water Act only allows on-shore surface discharge to navigable waters west of the 98th Meridian (a north-south line approximately running just west of Minnesota and through Dallas, Texas) if the produced water is of acceptable quality for beneficial uses such as stream flow augmentation. Other potential beneficial uses of produced water include water source for cogeneration or cooling, agricultural irrigation, drinking water supply, and groundwater recharge.

1.2 Project Objective

This project, jointly funded by the U.S. Department of Energy, National Energy Technology Laboratory (No.DE-FC26-02NT15463), Aera Energy LLC, and Kennedy/Jenks Consultants evaluated the potential for treatment and beneficial reuses of produced water from an oilfield near San Ardo in Monterey County, CA. Around San Ardo, the Salinas Valley groundwater basin provides most of the water supply needs. Due to high water demands from population growth and agriculture groundwater, extraction exceeds the sustainable yield of this basin. The high dependence on groundwater has resulted in a long-term average overdraft of about 19,000 acre-foot per year (AFY) in the groundwater basin. The overdraft conditions have resulted in seawater intrusion for about 6 miles in the northern Salinas valley, where the river empties into the Pacific Ocean. A successful produced water treatment process could make available more than 4,000 AFY of water from Aera's San Ardo oilfield. This is nearly one fifth of the annual overdraft.

The overall project was divided into two phases (Phase I & Phase II). Phase I activities started in October 2002 and completed in October 2003. Phase II activities were initiated in October 2003 and completed in April 2005. The major objectives of Phase I were the following:

- Identify potential end uses for the treated produced water

- Identify regulations related to treatment, delivery and use of treated water for the identified end uses

- Evaluate process alternatives to meet the water quality goals and develop planning level cost estimates, work plans, sample analyses plans and a health & safety plan for the pilot study

- Develop engineering drawings for the Phase II pilot plant study

The major objectives of Phase II of this project were to:

- Perform pilot study to verify the findings from Phase I study

- Develop process design criteria for full scale plant based on the pilot study findings, and

- Revise the cost estimates based on the pilot study results

1.3 Project Site Description

The project site, San Ardo oilfield, is located in Monterey County, California within the city limits of San Ardo. The field is adjacent to the Pacific Coast Highway (Hwy 101) and is located on the in the county of Monterey, State of California. Figure 1-2 is a location map of the project site. The majority of the field is owned by two oil companies, Aera Energy LLC (~ 60 %) and Chevron Texaco (~ 40%). Figure 1-3 summarizes the current water balance of the Aera Energy LLC activities in the San Ardo Field.

1.4 Potential Project Benefits

The benefits of produced water treatment and removal at the San Ardo oilfield are primarily related to oil production. By reducing the volume of produced water reinjected into disposal wells within this oilfield, reservoir pressures will drop significantly. This in turn will lead to improved thermal (steam) efficiency and lower costs in the oil recovery process. In addition, costs associated with current reinjection of the full produced water stream will be reduced. A successful produced water treatment process may also provide a secondary benefit in creating a new, usable water supply; however the end use of this water is uncertain.

1.5 Project Entities

The project consisted of a team made up of the following participants:

- Aera Energy LLC, a California limited liability company, headquartered at Bakersfield, CA was the prime contractor with DOE.
- First tier subcontractor included Kennedy/Jenks Consultants, Inc. which is a privately owned, full service environmental engineering firm.

1.6 Project Staff

Mr. Robert A. Liske of Aera Energy LLC was the Project Manager. Ms. Debra Bias and Mr. Prentice Patterson, the facility supervisors, provided assistance at the San Ardo Oil Field. The technical project team was led by Dr. Lawrence Y.C. Leong of Kennedy/Jenks Consultants. Key support staff include Dr. Rajagopalan Ganesh, Dr. Joseph A Drago, Mr. Sunny Huang, Ms. Roxanne Nagle and Mr. Josh Anderson of Kennedy/Jenks Consultants.

1.7 Organization of Final Report

Section 1 of the Final report describes the general background and goals of the project. Section 2 presents efforts to identify the possible end uses and disposal options for treated produced water near the San Ardo oilfield. Section 3 reviews regulatory requirements for treatment, delivery, storage, use and disposal of produced water in the project area. Section 4 summarizes screening and selection of treatment processes. Section 5 presents the results of bench scale tests conducted to optimize the pilot process as well as to facilitate pre- and post treatment process train evaluation. Section 6 describes the pilot plant unit processes, the analytical methods, and the operational plan. The results of the pilot plant study are presented in Section 7. The recommended full scale process train and the estimated cost are presented in Section 8. A summary of technology transfer activities from this project are presented in Section 9. The bench and pilot study work plan and pilot study results are presented in Appendixes A and B, respectively. Correspondence with various regulatory agencies is presented in Appendix C. Appendix D contains copies of the material that have been presented at DOE or national meetings to fulfill the technology transfer requirements of this project.

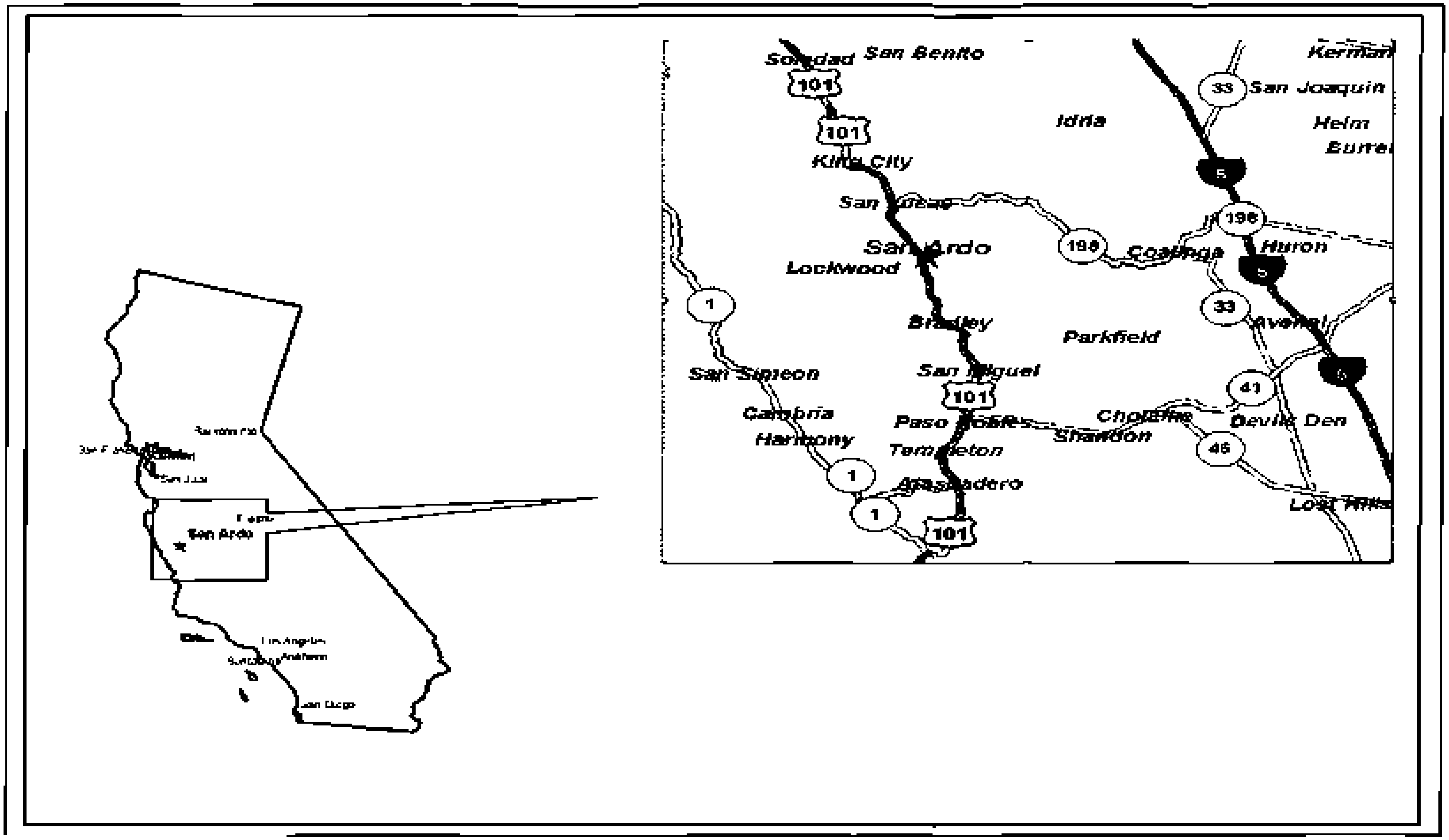


Figure 1-1. Project Site Location

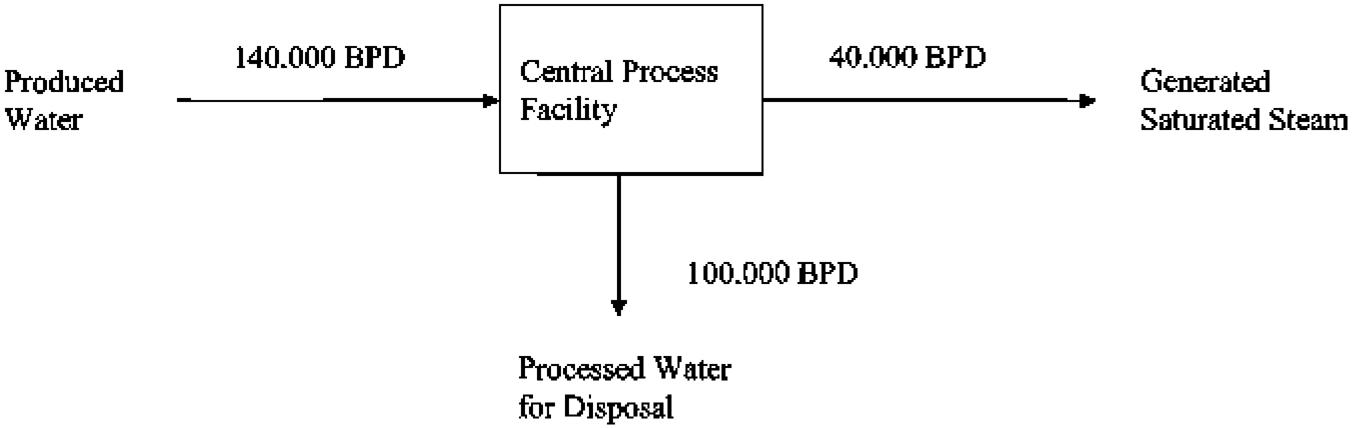


Figure 1-2. Current Aera Energy LLC San Ardo Oilfield Produced Water Balance

Section 2: Evaluation of End Use and Offsite Disposal of Treated Produced Water in the Project Area

This section summarizes various possible end uses and disposal options identified for the treated produced water from the San Ardo oilfield. The potential purchasers of treated oilfield-produced water in the San Ardo area are limited because currently there are no regional conveyance facilities in the Salinas Valley, other than the Salinas River. Furthermore, the Clean Water Act significantly restricts such on-shore surface discharge of treated produced to navigable waters in areas west of the 98th Meridian (a north-south line approximately running from just west of Minnesota down through Dallas, Texas). The surface water discharge of treated produced water to navigable waters is allowed only if the treated water is put to actual use for agricultural use or wildlife propagation. For uses other than agriculture or wildlife propagation, the treated water must be delivered through direct piping or some other alternate means. Initial evaluation of potential options for treated water use or disposal yielded the following opportunities:

- Agricultural growers, including those who currently utilize groundwater, and those landowners who desire to bring land into agricultural production,
- Monterey County Water Resources Agency (MCWRA) for the Salinas Valley Water Project or Castroville Seawater Intrusion Project, and/or
- Use for industrial (power plant) application in King City.
- Use of treated produced water for creation of wetlands in the Salinas Basin

With the exception of groundwater recharge, all opportunities listed above have major obstacles to full-scale implementation. The limitations of each of these alternatives are presented below.

Subsequently, an additional option of using the treated water to recharge groundwater adjacent to the project area and away from the oil formation has been identified as another potential reuse option. As discussed below, this option may avoid the major obstacles to full-scale implementation that the previously-identified reuse options face.

2.1 Use of Treated Produced Water for Agricultural Irrigation in the San Ardo Area

The San Ardo oilfield is located in Salinas Valley in the central coastal region of California. San Ardo is a highly productive agricultural region, producing approximately two billion dollars in revenue each year in Monterey County. The Salinas Valley has a southeast-northwest trend, and is bordered by the Santa Lucia Range on the west and the Gabilan and Diablo Ranges on the east. The oilfield, located in the southeastern stretch, is part of the Upper Salinas Valley.

2.1.1 Agricultural Acreage in the Salinas Valley

Agricultural land in the entire Salinas Valley in 1995 extended across an area of approximately 200,000 acres (MCWRA, 1998). Within the Upper Salinas Valley, agricultural land in 1995 occupied 48,000 acres (MCWRA, 1998). Field and truck crops occupy the most land (26,000 acres), and vineyards are the second largest land-users (16,000 acres). The breakdown of the Upper Valley agricultural acreage into land use types is shown in Table 2-1.

Table 2-1: Upper Valley Sub-Area Crop Acreage (1995)

Type of Crops	Upper Salinas Valley (Acres)	Total Salinas Valley (Acres)
Pasture	1,900	4,200
Field	450	7,000
Truck	25,800	143,000
Orchards	450	1,100
Vineyards	16,300	35,000
Grain	3,000	5,000
Total Acreage	**48,000**	**196,000**

Source: MCWRA (1998)

2.1.2 Agricultural Acreage Within a Five Mile Radius of San Ardo Oilfield

Preliminary evaluations indicated that, in order to economically deliver the treated water for agricultural irrigation, the farmland must be within a radius of 5 miles from the oilfield. Therefore, a Geographical Information System (GIS) analysis was performed to identify farmland within this boundary. Evaluations indicated that there are about 3,500 acres of farmland within 5 miles north of the oilfield and east of the Salinas River (Table 2-2). Since these farms are located downstream from the oilfield area, water can either be delivered through the Salinas River or directly by hard pipe. Hence, these farms were identified as the most likely agricultural users for the treated produced water. Figure 2 - 1 shows the location of the farmland within five miles north of San Ardo oilfield.

Table 2-2: Agricultural Land Owners and Acreage Within Five Miles to the North of San Ardo Oilfield

Owner	Parcel Ref. Nos.	Acreage
Albert A Oliveira	6,12	73
Arvid J & Ann R Myhre	37	71
Arvid J Myhre	38	18
Arvid J Tr Myhre	23, 24, 27	211
Bonifacio & Josefina Rubio	40	64
Dudely & Grimes Co.	36, 45	33
Harold C & Ester M Lombardi	8, 15, 16, 19	283
Jerry J Sr & Suzanne Rava Rava	29	200
Lawrence R Glau	22	392
Orradre Ranch	30, 31, 32	117
Rosenberg Family Ranch LL	2, 5, 7, 11, 20, 21, 25, 26, 28	1,775
Others	1, 3, 4, 8, 9, 14, 33, 34, 39, 41, 43, 44	200
Total		**3,500**

Figure 2-1. Agriculture Land Within 5-mile Radius of San Ardo Oilfield

Out of the 3,500 acres of farmland, water can be delivered using a 2.5-mile pipe line from the San Ardo oilfield and service about 2,700 acres. Only one owner owns nearly 50% of the 3,500 acres of farmland. Four owners own approximately 2,600 acres within a 2.5-mile pipe service area. Data from MCWRA indicate that the average amount of water applied for irrigation in 1995 in the Upper Salinas Valley was about 2.75 AF/acre (MCWRA, 1998). The peak irrigation months are June through August. Based on annual water usage, all of the proposed treated produced water from the oilfield can be utilized by less than 2,000 acres of farmland.

2.1.3 Agricultural Crops in the San Ardo Oilfield Area

Table 2-3 shows the perennial and annual row crops grown or intended to be grown in the project area. Alfalfa, asparagus, grapes and walnuts are among the perennial crops cultivated in this area and beans, broccoli, cabbage, cauliflower, garlic and lettuce are among the annual crops grown.

Table 2-3: Crops Grown In San Ardo Area

Type of Crop	Name of Crop
Perennial	alfalfa, asparagus, grapes (predominantly wine grapes, such as cabernet, merlot, and chardonnay), and walnuts
Annual "Row"	beans (lima, seed), broccoli, cabbage, cauliflower, garlic, lettuce (leaf, head, Romaine), onions, parsley, peppers, spinach, tomatoes.

2.1.4 Water Quantity Needs of Agricultural Crops

Data from MCWRA indicate that the average amount of water applied for irrigation in 1995 in the Upper Salinas Valley was about 2.75 AF/acre (MCWRA, 1998). The seasonal variation in water demand is not currently available. In general, the peak irrigation months are June through the end of August, due to the heat in the Salinas Valley. Table 2-4 summarizes the estimated water use per acre of irrigation for the types of crops grown in the project area.

Table 2-4: Water Quantity Estimates for Specific Crops Grown in the San Ardo Area

Crop	Estimated Total Water Use (AFY/Acre)[a]	Number Of Days And/Or Season	Irrigation Method	Crops Per Year
Perennial Crops				
Alfalfa				
Asparagus				
Grapes (Wine)[b]	2.0 – 3.0	180	Drip	1
Walnuts				
Annual Crops				
Beans				
Broccoli[c]	2.0 – 3.0	- - -	Sprinkler/Furrow	2
Cabbage				
Cauliflower				

Crop	Estimated Total Water Use (AFY/Acre)[a]	Number Of Days And/Or Season	Irrigation Method	Crops Per Year
Garlic				
Lettuce (Head)[d]	1.0 – 1.5	60 - 70 Summer; 100 - 130 Winter	Sprinkler	2
Lettuce (Leaf)[e]	1.0 – 1.5	60 - 70 Summer; 100 – 130 Winter	Sprinkler	2
Onions[f]	2.5 – 3.0	- - -	Sprinkler/Furrow	1
Parsley				
Peppers				
Spinach (Fresh)[g]	0.5 – 1.0	30 – 55	Sprinkler/Furrow	3
Spinach (Processed)[g]	1.5 – 2.0	70 – 120	Sprinkler/Furrow	2

(a) Estimated total water use = ETc + runoff + drainage. ETc is crop evapo-transpiration under standard conditions, and refers to the evapo-transpiration from disease-free, well-fertilized crops, which are grown in large fields under optimum soil water conditions, excellent management and environmental conditions, and achieving full production under the given climatic conditions.
(b) Wine Grapes: Water Management and Irrigation Scheduling, Tulare County Publication IG9-98
(c) Broccoli: Broccoli Production in California, UC DANR Publication 7211
(d) Head Lettuce: Iceberg Lettuce Production in California, UC DANR Publication 7215
(e) Leaf Lettuce: Leaf Lettuce Production in California, UC DANR Publication 7216
(f) Onions: Fresh market Onion Bulb Production in California, UC DANR Publication 7242
(g) Spinach: Spinach Production in California, UC DANR Publication 7212

2.1.5 Water Quality Requirements

Tables 2-5 compares untreated oilfield produced water quality and Central Coast Regional Water Quality Control Board (CCRWQCB) water quality requirements for irrigation use. In addition, if the treated water is delivered through the Salinas River, treated produced water must also meet requirements of the National Toxicity Regulation (NTR). As shown in Table 3 concentrations of ammonia, nitrogen, boron, chloride, fluoride, salinity, sodium and TOC in the untreated produced water exceed CCRWQCB requirements. The San Ardo produced water must be treated to remove these constituents if the treated water were to be used for irrigation.

Table 2-5: San Ardo Produced Water and CCRWQCB Water Quality Requirements

Compound	San Ardo Produced Water (mg/l)	CCRWQCB Basin Plan (Agricultural use) Criteria
Alkalinity	367	
Aluminum	0.2	5[a]
Arsenic		0.1[a]
Ammonia - Nitrogen	31.1	5 – 30[b]
Barium	0.41	
Beryllium	<0.0005	0.1[a]
Bicarbonate	448	90 – 520[b]
Boron	26.8	0.75 [a]
Cadmium	<0.0005	0.01[a]
Calcium (Ca^{+2})	111	
Carbonate	1	
Chloride	4,050	150[c]
Chromium		0.1[a]
Cobalt		0.05[a]
Copper	0.0008	0.2[a]

Compound	San Ardo Produced Water (mg/l)	CCRWQCB Basin Plan (Agricultural use) Criteria
Fluoride	1.8	1[a]
Hardness, Total	303	
Iron	0.17	5[a]
Lead		5[a]
Lithium		2.5[a]
Magnesium (Mg^{+2})	6.07	
Manganese	0.105	0.2[a]
Molybdenum	0.008	0.01[a]
Nitrate-Nitrogen	4	5 – 30[b]
pH	7.54	6.5 – 8.4[b]
Potassium	61.6	
Salinity (mmho/cm)	10.7	0.75 – 3[b]
Selenium	<0.0005	0.02[a]
Silica (SiO_2)	227	
Sodium	2,540	70[c]
Sodium Adsorption Ratio		3 - 9
Strontium	2.68	
Sulfate	63	150[c]
Sulfide	12	
TDS	7,540	600[c]
TPH (oil and grease) for NPDES Discharge	1.9	35
TOC	80	<2[d]
Vanadium		0.1[a]
Zinc		2[a]

(a) CCRWQCB Water Quality Objective for Agricultural Water Use

(b) Guidelines for interpretation of quality of water for irrigation. The range shown is for "increasing problems" for crops.

(c) Median groundwater quality objective for upper Salinas Basin

(d) Adapted based on anti-degradation policy

Although the evaluation indicated the potential for using the treated San Ardo oilfield produced water for agricultural use, there are several concerns that must be addressed prior to implementation of this concept. For example, there is a significant variation in seasonal water demand for agriculture, with the peak demand period extending from June through August only. The treated produced water from oilfield operation is, however, generated continuously throughout the year. Surface or underground storage facilities of hundreds of million gallon capacity may be required to store water generated during non-peak demand periods. Secondly, significant effort may be required to convince the farmers to accept the recycled water source for irrigation. Finally, the cost of treating and delivering the water must be compared with the benefit of increased oil production prior to implementation of this project.

2.2 Monterey County Water Resources Agency Use

The Monterey County Water Resources Agency is a public agency that has been charged with the long-term management and preservation of water resources in Monterey County. In order to prevent seawater intrusion into the Salinas Valley Basin and protect agricultural water use, MCWRA has undertaken two major projects i) the Salinas Valley Water Project (SVWP) and ii) the Castroville Seawater Intrusion Project (CSIP). The key components of these projects are to identify alternate sources of water for agricultural use in the Salinas Valley Basin and prevent seawater intrusion by reducing groundwater drawdown in the lower Salinas Valley Basin. The main objective of the SVWP is to increase the capacity of the Nacimiento Dam reservoir by i) modifying the Naciemiento Dam spillway and ii) construct a facility to divert part of Salinas River water for the Castroville Sea Water Intrusion project. Under the CSIP project, the excess water from the Salinas River diversion will be diverted to the Castroville service area for agricultural use. This will replace the groundwater that is currently pumped for agriculture irrigation in this area, and will help prevent sea water intrusion into drinking water aquifers. The operational objective of the project is to stop sea water intrusion into the Salinas Basin and provide up to 1000 AFY net groundwater outflow to Monterey Bay. In addition, the average annual Salinas River diversion capacity is about 12,000 AFY. By comparison, the amount of water anticipated to be generated by treatment of produced water in this project is about 4000 AFY.

Use of treated produced water by MCRWA for the Salinas Valley Project or Castroville Project will involve delivery by the Salinas River to the Salinas River diversion facility followed by delivery to lower basin users by the MCWRA distribution system. The 40 CFR 435.30 of the Clean Water Act requires that the use of oil field treated water must involve beneficial uses such as agriculture and wildlife propagation. Hence, the CCRWQCB, under some conditions, may permit the delivery of treated produced water into the Salinas River for supplementing agricultural use under these MCWRA projects. The water thus discharged must meet all the water quality criteria described earlier for discharge of water for agricultural use. Although the use of treated produced water for MCWRA initially appeared to be a viable option, upon further discussion with MCWRA, it was observed that the loss of water during conveyance (evaporative and percolation) from the oilfield is significant compared to the water generated in this project. For example, the average flow in the Salinas River is about 60 cfs while the amount of water generated by this project is about 1.5 cfs. The loss during conveyance in this stretch is estimated by MCWRA to be about 5 cfs. Since the water generated from this project is significantly smaller than the water lost during conveyance, MCWRA staff indicated potential difficulties in estimating the quantity of water received at the end use location. Hence, the use of treated water for MCWRA does not appear to be a viable option.

2.3 Industrial Use

For cooling and make-up water needs, a power plant located at King City was initially considered as a candidate for using the treated produced water. This plant is located about 30 miles north (downstream side of the Salinas river) of San Ardo. Delivery of water through the Salinas River is not possible due to 40 CFR 435.30 beneficial use requirements. In addition, delivery of water by a new, unsubsidized 30-mile pipeline is cost prohibitive. Hence, this option is not pursued further in this project.

2.4 Use of Treated Produced Water for Creation of Wetlands in the Salinas Basin

One possible option for the use of treated produced water is to create wetlands to preserve riparian oak. Seasonal (vernal) ponds to preserve native amphibians are also an option. Either of these options will require a survey by biologists to identify the presence of endangered species in the project location. United States Fish & Wildlife Services (USFWS) and California Department of Fish and Game may encourage such use. However, creation of wetlands for endangered species restoration/preservation will require a long term commitment of water supply from the oilfield. This may be a concern if the oilfield operations are curtailed for any reason or terminated at the end of the economic life of the oil field or other reasons.

2.5 Groundwater Recharge of Treated Water Adjacent to Project Area and Away From the Formation

Under this option, the treated produced water is discharged outside the oilfield for groundwater recharge, rather than for a specific end use such as agricultural use or endangered species preservation. A key requirement for this option is the availability of land for such recharge and its capacity to percolate the water at a reasonable rate. In the area around San Ardo oilfield, a large amount of land is available for construction of such recharge (percolation) basins. The soil in this area is generally amenable for agriculture. It is composed of sand, loamy sand, silt loam and fine sandy loam with moderate infiltration rates. Some initial evaluations indicate that for discharge of 50,000 barrels per day of water in these percolation ponds, approximately 20 acres of land may be required.

The water quality requirements for such disposal are set forth in the CCRWQCB Basin Plan. However, because the recharge option should not involve the discharge of the treated water to navigable waters, the Clean Water Act prohibition against discharging treated produced water should not be applicable to this option.

Section 3: Regulatory Requirements for Beneficial Uses

3.1 Introduction

The objective of this section is to summarize the regulations related to the use of treated oilfield produced water for various end use/disposal options identified in Section 2. Furthermore, for the convenience of the reader, regulations related to treatment of the produced waters are also presented in this section.

The regulatory requirements for water and wastewater treatment processes generally address the use of treatment chemicals, air emissions and waste disposal. The specific issues identified for San Ardo oilfield produced water include:

- Use of spent-caustic generated in an off-site facility for softening of produced water
- Regulation of air emissions (e.g. VOC, NH3) during treatment
- Disposal, in Class II injection wells, of wastes generated during treatment of produced water

The key regulatory issues related to the use of treated produced water include

- Water quality issues
- Water delivery/water rights issues if treated produced water is delivered through Salinas River
- Storage of treated water

Table 3-1 shows the agencies responsible for regulation of various activities in the San Ardo area. The details of regulations are summarized in the following sections.

Table 3-1: Agencies Involved With Permit Processes for Treatment of San Ardo Oilfield Produced Water

Agency	Activities Regulated
Agencies Related to Treatment of Produced Water	
California Department of Toxic Substance Control (DTSC)	Transport and use of waste caustic for produced water treatment
Monterey Bay Unified Air Pollution Control District (MBUAPCD)	Air pollution control during treatment (warm softening, cooling) processes
California Department of Oil, Gas and Geothermal Resources (CDOGGR)	Deep well disposal of non-hazardous wastes within an oilfield in California
Monterey County Planning Department	Building facilities in the treatment plant facilities
Agencies Related to Delivery, Storage and Use of Treated Produced Water	
Central Coast Regional Water Quality Control Board (CCRWQCB)	Water/waste quality issues related to treatment, delivery, storage and end use

California Water Resources Department – Water Rights Division	Water rights/water allocation issues if treated water is discharged into Salinas River
California Water Resources Department –Division of Dam Safety	Storage of treated water near navigable waters
US Army Corps of Engineers	Storage facilities near navigable waters for federal funded projects
Monterey County Planning and Building Inspection Department	Grading permits for decentralized storage of treated produced water

3.2 Agencies/Regulations Related to Treatment of Produced Water

3.2.1 California Department of Toxic Substance Control

San Ardo produced water contains high level of hardness (250 mg/l as $CaCO_3$) which may require removal by precipitation at elevated pH conditions. One of the options considered for such a precipitative softening process is the use of "spent-caustic" generated in an offsite facility. Such a use, if viable, will facilitate waste minimization due to reuse of spent caustic. Transportation and use of such off-site generated spent caustic is regulated by the California Department of Toxic Substance Control (DTSC). A key factor that will influence such use is the classification (hazardous or non-hazardous) of the spent caustic. As per the provisions of the California Health and Safety Code (H&SC) section 25143.2(b)(2), a material such as the "spent caustic" is exempted from classification as waste material if it "is used as a safe and effective substitute for commercial products if the material is not being reclaimed". Based on this criterion the spent caustic, if used for produced water treatment, is considered a recyclable material. However, this provision of the H&SC requires that the material must be stored in containers or tanks that are properly labeled with the words "recyclable material", the facility has a business plan, and the facility must handle the material in accordance with all local ordinances and codes. In addition, every two years the facility must file a claim that the material qualifies for exclusion or exemption with the local Certified Unified Program Agency (CUPA).

3.2.2 Monterey Bay Unified Air Pollution Control District

During the treatment of oilfield produced water, there is a potential for emission of volatile compounds such as VOC or ammonia from the oilfield produced water. The Monterey Bay Unified Air Pollution Control District (District) regulates air emissions from stationary sources within the three County North Central Coast Air Basin (Monterey, Santa Cruz and San Benito Counties). The District develops rules and regulations to work towards attainment and maintenance of Federal and State ambient air quality standards, and is the primary enforcement agency for air pollution control in the project area.

Any facility which has the potential to emit air contaminants must apply for a permit from the District. The District determines the applicable permit requirements. There are two types of permits: the Authority to Construct (A/C) and Permit to Operate (P/O). The A/C is a certification that the emissions from the proposed project will meet all applicable District requirements and not interfere with air quality standards when constructed. The P/O is issued after construction is completed and operation of the equipment has begun. It certifies that the construction and actual operation meets the terms and conditions of the A/C and that emissions are consistent with those estimated in the A/C.

3.2.3 California Department of Oil, Gas Geothermal Resources

At present, a large portion of the produced water generated in the oilfield is disposed through injection into Class II wells within the oilfield. It is likely that the proposed treatment will include disposal of the waste streams (e.g. RO reject stream) in Class II injection well within the oilfield. Such activities within the oilfield are regulated by the California Division of Oil, Gas and Geothermal Resources (CDOGGR)

CDOGGR oversees the drilling, operation, maintenance and plugging and abandonment of oil, natural gas and geothermal wells throughout California. In 1993, the Division received primacy from the United State Environmental Protection Agency (USEPA) to regulate Class II injection wells, under the provisions of California Public Resource Code and the Federal Safe Drinking Water Act. The main features of the UIC program include permitting, inspection, mechanical integrity testing, plugging and abandonment oversight, data management and public outreach. Federal and State regulations allow nonhazardous fluids integrally associated with the production of crude oil and natural gas to be injected into Class II injection wells.

Discussions were held with CDOGGR regarding the regulations related to deep well injection of waste streams generated in the treatment of oil field produced water within the oilfield boundaries. The CDOGGR responded that as long as the waste streams are not hazardous they can be deep well injected in the oilfield. Correspondence with CDOGGR is included in Appendix C.

3.2.4 The Monterey County Planning Department

Approval from Monterey County Planning Department must be obtained for all construction projects in the project area. Engineering drawings for full-scale treatment plant buildings must be approved by Monterey County Planning, Building, Fire and Public Works departments.

3.3 Regulations Related to Water Quality of Treated Water

3.3.1 Central Coast Regional Water Quality Control Board

The Central Coast Regional Water Quality Control Board (CCRWQCB) is the principal regulatory agency responsible for overseeing the discharge of any water that could impact California water resources in this region. This authority comes from the Porter-Cologne Water Quality Control Act (Porter-Cologne) that established the California State Water Resources Control Board (CWRCB) and nine Regional Water Quality Control Boards. The CCRWQCB is one of these nine regional boards.

The CCRWQCB, in its role of implementing the State Policy for Water Quality Control, has adopted a Basin Plan that identifies the beneficial uses of the various existing water resources in the region, including surface and ground water. Any discharge from this project would most likely occur within the Salinas Hydrologic Unit. This hydrologic unit is subdivided into various sub-units and each sub-unit has its own set of beneficial uses.

All beneficial uses are protected by the development of water quality objectives that, in turn, are used to establish local waste discharge requirements (WDRs). The WDRs must also comply with the existing State Implementation Policy related to the National Toxics Rule (NTR) and the specific California Toxics Rule (CTR).

Authorization from the CCRWQCB is required for any discharge that may have an impact on the region's water resources. Two types of authorization are issued. The first is the

National Pollutant Discharge Elimination System (NPDES) permit, a national program delegated to the State and Regional Boards for implementation. This permit affects any discharge to a water of the U.S. (primarily surface waters). The second is a set of WDRs which are a California authorization intended to protect state waters not covered by the NPDES permit program. In practice, it is common for the CCRWQCB to issue one permit that covers both program requirements.

The permit requirements under various water discharge (delivery) and water use scenarios are described below:

3.3.1.1 Water Quality Regulations Related to Delivery of Treated Produced Water Through the Salinas River

In this scenario, produced water for irrigation would be treated and then discharged directly to the Salinas River. The treated water would need to meet the requirements found in the following regulations and/or policy documents:

- 40 CFR 435.30 et seq,
- 40 CFR 435.50 et seq,
- NTR)the CWRCB Policy for Implementation of Toxics (Resolution 2000-015 as amended by Resolution 2000-30),
- The Anti-degradation Policy (Resolution 68-16), and
- The narrative and specific numeric water quality objectives contained in the Central Coast Basin Plan for the Salinas River and any groundwater that might be impacted by the discharge.

<u>40 CFR 435.30 et seq.</u>

This is a federal regulation promulgated by the Environmental Protection Agency (EPA) in which effluent guidelines for the oil and gas extraction industry were developed. Specifically, 435.30 et seq. addresses discharges from the "onshore" subcategory of the oil and gas extraction industry that are located landward of the inner boundary of territorial seas. In section 435.32, the effluent guideline states, "there shall be no discharge of waste water pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion, or well treatment" to the west of the 98th meridian. Unless wastewater discharge to the Salinas River is subject to other provisions contained in 40 CFR 435 (see below), the Water Board will not allow any discharge of wastewater to the Salinas River.

<u>40 CFR 435.50 et seq.</u>

This section of the federal regulations addresses onshore facilities "located in the continental United States and west of the 98th meridian for which the produced water has a use in agriculture or wildlife propagation when discharged into navigable waters". Onshore facilities in the San Ardo Field are located in the continental United States and they are located west of the 98th meridian. The wastewater would be treated before discharge to meet quality standards for use in agricultural applications. In 435.51, the term "use in agricultural or wildlife propagation" is defined to include produced water of sufficient quality to be used for agricultural uses. Discharge would be subject to certain limitations specified in 40 CFR 435.52, namely, that the produced water (after treatment) does not exceed a daily maximum limitation for oil and grease of 35 mg/l and other limitations as discussed below.

NTR and CTR, Water Board Implementation Policy

These two regulations and the State Board policy are intended to limit the discharge of "toxics" into navigable waters. CTR, promulgated in 2000, specifies water quality criteria for 128 priority pollutants based on their toxicity to aquatic species. These limits, presented in EPA Federal Register (USEPA, 2000), are generally lower than NPDES discharge limits based on Basin Plan criteria. Compliance with some of these limits would require significant, additional treatment processes and increased treatment cost.

Anti-degradation Policy

The CWRCB adopted this policy in the late 1960s to maintain the quality of existing water resources. Under this policy, the discharge must not cause a degradation of the existing quality of the receiving water unless it has been demonstrated that the change will be consistent with maximum benefit to the people of California, that it will not unreasonably affect the present and anticipated beneficial use of such water, and that it will not result in water quality less than that prescribed in the policies.

Central Coast Basin Plan

The CCRWQCB is responsible for adopting and implementing the Basin Plan that defines beneficial uses of surface and groundwater in the project area and sets narrative and numerical water quality objectives for the designated use. Accordingly, the beneficial use designations for the Salinas River include Municipal and Domestic Water Supply (MUN) as well as Agricultural Water Supply (AG) and Industrial Water Supply (IND) uses among other uses. In addition, the Basin Plan defines narrative and numeric criteria for groundwater recharge and agricultural use when the water is not delivered through the river. The Water Board may require that the produced water be treated to meet the appropriate criteria of the narrative and specific numerical water quality objectives as identified in the Basin Plan prior to discharge.

3.3.1.2 Water Quality Requirements Related to Delivery of Treated Water for Agricultural Irrigation by Hard Pipe

In this scenario, the end user would get deliveries of treated water for agricultural irrigation by a hard pipe. The CCRWQCB would require a WDR for this use. The treated water must meet the following water quality criteria:

- Crop water quality requirements
- Water quality requirements of the Central Coast Basin Plan

Compared with delivery through the Salinas River, there would be fewer monitoring requirements. For example, a shorter list of parameters may be issued to routinely treat and report. These differences may or may not alter the treatment process train for the produced water.

3.3.1.3 Water Quality Requirements Related to Discharge of Groundwater Into the Salinas River Through Water Trade Agreement with Farm Owners

Under this scenario, treated water delivered for agricultural use would be traded for groundwater. The "freed–up" groundwater would then be pumped into the Salinas River for conveyance to downstream users. The groundwater pumped into the river must meet all the requirements specified in an earlier section for the discharge into the Salinas River.

3.4 Water Rights Regulation

3.4.1 California Water Resources Control Board – Division of Water Rights

The CWRCB Division of Water Rights (DWR) is responsible for ensuring that water is shared equitably among all downstream users, based on historical or legally determined water rights. As such, the DWR establishes removal quotas or pumping limits based on the adjudicated volumes of water provided by the various sources. The addition of new sources of water, such as treated produced water, would likely need to be allocated to downstream users. The process requires identification of the volume of water and the potential downstream user. The permit to appropriate the released water by the identified user would be based on the amount of water delivered and potential losses during conveyance. The proposed use of the appropriated water must also be specified. The permit application must indicate the details of the diversion works (direct diversion by pump, storage dam, etc.). The permit application would have to be filed well in advance of the construction of diversion work.

The proposed project may be subject to the California Environmental Quality Act (CEQA) which requires agencies to consider environmental effects. This process may involve obtaining a certification of exemption, a negative declaration or a preparation of a full Environmental Impact Report (EIR). More details regarding the appropriation process is provided in the three pamphlets issued by the DWR (CWRCB 2000, 2000a, 2001).

3.5 Water Storage Regulations

Due to potential differences in supply and demand for the treated produced water storage facilities may be required to store the water produced during non-peak demand period. For example, the peak water demand for agricultural use is between June and August. Depending on the location, size and funding source various agencies would be involved in the permit process for construction of storage facilities. Permit requirements from these agencies are briefly discussed below:

3.5.1 California Department of Water Resources – Division of Safety of Dams

The Division of Safety of Dams (DSD) would be involved with any project that creates a structure to impound water in a "navigable" water as defined by EPA if the structure is greater than 25 feet high or the impoundment contains more than 50 acre-feet of water. In this role, the DSD would ensure that the structural integrity of any jurisdictional dam (storage structure) is adequate for its intended purpose. Furthermore, the DSD would usually be the State representative for the US Army Corps of Engineers.

Water storage structures that are built solely for agricultural use and not located across a stream channel, watercourse, or natural drainage area are not considered to be a dam and not subject to the jurisdiction of the DSD. (California Water Code (CWC), Division 3, Part 1, Chapter 1, §6004(b)). The jurisdiction of the DSD normally applies to any structure that is 25 feet or more in height or has or will impound a capacity of 50 acre-feet or more. (CWC, §6002). However, the CCRWQCB would be involved because any water discharge into the storage area could have the potential to impact waters of the state, i.e. groundwater.

3.5.2 US Army Corps of Engineers

The Corps of Engineers is not normally involved in such projects unless there is direct U.S. Government funding for the construction of a dam. As such, the Corps of Engineers would rely upon the DSD to oversee any construction that does not involve federal funding (i.e., the COE will be directly involved only if the project receives federal funding).

3.5.3 Monterey County Planning and Building Inspection Department

The feasibility of local water storage in surface impoundments (ponds) on individual farmlands was explored. In order to install a pond, a farmer would be required to obtain grading permits from the Monterey County Planning and Building Inspection Department. As part of the permit process, the farmer must submit five sets of plans for each area where ponds are planned.

3.5.4 Central Coast Regional Water Quality Control Board

Chapter 3 of California Code of Regulations (Title 27, Division 2, Subdivision 1) classifies wastes to determine where the wastes can be discharged (stored). This chapter presents geologic and siting criteria for waste management units to store various waste streams. The CCRWQCB is responsible for defining the storage siting criteria if seasonal storage is required for treated produced water. However, an exemption from this requirement might be available if the waste (treated produced water) meets the criteria for inert waste as defined by section Ch15:§2524. An "inert waste" is a subset of waste that does not contain hazardous substances or soluble pollutants at concentrations in excess of applicable water quality objectives and does not contain significant quantities of decomposable waste.

3.6 Regulations Related to Wildlife Protection – California Department of Fish and Game

Any structure constructed for discharge of treated water into a waterway would require a stream alteration permit from the California Department of Fish and Game (CDFG). In addition, CDFG is responsible for ensuring sufficient water flow downstream of any water diversion point at all times in order to protect fish and wildlife resources. (Section 5937, Article 2, Chapter 3, Part 1, Division 6 of the California Fish and Game Code). Approval from the CDFG may be required to obtain water appropriation by an end user.

In summary, an evaluation of regulations indicates that, for delivery of treated water to agricultural land by hard pipe, the treated water quality must meet crop water quality and basin plan water quality requirements. WDRs must be obtained from the CCRWQCB. For delivering water via the river the following would be required:

- The released water must facilitate agricultural or wildlife restoration requirements.
- The water quality must be in compliance with NPDES, NTR, CTR and anti-degradation requirements.
- A permit from the CWRCB must be obtained for water appropriation.
- Approval from the CDFG may be required for the appropriation of water to verify that the loss of water will not have an adverse effect on fish and wildlife resources.

Finally, storage of water during periods of low demand may involve regulations from the DSD, Monterey County Environmental Health & Planning Department, and the CCRWQCB depending on storage location and water quality.

Section 4: Pilot Process Selection

4.1 Background

This section reviews treatment processes that are potentially applicable for treatment of San Ardo produced water and presents the process train selected for the pilot study. A key goal of this project is to lower the Operations & Maintenance (O&M) costs for the treatment of San Ardo oilfield produced water based on the findings of the previous DOE pilot study at Placerita Canyon (Doran, 1998).

Table 4-1: Representative Water Quality Characteristics of Placerita and San Ardo Oilfield Produced Waters

Parameter*	Placerita Canyon Produced Water	San Ardo Produced Water
Alkalinity (mg/l as $CaCO_3$)	482	367
Aluminum	-	0.2
Ammonia - Nitrogen	15	31.1
Barium	1.5	0.41
Bicarbonate	-	448
Boron	20	26.8
Calcium (Ca^{+2})	260	111
Chloride	3,180	4050
Fluoride	-	1.8
Hardness, Total (mg/l as $CaCO_3$)	1,100	303
Iodide		3.1
Iron	0.16	0.17
Magnesium (Mg^{+2})	97	6.07
Manganese	-	0.105
Nitrate	-	4
Oil and Grease	-	46.2
pH (units)	7.02	7.54
Potassium	75	61.6
Silica (SiO_2)	206	227
Sodium	1,650	2,540
Sulfate	82	63
Sulfide	-	12
TDS	6,000	7,540
Temperature (° F)	152	190
TPH	-	1.9
Turbidity (NTU)	-	4.3
TOC	99	80

* - units in mg/l, unless specified otherwise; - No data

Table 4-1 summarizes the water quality characteristics of the Placerita and San Ardo produced waters. In both the waters TDS, ammonia, boron and organics are the key water quality parameters of concern based on end use criteria. The general approach for treating of these waters involves selection of a treatment process for TDS removal, and removal of other contaminants by optimization of desalination process conditions and selection of appropriate pre/post treatment processes. Thermal and membrane processes are the most commonly used desalting technologies for treatment of brackish and sea waters for agricultural or potable water use. Both of these processes require pretreatment to remove hardness and silica to minimize scaling problems and improve desalination efficiency.

In the earlier Placerita Canyon produced water pilot study, detailed technical and economic evaluations of two thermal processes (Multi-stage Flash Distillation (MSF) and Multiple Effect Distillation (MED)) and one membrane technology (Reverse Osmosis) were performed. Results indicated that the planning level cost estimate for RO based process was significantly lower (three fold) than the cost estimate for the thermal processes. Thermal processes are generally cost effective for waters with high TDS (>30,000 mg/l) such as seawaters. Hence, thermal processes were not considered for evaluation for treatment of San Ardo produced water.

The feasibility of two membrane based processes i) Reverse Osmosis and ii) Electro Dialysis Reversal, were evaluated for treating San Ardo oilfield produced water: RO was selected due to its successful application in the Placerita Canyon produced water project. EDR was selected for evaluation due to some recent developments in this desalination technology. A discussion of each of these processes, pre/post treatment requirements, benefits and limitations are presented below. In addition, a planning level cost estimate for the two processes is also developed. Finally, the process selected for the pilot study and rationale for selection is also presented.

4.2 Reverse Osmosis

RO is a membrane separation process in which the water from a pressurized saline solution is separated from the solutes (the dissolved material) by flowing through a membrane. No heating or phase change is necessary for this separation. The major energy required for desalting is for pressurizing the feed water.

In practice, the saline feed water is pumped into a closed vessel where it is pressurized against the membrane. As a portion of the water passes through the membrane, the remaining feed water increases in salt content. The fraction of the water that passes through the membrane is called the "permeate" and the concentrated fraction that is discharged as waste is the "RO reject".

Without the controlled discharge of RO reject, the pressurized feed water would continue to increase in salt concentration, creating such problems as precipitation of supersaturated salts and increased osmotic pressure across the membranes. The amount of the feed water discharged to waste in this brine stream for brackish water varies from 10 to 40 percent of the feed flow, depending on the salt content of the feed water.

An RO system is made up of the following basic components:

- Pretreatment
- High-pressure pump
- Membrane assembly
- Post-treatment

Pretreatment of the water is important in RO because the feed water must pass through pores of the membrane. Pretreatment processes typically include removal of suspended solids and chemical conditioning to inhibit salt precipitation and microbial growth. The suspended solids are generally removed by installation of cartridge filters upstream of the RO unit, and membrane scaling and fouling are minimized by addition of anti-scalent and anti-foulant chemicals to the feed water.

The high-pressure pump supplies the pressure needed to enable the pretreated water to pass through the membrane. This pressure ranges from 17 to 27 bar (250 to 400 psi) for brackish water and from 54 to 80 bar (800 to 1,180 psi) for seawater.

The membrane assembly consists of a pressure vessel and a membrane that permits the feed water to be pressurized against the membrane. The membrane must be able to withstand the pressure drop involved. The semi-permeable membranes are fragile and vary in their ability to pass fresh water and reject the passage of salts. Based on the characteristics of the feed water and the membrane, most of the salts are rejected while allowing most of the water to pass through. RO membranes are made in a variety of configurations. Two of the most commercially successful are spiral-wound and hollow fine fiber. Both of these configurations are used to desalt both brackish and sea water, although the construction of the membrane and pressure vessel will vary depending on the manufacturer and expected salt content of the feed water.

Post-treatment consists of stabilizing the water and preparing it for distribution. This post-treatment might consist of removing gases such as carbon dioxide and hydrogen sulfide and adjusting the pH.

Two developments have helped to reduce the operating cost of RO plants during the past decade: the development of membranes that can operate efficiently with lower pressures and the use of energy recovery devices. The low-pressure membranes are being widely used to desalt brackish water. The energy recovery devices are connected to the concentrate stream as it leaves the pressure vessel. The water in the concentrate stream loses only about 1 to 4 bar (15 to 60 psi) relative to the applied pressure from the high-pressure pump. These energy recovery devices are mechanical and generally consist of turbines or pumps of some type that can convert pressure drop to rotating energy.

As discussed earlier, in addition to removing TDS, the San Ardo produced water must be treated for organics, ammonia and boron to meet the water quality goals of the selected end use. Furthermore, to minimize scaling of the RO membrane, pretreatment is required to remove hardness and silica from the water. A brief discussion of the mechanism/processes to remove these constituents is presented below:

4.2.1 Removal of Scale-Causing Hardness and Silica

Membrane desalting processes require pre-treatment to prevent inorganic scaling. Inorganic scaling occurs when the concentration of inorganic compounds such as calcite exceed their solubility product in the concentrated brine. Calcium and magnesium hardness, as well as silica, are the primary compounds of concern for inorganic scaling.

The most prevalent approach to address scaling in RO processes is to decrease the pH of the feed water to less than 7 and add an anti-scalant. The solubility of calcium and magnesium increases at a lower pH, and the anti-scalant helps prevent silica and other compounds from precipitating as solids.

While lowering pH may mitigate hardness and silica problems, it is not a desirable approach for treating produced water of high organic and boron content. The organics present in the water may adsorb to the membrane and provide nutrients for biological activity within the pores of the membrane or on the membrane surface as a biofilm. Results from produced water treatment using RO has shown that reducing feed water pH can cause operational problems due to increased organic fouling (Dyke et al. 1992). In addition, the efficiency of boron removal also decreases with lower pH because boron exists primarily in an un-ionized form of boric acid at pH below 9.5. Therefore, for effective treatment of produced water, hardness and silica are usually removed from the water by precipitative softening and/or ion exchange. prior to the RO process

4.2.1.1 Precipitative Softening

In precipitative softening, hydrated lime ($Ca(OH)_2$) or caustic soda (NaOH) is added to the feed water to raise the pH and convert bicarbonate alkalinity into carbonate and hydroxide alkalinity. Soda ash, Na_2CO_3 may also be added as a source of carbonate. Calcium then precipitates with carbonate and magnesium precipitates with hydroxide. Silica precipitates directly with magnesium or co-precipitates with magnesium hydroxide, so additional magnesium is sometimes added to increase silica removal.

Produced water is typically warm when extracted, and precipitative processes are usually operated at either warm (90° to 170° F) or hot (215° to 230° F) temperatures rather than ambient temperatures (40° to 90°F). At high temperatures, the solubility of calcium carbonate is lower, the solubility of magnesium salts is higher, chemical kinetics are faster, and precipitates settle more quickly.

Effluent hardness concentration is controlled by the availability of carbonate for precipitation and the solubility of calcium and magnesium at the operating pH and temperature. At warm temperatures, effluent hardness concentrations can be reduced to less than 20 mg/L $CaCO_3$ by adding excess soda ash to react with hardness (DeSilva 1996, Doran et al., 1997).

4.2.1.2 Silica Removal Mechanisms

Silica removal in precipitative softening is often characterized in the literature as adsorption to or co-precipitation with magnesium hydroxide. Mujeriego (1976) suggests that silica is also removed by forming metal silicates, such as magnesium silicate shown in the following reaction:

$$2Mg^{2+} + 3SiO_2(aq) + 5.5\ H_2O = Mg_2Si_3O_8(H_2O)_{3.5}\ (s) + 4H^+$$

Mujeriego's research indicated that silica removal by magnesium is controlled by the $H_3SiO_2^-$ while silica removal by calcium is controlled by $H_2SiO_2^{2-}$. He found that silica removal was optimized at pH levels that corresponded to the maximums of the controlling species. For example, silica removal with magnesium was greatest when at a pH where $H_3SiO_2^-$ dominates: $(p^*K_1 + p^*K_2)/2$ where p^*K_1 and p^*K_2 represent the first and second dissociation constants for orthosilicic acid. The temperature-dependent equations for these constants are given below, for **T** in Kelvin:

$$p^*K_1 = 3405.9 / \mathbf{T} - 6.368 + 0.016346 \times \mathbf{T}$$

$$p^*K_2 = 8949.2 / T - 33.11 + 0.049581 \times \mathbf{T}$$

Table 4-2 provides values for these dissociation constants at room temperature and at temperatures indicative of produced water.

Table 4-2: Dissociation Constants for Orthosilicic Acid *

T (°C / °F)	p*K$_1$	p*K$_2$	(p*K$_1$ +p*K$_2$) /2
25 / 77	9.93	11.69	10.81
50 / 122	9.45	10.61	10.03
60 / 140	9.30	10.27	9.78
65 / 149	9.25	10.15	9.70
70 / 158	9.17	9.98	9.58

*For the reactions

$H_4SiO_2 = H_3SiO_2 + H^+$

$H_3SiO_2 = H_2SiO_2^{2-} + H^+$

$p^*K_1 = [H_3SiO_2] / [H_4SiO_2]$

$p^*K_2 = [H_2SiO_2^{2-}] / [H_3SiO_2]$

The amount of sludge produced by a precipitative softening process depends on the amount of hardness removed and the amount of lime added, if any. For silica removal, sludge is often recycled or allowed to form a sludge blanket.

4.2.2 Removal of Boron

Boron must be removed from water that will be used for agricultural irrigation, especially for citrus crops. Boron is often found at levels over 20 mg/L B in produced water, while irrigation goals are between 0.7 and 0.5 mg/L B, thus necessitating more than 95 percent removal.

Boron is difficult to remove as an un-ionized form of boric acid at pH below 9.5. At higher pH, the ionized boron can be removed from produced water with precipitation, boron-selective ion exchange resins or reverse osmosis.

4.2.2.1 Precipitative Softening

Boron is removed during precipitative softening in a process similar to silica removal. The chemical precipitation behavior of boron is similar to silica, as Table 4-3 indicates.

Table 4-3: Dissociation Constants for Boron*

T (°C / °F)	pK$_1$	pK$_2$	(pK$_1$ +pK$_2$) /2
25 / 77	9.2	12.74	10.97
50 / 122	8.48	11.74	10.11
60 / 140	8.23	11.39	9.81
65 / 149	8.11	11.21	9.66
70 / 158	7.99	11.05	9.52

*For the reactions

$_3BO_3 = H_2BO_3^- + H^+$ $pK_1 = [H_2BO_3^-] / [H_3BO_3]\backslash$

$H_2BO_3^- = HBO_3^{2-} + H^+$ $pK_2 = [HBO_3^{2-}] / [H_2BO_3]$

This table shows that the average of the first and second dissociation constants of boric acid is similar to values for orthosilicic acid. If boron is removed through a mechanism similar to silica, removal for both constituents should be optimized at the same pH.

Results from earlier studies using Placerita Canyon oilfield produced water had influent boron concentrations of 18 to 20 mg/L that were reduced to 5 to 10 mg/L in the precipitative softening effluent by adjusting pH and adding magnesium chloride (Drago et al., 1997, Doran et al., 1997). However, these treated levels are significantly higher than the water quality goal of 0.5 – 0.75 mg/l for boron for agricultural irrigation.

4.2.2.2 Ion Exchange

The Rohm and Haas Company manufactures an ion exchange resin Amberlite IRA-743 that selectively removes borate. Under laboratory conditions, a variety of solutions containing boron have been treated with a cross-linked polymer resin. In one experiment, a solution of 500 mg/L sodium chloride and 10 mg/L boron was passed through a bed of the Amberlite IRA-743 resin. Effluent boron concentrations were less than 1 mg/L. At a flow rate of 2 gallons per minute per cubic foot of resin (gpm/ft3), the resin absorbed 55 grams per ft3, equivalent to 1,500 gallons of water per ft3 of resin (Rohm and Haas 1993.)

While the boron removal results are promising, costs for this technology are high. Extrapolating these and other similar results, approximately 2,000 ft3 of resin would be required to treat 3 MGD of permeate water from reverse osmosis or thermal process from an average boron concentration of 10 mg/L to less than 1 mg/L. At approximately $1,000 per ft3 of resin, a planning level capital cost estimate for a boron-selective ion exchange system is $4 to $5.75 million including installation (in year 1996) (Crossen, 1996).

4.2.2.3 Reverse Osmosis

When operated at a pH where boron is present as borate (disassociated boric acid), reverse osmosis (RO) removes a significant fraction of boron in produced water. Greater than 99 percent boron rejection has been reported around pH 10.6 and 11.0 (Dyke et al. 1992). Boron levels in the RO treated water at pH 10.5 was about 1 mg/l in the Placerita Canyon pilot study. At a lower pH, the RO process was less successful in removing boron.

4.2.3 Removal of Organics from Produced Water

Reported values of dissolved organics in produced waters range from 10,000 mg/L to less than 100 mg/L (Giordano and Kharaka 1994). More than 80 percent of the dissolved organics are monocarboxylic (e.g., acetate, proprionate, and butyrate) and dicarboxylic (e.g., oxalate, malonate, and succinate) acid anions (Giordano and Kharaka, 1994).

Processes such as biodegradation, adsorption, air stripping and reverse osmosis can remove organics. Adsorption processes are more effective for removing less soluble (hydrophobic) organic compounds. However, the majority of organics in produced water are polar organic acids that are more soluble in water. Hence, the empty bed contact time required for adsorption processes may be very high. Air stripping is very effective for removing volatile or semi-volatile organic compounds. However, the majority of organic compounds typically present in the produced water are organic acids (not volatile or semi-volatile compounds). Hence, they can not be removed effectively under most practical design and operating conditions.

In the Placerita Canyon pilot study, biodegradation of organic compounds from the produced water was evaluated using a trickling filter. Results showed that less than 10% of organics were removed by biodegradation. This indicated that a significant amount of organics present in the produced water are complex organic compounds that are not readily biodegraded.

Under the current study, samples from San Ardo produced water were analyzed for TOC and biochemical oxygen demand (BOD) levels to evaluate the biodegration potential of organics. The concentration of TOC provides an estimate of total organic compounds in the water and the concentration of BOD provides an estimate of biodegradable organics. The TOC and BOD of the San Ardo produced water were 80.7 and 69 mg/l, respectively.

Subsequently, the following standard equation relating the concentration of organic substance in wastewater and O2 requirement for breakdown was used to normalize the TOC and BOD concentrations:

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6CO_2 + 6\,H_2O$$

According to the above equation, 72 mg of carbon represents 1 mM of organic compound, and 192 mg of oxygen is required to mineralize this amount of organic compounds. Hence, a TOC of 80.7 mg/l in the San Ardo produced water represents about 1.12 mM of total organic compound, and a BOD of 69 mg/l represents about 0.36 mM (69 / 192) of organic matter available for biodegradation. This indicates that only about 32% of the organics (equivalent of 25.8 mg/l of TOC) in the water is available for biotreatment. In addition, all of the BOD are not removed in most biotreatment plants. It is reasonable to assume that about 80% of the BOD is removed in the biotreatment processes. This means that only about 20 mg/l of the 80.7 mg/l of the TOC may be removed from San Ardo produced water by biotreatment processes.

Results from the pilot study indicated that RO membranes effectively removed organics from the produced water. Approximately 97% of the organics was removed by the RO membranes. The average TOC in the RO feed water was 97 mg/l and the average permeate TOC was about 3 mg/l.

4.2.4 Ammonia Removal

The agricultural irrigation water quality goal for ammonia is about 5 mg/l (Table 2-5). Possible ammonia treatment technologies include break point chlorination, air stripping, ion exchange, RO and biological oxidation.

Ammonia removal using breakpoint chlorination may have some limitations. For example, chlorine requirements for this process increase outside of the optimal range of pH 6 - 7. In addition, this may create major water quality concerns including elevated levels of disinfection by-products (DBPs) and taste and odor causing compounds. For example, under the recently implemented California Toxics Rule, the discharge limit for chloro-dibromo-methane, a disinfection by-product, is 1 µg/l. Bench scale studies must be performed to verify compliance with these limits prior to use of this process for ammonia removal. Air stripping of ammonia generally requires a pH above 10 to ensure that the majority of it is in the strippable NH_3 form. RO is not generally used when ammonia is the only parameter for removal, but this process is effective when operating at a pH where ammonia is in the form of NH_4^+. Ammonia is generally removed by RO with efficiencies exceeding 85 percent when operating below pH 8.5. However, if RO is operated at a pH of about 10.5 to facilitate boron removal, ammonia removal will be insignificant. Post treatment, including pH adjustment and ion-exchange, may be required for ammonia removal under those conditions. Ammonia removal with ion exchange is more effective when operating at a pH below 8.5. Yet another process for ammonia removal, depending on the treated water end use, is biological oxidation of ammonia in wetlands. In this process ammonia is oxidized to nitrate and subsequently denitrified to nitrogen by microorganisms in the wetlands. However, this is not a viable option if the treated water is used for industrial applications or if sufficient land is not available for creation of wetlands.

4.3 Electrodialysis Process

Electrodialysis was commercially introduced in the early 1960s, about 10 years before RO. The development of electrodialysis provided a cost-effective way to desalt brackish water and spurred considerable interest in this area. Electrodialysis depends on the following general principles:

- Most salts dissolved in water are ionic, with positive (cationic) or negative (anionic) charge.
- These ions are attracted to electrodes with an opposite electric charge.
- Membranes can be constructed to permit selective passage of either anions or cations.

When electrodes connected to an outside source of direct current (like a battery) are placed in a container of saline water, electrical current is carried through the solution, and ions such as sodium (+),calcium (++), chloride (-), and bi-carbonate (-) tend to migrate to the electrode with the opposite charge.

In the electrodialysis process, membranes that will allow either cations or anions (but not both) to pass are placed between a pair of electrodes. These membranes are arranged alternately with an anion-selective membrane followed by a cation-selective membrane. A spacer sheet that permits water to flow along the face of the membrane is placed between each pair of membranes.

One spacer provides a channel that carries feed (and product) water, while the next carries reject stream. As the electrodes are charged and saline feed water flows along the product water spacer at right angles to the electrodes, the anions in the water are attracted and diverted towards the positive electrode. This dilutes the salt content of the water in the product water channel. The anions pass through the anion-selective membrane, but cannot pass any farther than the cation-selective membrane, which traps the anion in the brine. Similarly, cations under the influence of the negative electrode move in the opposite direction through the cation-selective membrane to the concentrate channel on the other side. Here, the cations are trapped because the next membrane is anion-selective and prevents further movement towards the electrode.

By this arrangement, concentrated and diluted solutions are created in the spaces between the alternating membranes. These spaces, bounded by two membranes (one anionic and the other cationic), are called cells. The cell pair consists of two cells, one from which the ions migrated (the dilute cell for the product water) and the other in which the ions concentrate (the concentrate cell for the brine stream).

The basic electrodialysis unit is referred to as a membrane stack and consists of several hundred cell pairs bound together with electrodes on the outside . Feed water passes simultaneously in parallel paths through all of the cells to provide a continuous flow of desalted water and brine from the stack. Depending on the design of the system, anti-scalent chemicals may be added to the streams in the stack.

An electrodialysis unit is made up of the following basic components:

- Pretreatment train
- Membrane stack
- Low-pressure circulating pump
- Power supply for direct current (a rectifier)
- Post-treatment

The raw feed water must be pre-treated to remove materials that could harm the membranes or clog the narrow channels in the cells.. The feed water is circulated through the stack using a low-pressure pump with enough power to overcome flow resistance as the water passes through the narrow passages. A rectifier is used to transform alternating current to the direct current supplied to the electrodes on the outside of the membrane stacks.

Post-treatment consists of stabilizing the water and preparing it for distribution. This post-treatment might consist of removing gases such as hydrogen sulfide and adjusting the pH.

4.4 Electrodialysis Reversal

In the early 1970s, an American company commercially introduced the Electrodialysis Reversal (EDR) process. An EDR unit operates on the same general principle as a standard electrodialysis plant except that both the product and the brine channels are identical in construction. Several times an hour, the polarity of the electrodes is reversed, and the flows are simultaneously switched so that the brine channel becomes the product water channel, and the product water channel becomes the brine channel.

The result is that the ions are attracted in the opposite direction across the membrane stack. Immediately following the reversal of polarity and flow, enough of the product water is dumped until the stack and lines are flushed out, and the desired water quality is restored. This flush takes about 1 or 2 minutes, and then the unit can resume producing water. The reversal process is useful in breaking up and flushing out scales, slimes and other deposits before they can build up and create a problem. Flushing allows the unit to operate with fewer pretreatment chemicals and minimizes membrane fouling.

4.4.1 Application

EDR has the following characteristics that lend it to various applications:

- Capability for high recovery (more product and less brine)
- Energy usage that is proportional to the salts removed
- Ability to treat water with a higher level of suspended solids than RO
- Not affected by non-ionic substances such as silica
- Low chemical usage for pretreatment

The major energy requirement is the direct current used to separate the ionic substances in the membrane stack. The key benefit of EDR over RO membranes is that, due to its relatively large size pores, EDR membranes are less susceptible to silica fouling. A majority of calcium and magnesium is removed by the electrode and silica passes through the membrane in the permeate. However, the EDR process is unable to remove organics. A significant amount of the organics pass through the membrane and are present in the permeate. Therefore, a pretreatment process to remove organics may be required prior to treatment of produced water using EDR technologies.

4.4.2 Pretreatment to Remove Organics During EDR Treatment

The EDR process alone is not very effective in removing organic compounds from waste streams. Processes such as adsorption and biodegradation may enhance removal of select organics. Ondeo Industrial Solutions (Richmond, VA) has patented an EDR based process train for brackish water treatment and has proposed use of a Membrane Bio Reactor (MBR) process to remove organic compounds. However, data regarding estimated removal of organic compounds from oilfield produced water using MBR is not currently available. However, evaluations by Kennedy/Jenks (Section 5) indicated that only about 30% of the organics in San Ardo oilfield produced water can be biodegraded.

4.4.3 Removal of Boron

The water quality goal for boron for agricultural use is 0.5 to 0.75 mg/l. Unless operated at high pH (> 10.5), EDR is not very effective for removing boron from produced water. Hence, an ion-exchange process to remove boron is required .

4.5 Economic Evaluation of RO and EDR Processes for Treatment of San Ardo Produced Water

Cost estimates for the two treatment processes were developed based on information from equipment vendors and cost estimate models. Capital cost, operation and maintenance (O&M) cost, and total annual cost (defined as the sum of amortized capital and operational costs) were compared. Capital costs were amortized over 20 years at an interest rate of 7 percent per year, yielding a capital recovery factor of 0.0936. These amortization rates are typical for municipal water utilities that often finance capital expenses through bonds.

The RO process train includes warm softening at pH 9.5 to remove scale forming compounds, cooling, pH adjustment to 10.5, reverse osmosis to remove dissolved solids and boron, pH adjustment to 8.5, and ion-exchange to remove ammonia (Figure 4-1). The EDR process train includes a walnut shell filter, cooling, membrane bioreactor, EDR, and ion-exchange to remove boron (Figure 4-2).

Table 4-4 shows the cost factors and assumptions used in developing the cost estimates. Total capital costs include equipment and direct constructions costs such as installation costs, as well as indirect costs such as legal fees and administration. Operating costs include chemicals, sludge disposal, energy, and labor. Kennedy/Jenks Consultants developed the cost estimates for the RO based process based on vendor quotes and previous project experience. Cost estimates for the EDR based process was obtained from Ondeo Industrial Solutions. Annual cost is the sum of amortized capital and operations and maintenance costs.

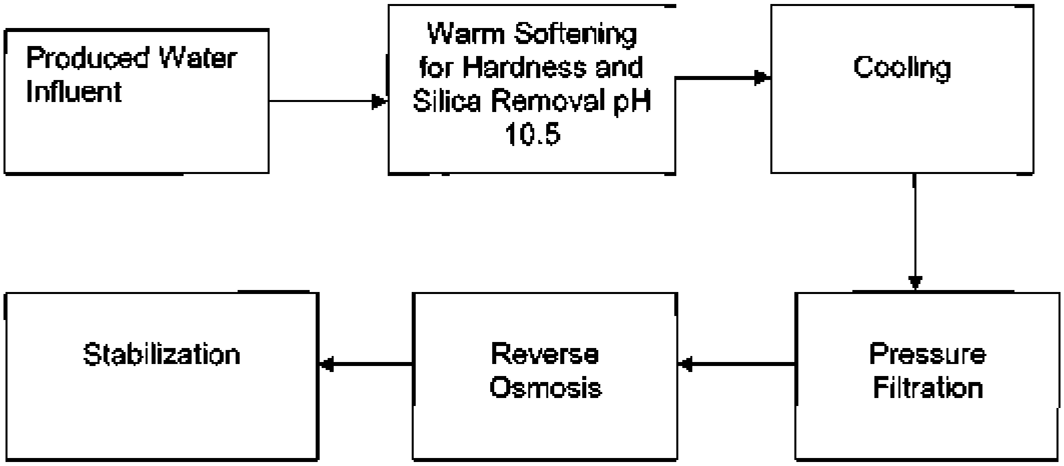


Figure 4-1. Simplified Schematic of RO Based Process for Treatment of Produced Water

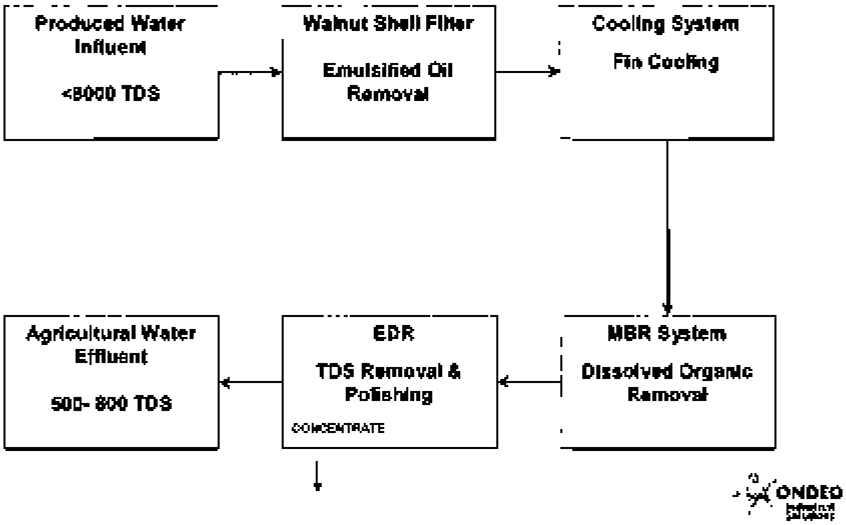


Figure 4-2. Simplified Schematic of EDR Based Process for Produced Water Treatment

Table 4-4: Cost Factors Used in Planning Level Cost Estimation

Parameter	Value	Unit
Dollar		
ENR Cost Reference	January 2003	index Year
Interest Rate	7	% per annum
Capital recovery period	20	Years
Capital		
Electrical & Instrumentation	15	% of process train costs
Site Work	10	% of process train + treatment bldg costs. Includes site development and internal piping.
Contractor's overhead & profit	12	% of direct construction cost
Mobilization and bonding	2	% of direct construction cost
Contingency	10	% of direct construction cost
Indirect construction costs	38	% of construction "bid" cost. Includes Engg. Design, CM, financial, legal, admin services, EIS, permit, utility connect fee and interest
O&M		
Sodium Hydroxide	0.25	$ per lb
Magnesium chloride	0.61	$ per lb
Polymer	2.6	$ per lb
RO antiscalent	2.6	$ per lb
RO antifoulant	3.6	$ per lb
RO chemical cleaning solution	4	$ per lb
Sodium hypochlorite	0.79	$ per lb Cl_2
Sulfuric acid	0.05	$ per lb
Electricity	0.10	$ per kW-hr
Labor rate	32	$ per hour
Replacement RO membrane	770	$ per element (18 months life)
Misc. maintenance materials	1	% of process train cost
Sludge Disposal	28	$ per wet ton (If sent to outside landfill)
Brine disposal	0.11	$ per bbl
Contingencies	10	% of direct annual O&M
Administrative Charges	2	% of capital cost
Property Tax	1	% of capital cost
Insurance	1	% of capital cost

Tables 4-5 through 4-7 present the summary of planning level capital (30% to +50%), O&M and annual cost estimates for the two processes. The overall treatment cost for the two processes were not significantly different. The estimated cost of treated water is about $2,500 per acre-foot. The capital cost for the EDR process is significantly higher than that of the RO process and the O&M cost for the RO process is higher than that of EDR.

Table 4-5: Planning Level Cost Estimates for 4.2 MGD Reverse Osmosis and Electrodialysis Reversal Systems

Desalting Technology	**Treated Water Recovery (Percent of 4.2 MGD)**	**Total Capital Cost *(Million* 2003 Dollars)**	**Annual Operating Costs *(Million* 2003 Dollars/yr)**	**Total Annual Cost *(Million* 2003 Dollars/yr)**	**Total Unit Cost (2003 Dollars/AF of Water Produced)**	**Total Annual Cost (2003 *cents/barrel* of Water Treated)**
Reverse Osmosis, including pretreatment	75	14.5	7.85	9.20	2,480	32
Electrodialysis Reversal, including pretreatment[1]	80	28.5	6.95	9.65	2,560	33

1. Cost for EDR based process obtained from Ondeo Industrial Solutions

Table 4-6: Cost Breakdown for Reverse Osmosis System

Process	**Total Capital Cost (Million 2003 $)**	**Annual Operations Cost (Thousand 2003 $)**	**Total Annual Cost (Thousand 2003 $)**	**Total Unit Cost (2003 $/AF of Water Produced)**	**Total Unit Cost (2003 cents/ barrel of Water Treated)**
Warm Softening*	1.2	3.75	3.86	1,038	13.4
Cooling	0.6	0.12	0.17	47	0.6
Sand Filtration	0.7	0.35	0.42	111	1.4
Reverse Osmosis	3.2	2.4	2.7	725	9.4
Ion-Exchange for Ammonia	1.0	0.10	0.19	52	0.7
Treatment Building & Indirect Expenses	7.8		0.73	196	2.5
Others		1.13	1.13	304	3.9
Total	14.5	7.85	9.21	2,475	31.9

Table 4-7: Cost Breakdown for Electrodialysis Reversal System with Pretreatment*

Process	Total Capital Cost (Million 2003 $)	Annual Operations Cost (Thousand 2003 $)	Total Annual Cost (Thousand 2003 $)	Total Unit Cost (2003 $/AF of Water Produced)	Total Unit Cost (2003 cents/ barrel of Water Treated)
Walnut Shell Filter	0.7		0.06	17	0.2
Cooling	0.6	0.13	0.18	50	0.6
Membrane Bioreactor	7.6	0.8	1.5	402	5.2
EDR	4.7	3.5	3.9	1,048	13.5
Ion-Exchange	1.1	0.1	0.2	54	0.7
Sludge Handling & Chemical	2.5	0.33	0.56	150	1.9
Treatment Building & Indirect Expenses	11.3		1.05	281	3.6
Others		2.1	2.1	558	7
Total	28.5	6.95	9.6	2,560	33

* Cost breakup derived from estimates obtained from Ondeo Industrial Solutions

4.6 Recommendations for Pilot Study

Based on the technical and economic evaluation of the RO and EDR processes, the RO process is recommended for pilot evaluation under Phase II of the project. RO is recommended due to uncertainty regarding the treatment of organics by the MBR system, EDR's lack of a cost advantage and previous good experience with treatment of produced water using RO processes.

Several bench-scale tests were conducted to evaluate the treatability of produced water from the San Ardo oil field. While most of these tests focused on chemical dosing for precipitative softening, studies also addressed other aspects of the treatment processes.

5.1 Goals

The goals of the bench scale studies were the following:

- Obtain the combination and concentrations of chemicals to maximize the removal of hardness and silica in the warm softening process;
- Assess the effectiveness of chlorine dioxide (ClO_2) to oxidize San Ardo oilfield organics (which may minimize the fouling of RO membranes); and
- Assess ammonia removal from RO treated water by break point chlorination.

5.2 Warm Softening Process

Earlier studies to treat produced water at Placerita Canyon oilfield indicated that optimum removal of silica and calcium hardness occurred at a pH of 9.5. However, the pH of the water had to be elevated to above 10.5 for boron removal in the downstream RO unit. In this study jar tests were conducted using San Ardo produced water to evaluate optimum chemical dosing conditions for the removal of hardness and silica in the warm softening unit at pH 9.5 to 11. Hardness removal was evaluated by adding i) caustic, ii) lime or iii) a combination of caustic and lime. Silica removal was facilitated by magnesium addition in all of these tests. Jar tests were performed in 1 liter jars containing 750 ml of produced water, using a standard Phipps and Bird jar testing apparatus. After chemicals were added, the contents of the jars were rapidly mixed at 150 rpm for two minutes, slowly mixed at 20 rpm for 20 minutes for flocculation, and then allowed to settle quiescently for 30 minutes. Total hardness, calcium hardness, alkalinity, and silica levels of the samples were measured before and after chemical addition. Magnesium hardness was determined as the difference between total hardness and calcium hardness.

Some of the initial jar tests, although performed immediately after sample collection, were conducted without trying to maintain sample temperature. A significant cooling was observed. For latter jar tests, the jar test water temperature was controlled by circulating hot filtered produced water in a water bath containing the jars.

5.2.1 pH Adjustment with Caustic

Figure 5-1 shows the results from two titration tests that were performed using caustic on two different days. No magnesium was added for silica removal in these tests. Produced water was collected from the inlet of the softening unit at the San Ardo treatment facility. The temperature of the produced water was not controlled during these tests. However, temperature and pH of the water were monitored during the test.

Results indicated that approximately 330 and 540 mg/l of caustic was required to increase the pH to 9.5 and 10.5, respectively.

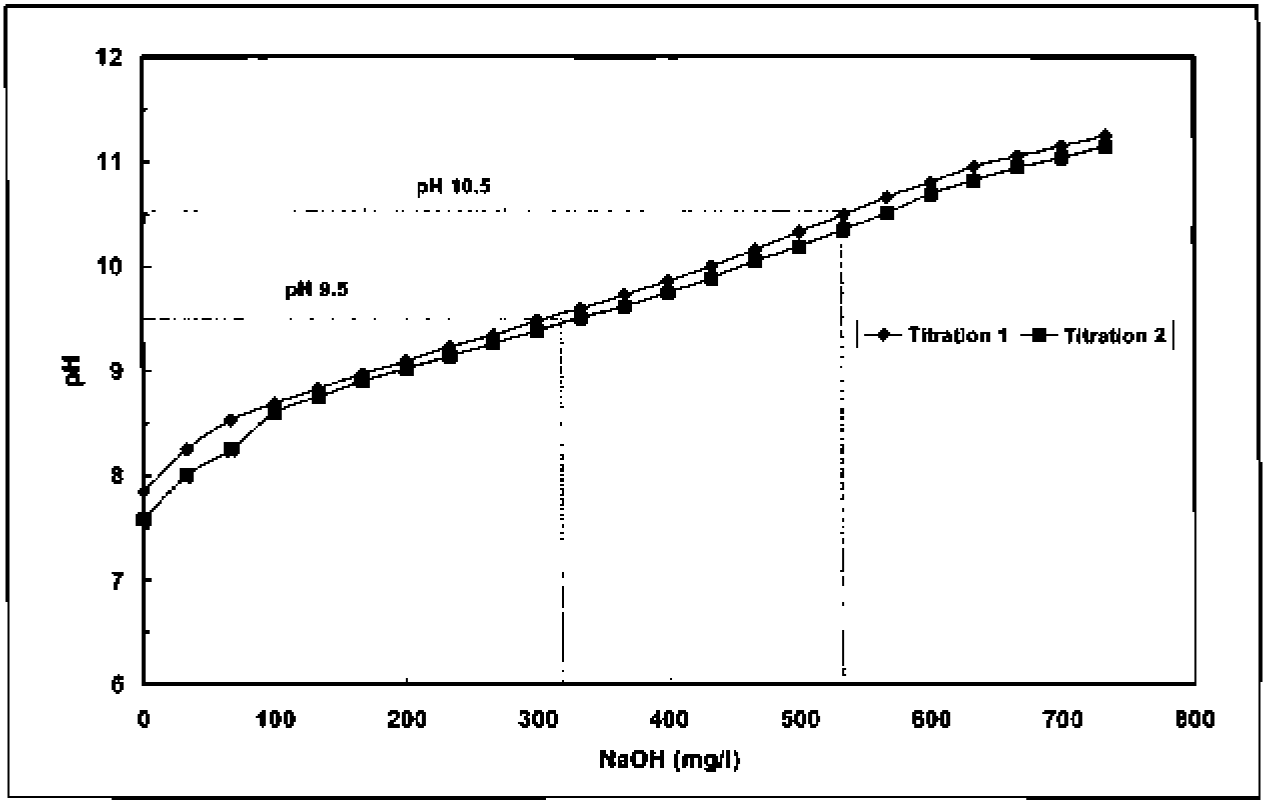


Figure 5-1. San Ardo Produced Water Titration Curve Using Caustic for Without Magnesium Addition

Figure 5-2 shows the titration curve for San Ardo produced water using 150 mg/l of magnesium and various amounts of caustic. Magnesium was added as $MgCl_2$ in these studies. Addition of magnesium lowered the pH of the water and increased the caustic required to elevate the pH to target level. Approximately 625 and 850 mg/l of caustic were required to raise the pH to 9.5 and 10.5, respectively in this test.

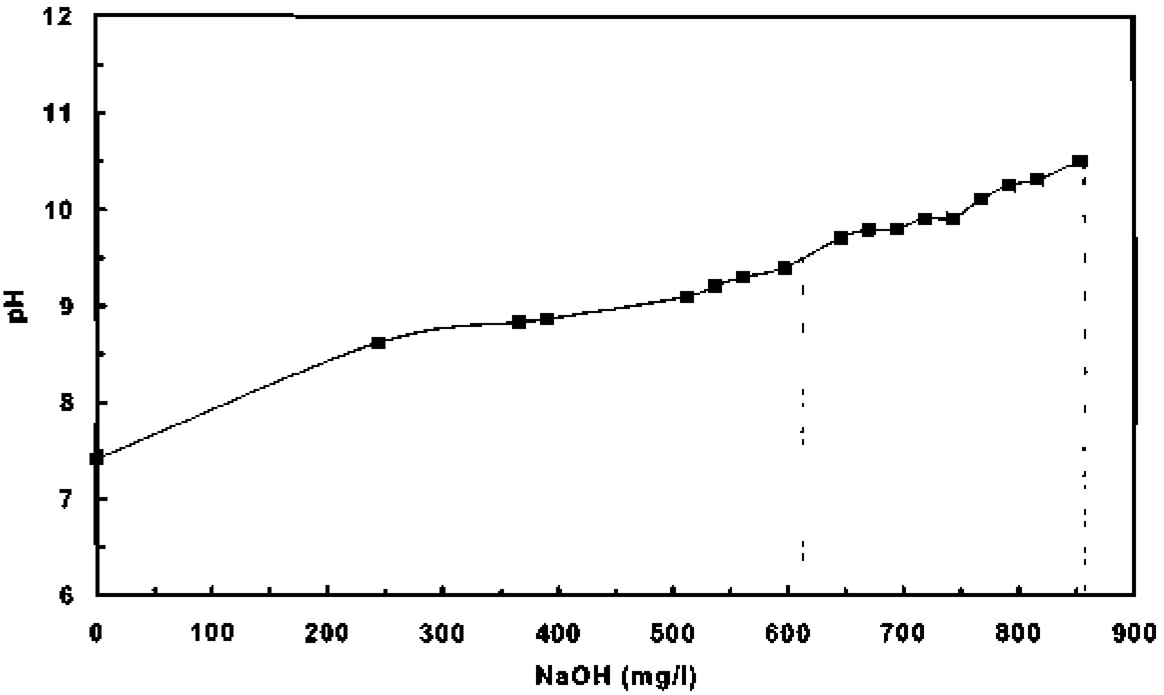


Figure 5-2. San Ardo Produced Water Titration Curve Using Caustic with 150 mg/l Magnesium Addition.

Results from titration tests were used to perform jar tests for hardness and silica removal. Initially three sets of jar tests were performed. In all the three tests magnesium chloride was added as the source of magnesium (0 – 420 mg/l). No caustic was added to the samples in the first set of tests. In the second and third sets, prior to adding magnesium, caustic was added to adjust the pH of the water to 9.5 and 10.5, respectively. The temperatures of all but two of the jars were not controlled during the jar test. In two jars (pH 10.5; Mg 70 and 105 mg/l) an attempt was made to maintain the temperature of the jars.

Figure 5-3 shows the residual silica and hardness levels in the test where no caustic was added. No significant removal of silica (~ 200 mg/l) was observed in any of the jars. Addition of magnesium increased the hardness (and slightly lowered the pH) of the water. The initial temperature of the water was about 140 °F and the final temperature was about 100 °F.

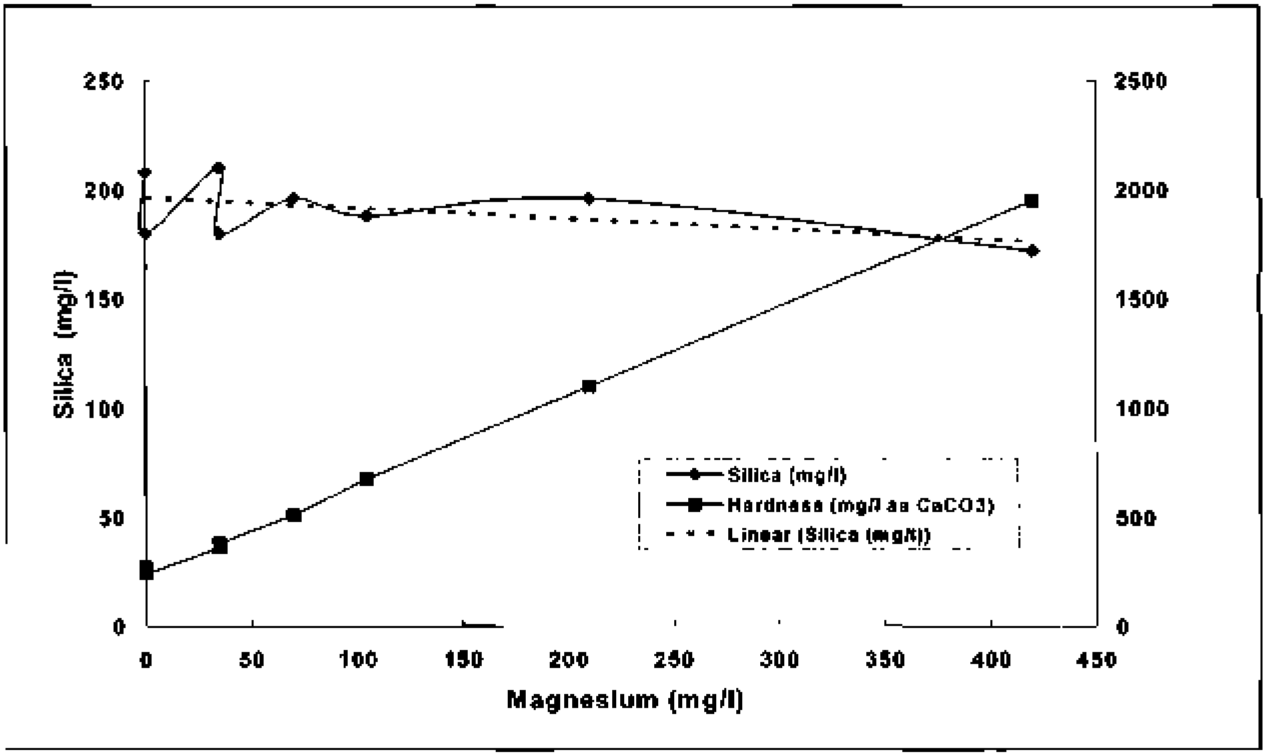


Figure 5-3. Silica and Hardness Concentrations with Increase in Magnesium Concentration Without Caustic Addition

In the second set of tests, the pH of the water was raised to about 9.5 using caustic, prior to addition of magnesium. The silica levels decreased from an initial concentration of 300 mg/l to about 90 mg/l when 420 mg/l of magnesium was added (Figure 5-4). However, magnesium addition increased the hardness of water from the initial level of 62.5 (after pH adjustment to 9.5) to 1,400 mg/l and the pH of the water decreased from 9.5 to 8.5.

In the third test, the pH of the water was raised to 10.5 prior to addition of magnesium. The silica levels significantly decreased with increase in magnesium concentration (Figure 5-5). Addition of 70 and 105 mg/l of magnesium (and insulation of the samples) reduced residual silica from 190 mg/l to 88 and 62 mg/l, respectively. The corresponding residual hardness was 22 and 58 mg/l, respectively. The initial temperature of the water was about 150 °F. The final temperatures in these two jars were 138 and 132 ° F, respectively.

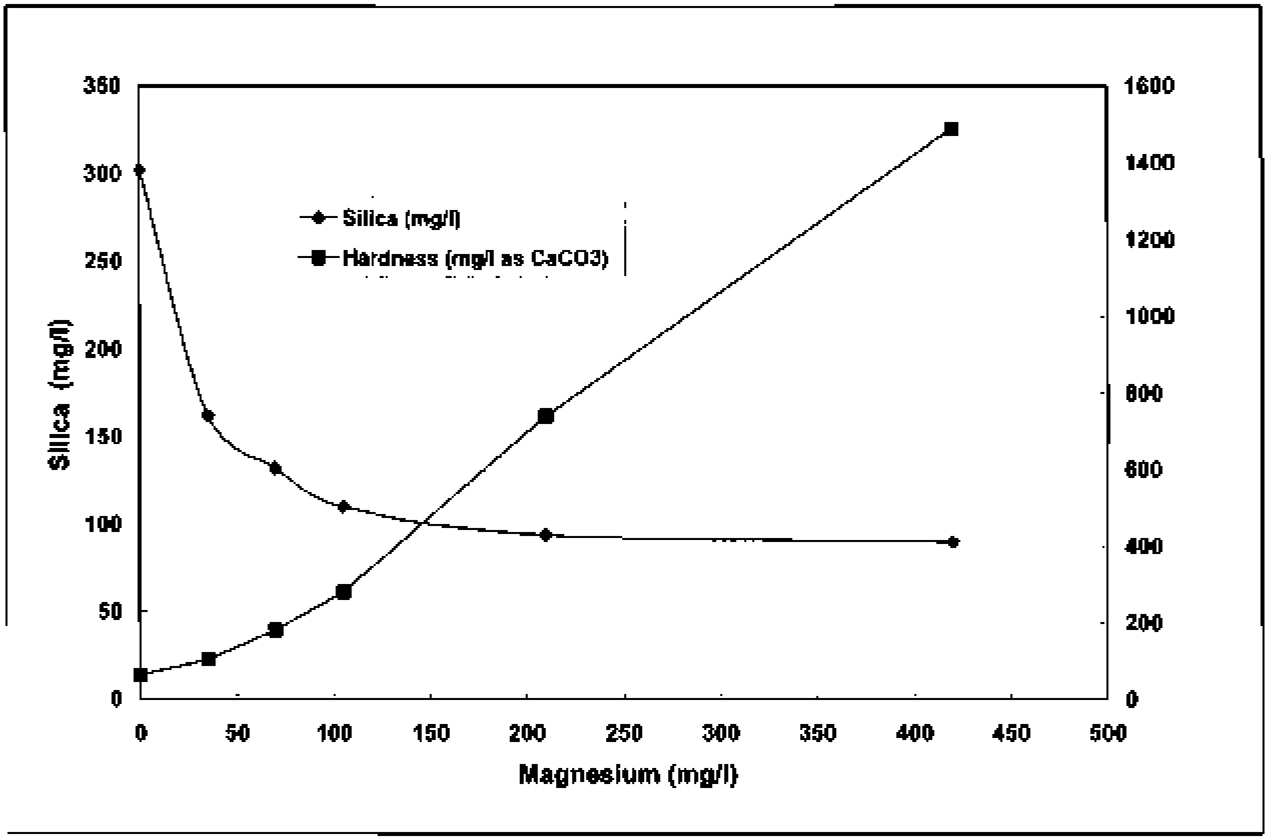


Figure 5-4. Silica and Hardness Concentrations as a Function of Added Magnesium with Initial pH Adjust to 9.5 Using Caustic

These screening test results indicated that addition of magnesium has multiple impacts on the treatment. While adding magnesium chloride facilitates silica removal, it also reduces the pH of the water and increases the hardness. Furthermore lack of temperature control during the preliminary jar tests may cause a decrease in silica and hardness removal. Therefore additional jar tests were performed to optimize the combined effects of caustic and magnesium, and also to control the temperature of the samples during precipitation. In these tests, magnesium addition (0 to 200 mg/l) was followed by appropriate amounts of caustic addition to yield a final pH of 10 in all the samples. Also, during these tests the jars were placed in a water bath, with the water bath temperature regulated by circulation of hot (filtered produced) water.

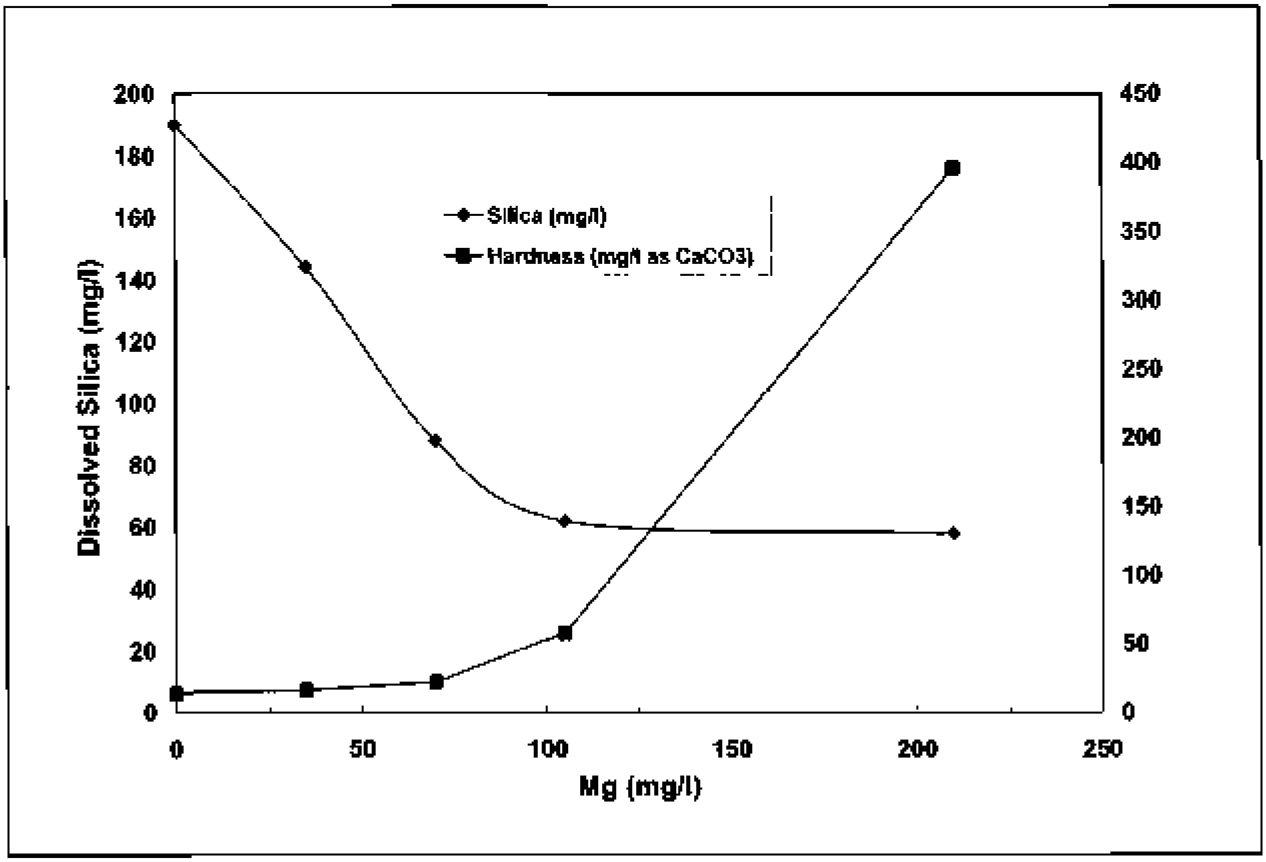


Figure 5-5. Silica and Hardness Concentrations as a Function of Added Magnesium with Initial pH Adjust to 10.5 Using Caustic

Approximately 660 and 780 mg/l of caustic were required to raise the pH to 10 when 100 and 160 mg/l of magnesium respectively, were added to San Ardo produced water (Figure 5-6). The residual silica concentration in these tests decreased with an increase in magnesium dose (Figure 5-7). The treated water silica concentrations were 88 and 36 mg/l, respectively at 80 and 160 mg/l of added magnesium concentration. The residual hardness was less than 10 mg/l as $CaCO_3$.

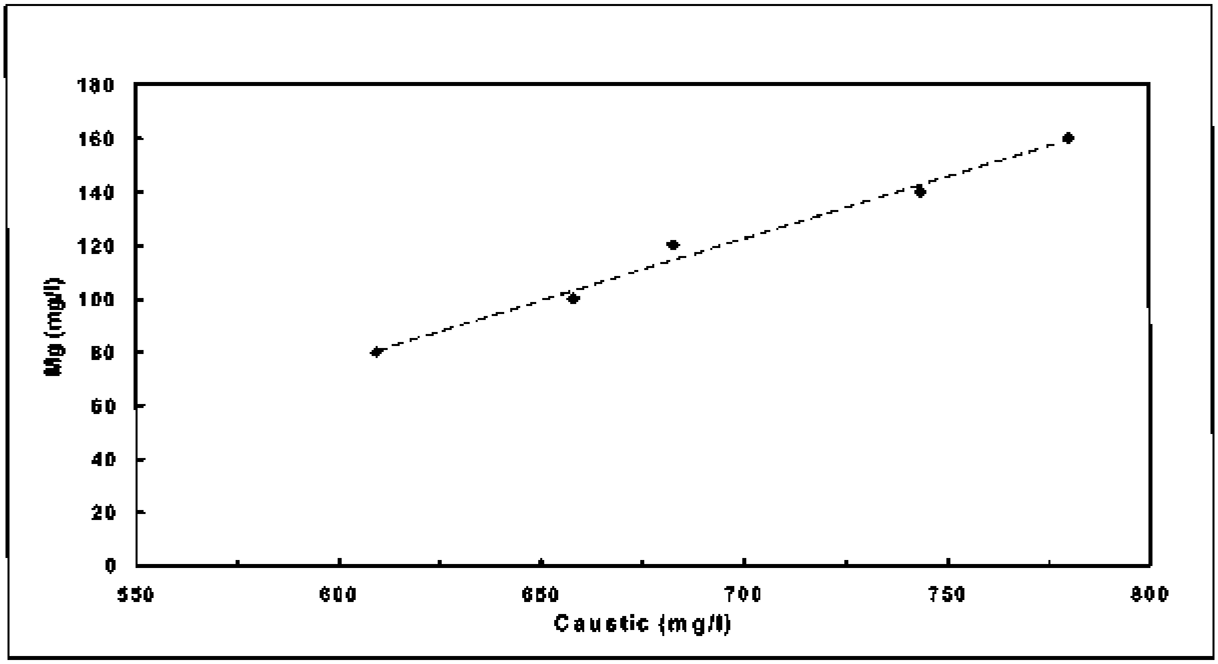


Figure 5-6. Caustic Addition Required to Raise the San Ardo Raw Filtered Produced Water pH to 10 as a Function of Magnesium Addition.

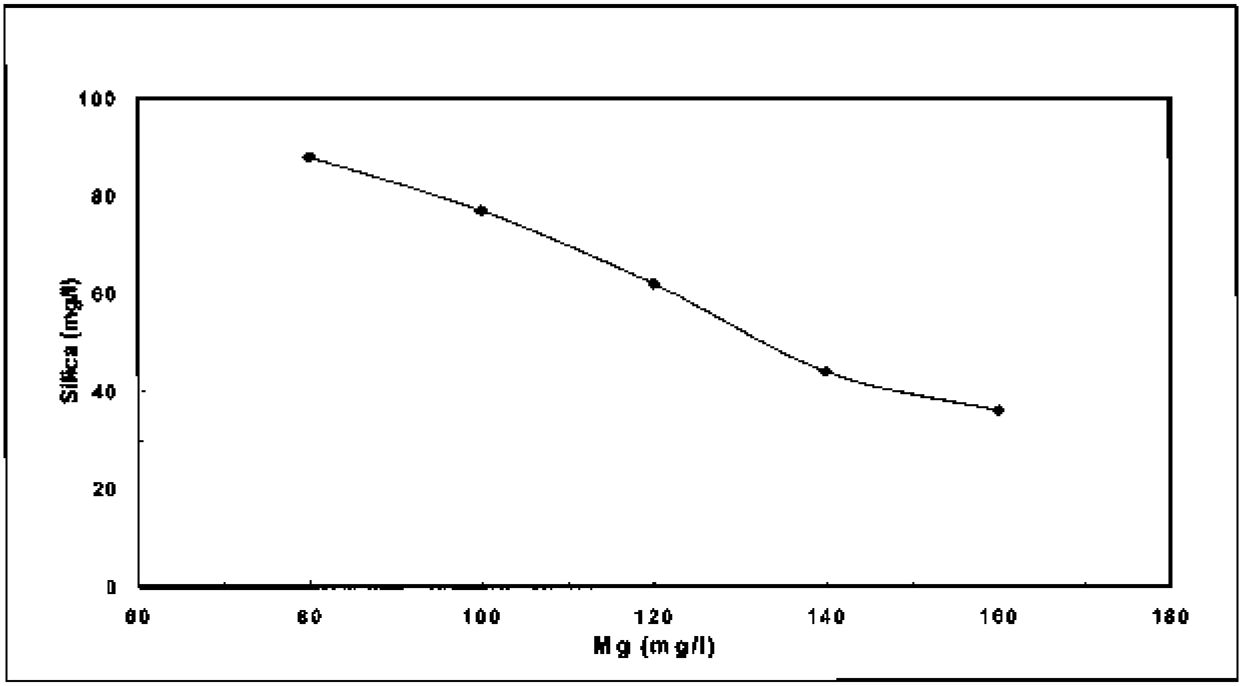


Figure 5-7. Silica Concentration in the Raw Filtered Produced Water as a Function of Magnesium Addition With Caustic Addition to pH 10.

The pilot unit is designed so that the influent water enters the warm softening unit (Claricone™ from CB&I Walker – Section 6) through two feed points. Approximately two thirds of the flow enters through one point and the remaining flow enters through the other. Another jar test was performed to identify the appropriate caustic feed point. The jar tests evaluated whether adding all the caustic through any one of the ports may result in better process performance than simultaneous caustic addition through both the ports. This jar test was performed using 100 mg/l magnesium. Three jars were used in this test. The sequence of caustic added to yield a pH of 10 was varied in these jars. In Jar #1, all of the caustic required to raise the pH of the 750 ml sample was added at once to the sample. However, in jars #2 and #3, after magnesium addition, the contents were split into two aliquots of 250 ml and 500 ml volumes. All of the required caustic was then added to the 500 ml aliquot of Jar #2, and 250 ml aliquot of Jar #3. The remaining caustic free aliquot was than added to bring the final sample volume to 750 mls in these jars. After rapid and slow mixing, the samples were allowed to precipitate. The filtered samples were analyzed for hardness, silica and alkalinity. Results indicated that the sequence of caustic addition did not significantly impact the hardness or silica levels (Table 5-1). In all of the samples the hardness was below 10 mg/l as $CaCO_3$, and silica levels varied from 55 to 65 mg/l. However, the alkalinity of the split samples was about 150 mg/l as $CaCO_3$ lower than that of the first sample.

Table 5-1: Hardness and Silica Levels in San Ardo Produced Water Using Caustic and Magnesium (100 mg/l) After Adjusting pH to 10

Sample	Method of Caustic Addition	Total Hardness (as mg/l $CaCO_3$)	Silica (mg/l)	Alkalinity (mg/l as $CaCO_3$)
#1	All at once	<10	54	835
#2	All Caustic added to 500 ml Aliquot	<10	64	682
#3	All Caustic added to 250 ml Aliquot	<10	58	656

5.2.2 pH Adjustment with Lime

As with the studies using caustic, titration curves were initially developed with lime. The results were then used to design lime softening jar tests.

Figure 5-8 shows the titration curve for San Ardo produced water using lime at different magnesium levels. Approximately 740 and 1,140 mg/l of lime were required to raise the pH to 9.5 and 10.5, respectively, when 70 mg/l of magnesium was added. About 750 mg/l and 980 mg/l of lime were required to raise the pH to 9.5 and 10.5, respectively, when 100 mg/l of magnesium was added.

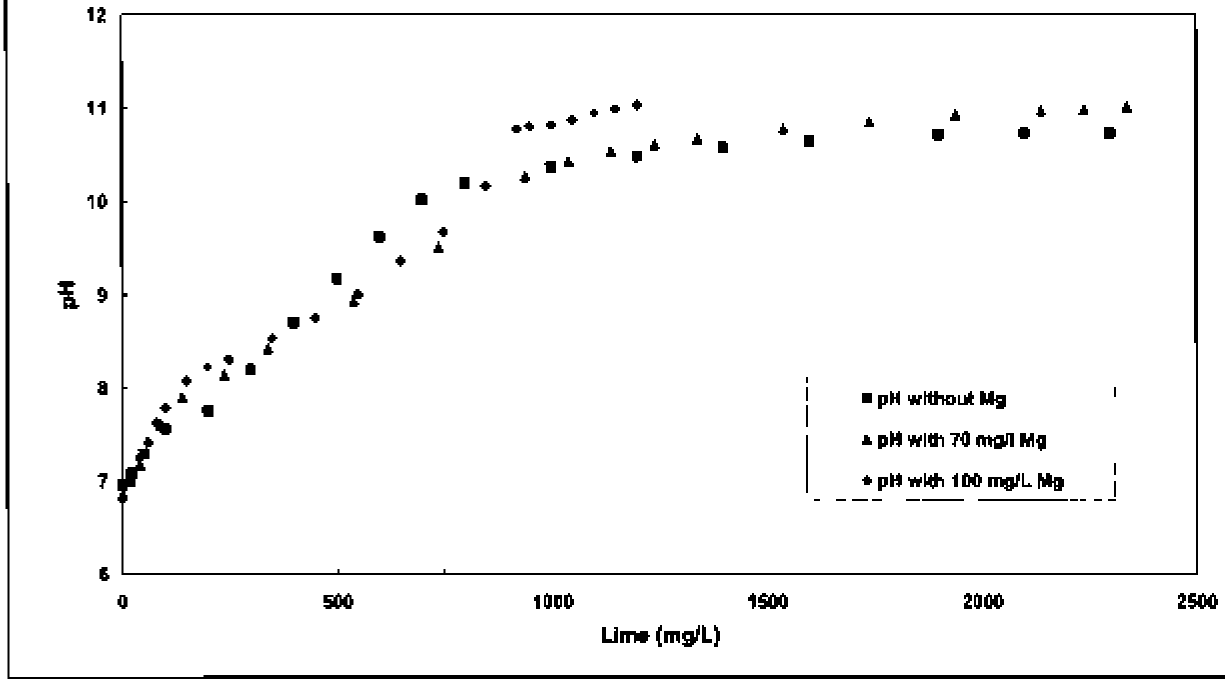


Figure 5-8. Titration Curve for San Ardo Produced Water Using Lime and Magnesium

Four sets of jar tests were performed using lime (Tables 5-2 to 5-5). They include i) pH 9.5, magnesium dosing 50 to 140 mg/l; ii) pH 10, magnesium dosing 50 to 140 mg/l; iii) magnesium 70 mg/l, pH 9 to 10.5; iv) magnesium 100 mg/l, pH 9 to 10.5. Results indicated that the residual silica levels were near or lower than the goal of 40 to 60 mg/l at pH 9.5 and 10 (Tables 5-2 & 5-3). However, silica was removed more effectively at pH 10 than at 9.5. Calcium hardness constituted more than 90% of the total hardness in the high pH samples indicating that most of the magnesium precipitated from solution. In the pH 9.5 samples, the ratio of total hardness to magnesium hardness increased with an increase in magnesium dose indicating partial removal of magnesium from these samples. The silica levels were below 10 mg/l at a magnesium dose of 135 mg/l at pH 10. However, both the total and calcium hardness levels were significantly higher than the hardness goal in all the lime precipitation studies. This is due to the presence of insufficient amount of carbonate in the produced water to precipitate all the calcium added (as calcium carbonate). The solubility of calcium hydroxide is significantly high at these pH levels resulting in unacceptable levels of hardness for RO operation.

Table 5-2: Jar Test Data Using Lime and Magnesium at pH 9.5

Magnesium (mg/l)	pH	Silica(mg/l)	Alkalinity*	Total Hardness*	Calcium Hardness*	Turbidity (NTU)
49	9.52	67	246	378	376	1.78
68	9.5	67	208	424	358	2.89
78	9.51	23	182	700	574	3.87
107	9.5	29	165	620	494	2
117	9.54	38	161	528	434	2.08
136	9.56	37	150	562	444	1.25

* - mg/l as $CaCO_3$

Table 5-3: Jar Test Data Using Lime and Magnesium at pH 10.5

Magnesium (mg/l)	pH	Silica(mg/l)	Alkalinity*	Total Hardness*	Calcium Hardness*	Turbidity (NTU)
49	10	56	234	420	430	1.67
68	10	56	230	422	432	3.57
78	10.1	31	256	560	566	2.24
107	10.1	21	230	630	636	4.54
117	10.02	13	184	625	622	7.16
136	10.03	7	190	785	740	4.54

* - mg/l as $CaCO_3$

Similar results were found in the bench tests with constant magnesium dose and varying pH levels (Tables 5-4 & 5-5). Silica removal increased with increase in pH at both magnesium levels. Also, lower silica levels were achieved by increasing the magnesium concentration from 70 to 100 mg/l. However, the hardness of these samples was significantly higher due to limitations in carbonate levels. Calcium hardness increased and magnesium hardness decreased with increase in pH. However, the total hardness was extremely high in all the cases. These results suggested that hardness removal from San Ardo water can not be achieved by using lime as the sole chemical for pH adjustment.

Table 5-4: Jar Test Data Using Lime and 70 mg/l Magnesium

Magnesium (mg/l)	pH	Silica (mg/l)	Alkalinity*	Total Hardness*	Calcium Hardness*	Turbidity (NTU)
68	9.02	159	236	530	270	3.62
68	9.5	102	240	500	380	7.62
68	10.02	48	270	550	570	2.93
68	10.62	51	406	650	655	1.59

* - mg/l as $CaCO_3$

Table 5-5: Jar Test Data Using Lime and 100 mg/l Magnesium

Magnesium (mg/l)	pH	Silica (mg/l)	Alkalinity*	Total Hardness*	Calcium Hardness*	Turbidity (NTU)
97	9.02	137	190	675	280	1.74
97	9.52	66	196	620	400	4.56
97	10.08	32	215	620	598	2.32
97	10.54	31	305	715	700	3.51

* - mg/l as $CaCO_3$

5.2.3 Bench Test Using Combined Lime – Caustic Addition

An effective and economic warm softening process to remove hardness and silica may require the use of a combination of chemicals. One such strategy involves optimization of lime dosing proportional to the carbonate concentration in the water. Caustic may be added to remove the remaining hardness and facilitate pH elevation. Finally, an appropriate amount of magnesium must be added to remove silica. A bench test was performed to evaluate silica removal by optimal use of lime, caustic and magnesium.

Based on the produced water quality characteristics and earlier bench test data, a lime dose of 90 mg/l and magnesium dose of 70 mg/l was selected for this study. The titration test was conducted to determine the amount of caustic required to adjust the pH to desired level. Figure 8-9 shows the titration curve for San Ardo water using lime and caustic for softening. Approximately 375 and 575 mg/l of caustic were required to raise the pH to 9.5 and 10.5, respectively.

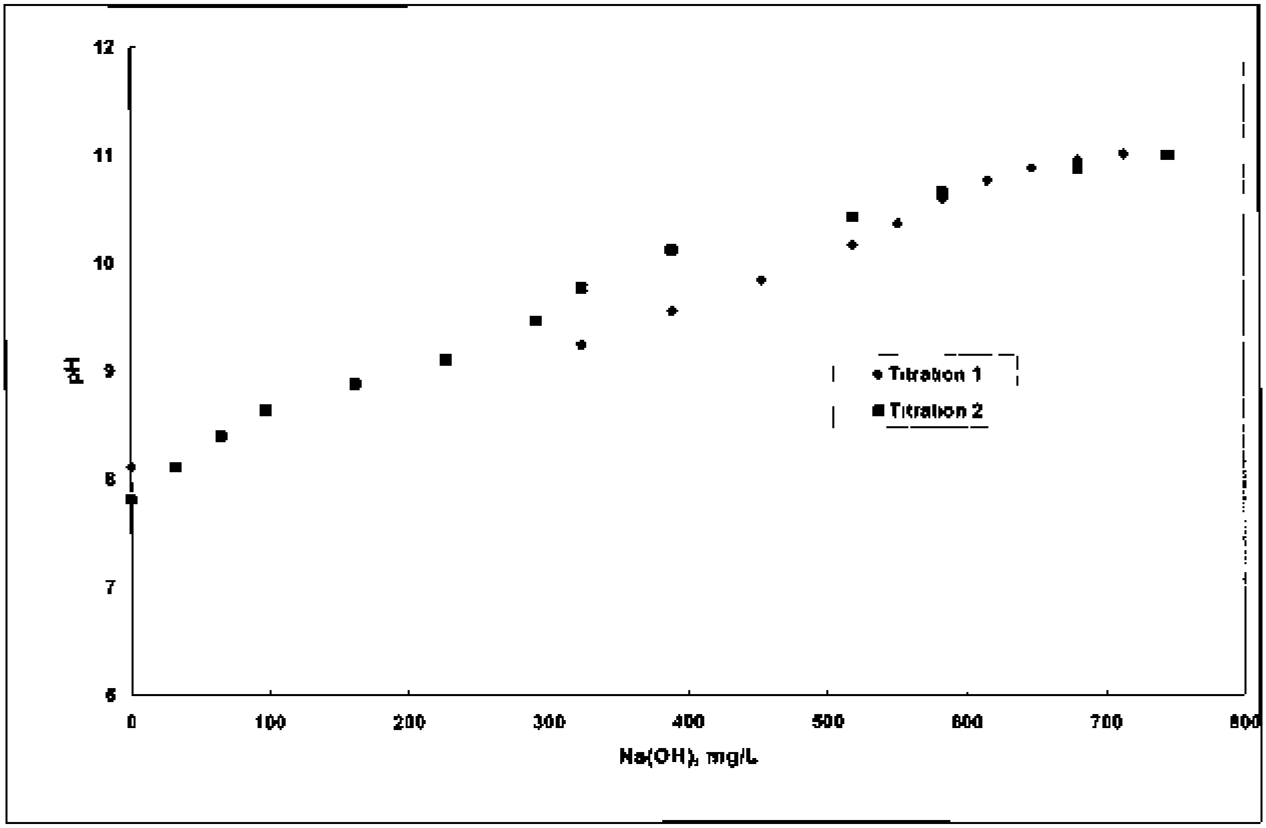


Figure 5-9. Titration Curve for San Ardo Water Using Lime (90 mg/l), Magnesium (70 mg/l) as a Function of Caustic Addition

Table 5-6 shows the jar test data for the combined lime, caustic and magnesium test. The silica and hardness of the raw water were about 200 mg/l and 260 mg/l as $CaCO_3$, respectively. About 90% of the hardness in the water was calcium hardness. Addition of lime and magnesium alone resulted in a small increase in calcium hardness and a significant increase in total hardness, indicating that most of the magnesium added remained in solution. About 10% of the silica was removed. Increase in pH to 9.5 using caustic removed more than 90% of the calcium hardness and 85% of the total hardness, which are below the hardness goal. Visual observation of the samples indicated settling of approximately 90% of the sludge within 5 minutes. A subsequent rise in pH to10 reduced the total hardness to below 10 mg/l as $CaCO_3$. However, in these samples more time (10 minutes) was required to settle 90% of the sludge. This may be due to the presence of relatively larger amount of magnesium floc. Magnesium floc is typically very flaky and does not settle well. At pH 9 or above, the silica levels decreased to about 80 mg/l. This is consistent with the silica removal for 70 mg/l magnesium in the other bench tests. Approximately 100 mg/l of magnesium was required to achieve the silica goal of 40 to 60 mg/l in those studies. Based on these results, it appears that effective hardness and silica removal can be achieved while producing sludge with better settling characteristics using 90 mg/l of lime, 100 mg/l of magnesium, and appropriate amount of caustic to raise the pH to about 9.5.

Table 5-6: Bench Test Data For Hardness And Silica Removal Using Combined Addition of Caustic, Lime and Magnesium

Magnesium (mg/l)	Lime (mg/l)	PH$^{(1)}$	Silica (mg/l)	Alkalinity*	Total Hardness*	Calcium Hardness*
0	0	6.98	200	344	260	230
70	90	7.71	187	328	572	250$^{(2)}$
70	90	9.01	101	368	212	50$^{(3)}$
70	90	9.27	84	390	96	25$^{(3)}$
70	90	9.53	84	446	40	<10$^{(3)}$
70	90	9.78	88	530	<10	<10$^{(4)}$
70	90	10.03	96	615	<10	<10$^{(4)}$

* - mg/l as $CaCO_3$

1 -Adjusted using caustic,

2- Cloudy, small amount of sludge precipitated

3 – 90% of sludge precipitated in 5 minutes,

4 – 90% of sludge precipitated in 10 minutes

5.3 Oxidation Tests Using Chlorine Dioxide (ClO_2)

Oilfield produced water may contain complex organic matter that is not readily biodegraded (Doran, 1997). These organics can potentially foul the RO membranes thereby shortening membrane life and increasing the O& M portion of the treatment cost. A pretreatment process that can remove organics may lower the potential for membrane fouling. Hence, a bench scale test was performed to evaluate oxidation of oilfield organics by ClO_2, a well known oxidizing agent.

The following were assumed in the design and data interpretation of the ClO_2 studies:

- Fouling of the membrane was predominantly caused by large organic molecules in the produced water,
- These larger molecules are not readily biodegradable
- Oxidation of these compounds by ClO_2 to smaller compounds may minimize their potential for fouling the membranes.
- Upon oxidation by ClO_2 to smaller organic compounds, the resultant organics would be more amenable for biodegradation

These tests were performed by Pureline Treatment Systems (Irvine, CA), a company that specializes in applying ClO_2 for water treatment. A five gallon sample of filtered produced water was shipped by overnight delivery to this facility, and the tests were performed the same day the samples were received.

The jar tests were performed in 1 L jars using 750 ml of sample. ClO_2 (5 – 25 mM) was injected into the jars over 8 hours. A control sample that received no ClO_2 was used for comparison purposes. The overall organic content of the samples was estimated by measuring the TOC, and the biodegradable fraction of the organics was estimated by measuring the BOD of the samples.

Table 5-7 shows the results from this test. The TOC and BOD of the control sample were about 58 and 49 mg/l, respectively.

Table 5-7: TOC and BOD Levels in San Ardo Produced Water After Dosing with ClO_2

ClO2 Dose (mM)	ClO2 Dose (mg/l)	TOC	BOD
0	0	58	49
5	335	68	92
10	670	61	93
15	1005	66	96
20	1340	71	92
25	1675	67	93

Organic degradation during BOD evaluation can be described by the following general equation.

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6CO_2 + 6\,H_2O$$

According to the above equation, 72 mg of carbon represents 1 mM of organic compound, and 192 mg of oxygen is required to mineralize this amount of organic compounds. Hence, a TOC of 58 mg/l in the control sample represents about 0.80 mM of total organic compound, and BOD of 49 mg/l represents about 0.25 mM (49 / 192) of organic matter available for biodegradation. This indicates that, prior to ClO_2 addition, only about 32% of the organics (equivalent of 18 mg/l of TOC) in the water were available for biotreatment. The remaining organics in the sample were not readily available for biodegradation. In the sample treated with 5 mM (or higher dosage) of ClO_2, the TOC levels were 3 to 13 mg/l higher than that of the control sample. This may be due to oxidation of some organic matter, which was not captured by TOC analyses in the control sample, to a form that is amenable for TOC analyses. The BOD of these samples was almost twice that of the control samples. This indicated that oxidation by ClO_2 facilitated transformation of about 0.23 mM ((92-49)/192) of initially non-biodegradable organic matter into a biodegradable form. However, approximately 50% of the organics still remained non-biodegradable after treatment with ClO_2. Increasing the ClO_2 dosing five fold did not significantly enhance oxidation of the oilfield organics to a biodegradable form. In summary, the results from this test suggested that while ClO_2 facilitated oxidation of a fraction (~32%) of the non-biodegradable organic matter into a bio-available form, approximately 50% of the organic matter was not oxidized even at extremely high doses of ClO_2.

5.4 Breakpoint Chlorination Studies

Unlike other bench studies that evaluated pretreatment requirements for the produced water this set of tests evaluated one of the post-treatment needs, i.e., possible removal of ammonia from the RO permeate using breakpoint chlorination. Breakpoint chlorination is a process by which residual ammonia is oxidized to nitrate and nitrogen trichloride by chlorine. The chlorine, in turn, is reduced to chloride ions. The theoretical ratio of chlorine to ammonia-N required to remove ammonia by breakpoint chlorination is 7.6:1 (ppm to ppm basis), excluding any chlorine demand from other compounds.

Chlorine stock was prepared by diluting 5 percent "bleach" with deionized water. Since water pH may impact the effectiveness of breakpoint chlorination, the initial permeate pH was adjusted to 7 prior to chlorine addition. Chlorine was added to four 750 ml samples to yield chlorine to ammonia nitrogen ratios of 5:1, 7.5:1, 10:1 and 15:1. The samples were stirred for an hour, allowed to settle for an hour and the supernatants were then analyzed for ammonia, nitrate, nitrite, free chlorine, total chlorine, pH, alkalinity and conductivity. The nitrate and nitrite analyses were performed in an external laboratory. The remaining analyses were performed in the field laboratory.

Table 5-8 and Figure 5-10 show the results from this test. The initial ammonia nitrogen concentration in the permeate was 14 mg/l. Adding 70 mg/l chlorine (5:1) decreased the ammonia nitrogen level to 8 mg/l. The residual chlorine level (after ammonia oxidation and meeting the chlorine demand) was about 28 mg/l. Adding 105 mg/l chlorine (7.5:1) resulted in complete oxidation of ammonia in the permeate. The residual chlorine level also decreased to about 1 mg/l in this sample, suggesting near complete breakpoint chlorination. Further increase in chlorine dose (10:1 and 15:1) increased residual chlorine levels to 38 and 100 mg/l, which are also consistent with breakpoint chlorination at the 7.5:1 dosing rate.

Table 5-8: Breakpoint Chlorination of San Ardo Produced Water

Chlorine : Ammonia-N Ratio	EC (umho/cm)	pH	NH3-N	Free Chlorine	Total Chlorine
No Chlorine	618	7.01	14*	0	0
5:1	794	5.93	8	28	32
7.5:1	1029	3.38	0	1.3	10
10:1	1052	4.66	0	38	61
15:1	1284	6.81	0	101	107

- Measured prior to pH adjustment to 7.

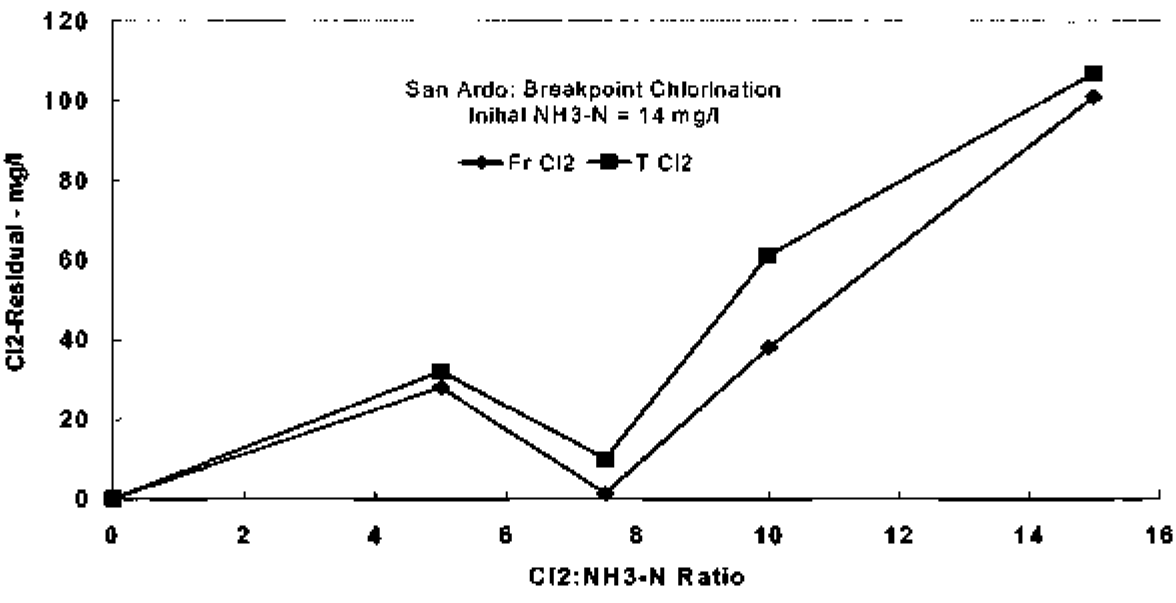


Figure 5-10. Breakpoint Chlorination Curve for RO Permeate of San Ardo Oilfield Produced Water.

Although these tests indicated possible ammonia removal using breakpoint chlorination of the RO permeate, several concerns must be addressed prior to use of this technique. For example, the water pH at breakpoint chlorination decreased to 3.38, possibly due to removal of NH_3 alkalinity in the water. Also, the water conductivity increased to above 1000 µmhos/cm, which indicates a high TDS concentration at this chlorine dosing. This is higher than the water quality criteria for most applications identified in the Central Coast Regional Water Quality Control Board Basin plan. Addition of caustic to neutralize the pH will further increase the TDS of this water. Finally, the results indicated that the total chlorine concentration in 10:1 and 15:1 ratio samples was 10 to 30 mg/l higher than the free chlorine level. These waters contained little or no ammonia and hence, it is unlikely that chloramines formed. Hence, it is not clear if the differences observed were due to chlorine demand exerted by other constituents in the permeate or due to experimental error caused by dilution of the samples or other limitations.

5.5 Conclusions of the Bench Scale Studies

5.5.1 Precipitation Studies

Results from the bench scale tests indicate that the hardness of the produced water can be reduced to about 40 mg/l by addition of 600 mg/l caustic. However, no significant amount of silica is removed without addition of magnesium. Addition of 600 mg/l caustic and 100 mg/l of magnesium at pH between 9.5 and 10 can reduce hardness and silica to desired levels. Lime and magnesium addition without caustic was not effective in meeting the hardness goal. The test using lime, caustic and magnesium indicated that 90 mg/l lime, 100 mg/l magnesium and sufficient caustic to adjust the water pH to 9.5 can be effective in meeting the hardness and silica goals.

Due to difficulties associated with feeding lime, it is recommended that the pilot studies be conducted using caustic (550 to 650 mg/l) to a target pH of 9.5-10.5 and a magnesium concentration of 100 mg/l. It is anticipated that such an operation will result in an effluent hardness level of about 10 mg/l and silica level of about 50 mg/l from the warm softening process.

5.5.2 ClO_2 Oxidation Studies

Only about 30% of the organic compounds in the untreated oilfield produced water were amenable to biodegradation. Treating the water with 5 mM of ClO_2 increased the fraction of organics that can be biodegraded to about 50%. However, further increase in ClO_2 dosing by up to 25 mM did not significantly increase the bioavailability of the organics. This suggested that a large fraction of organics in the produced water can not be oxidized by ClO_2, thereby limiting its effectiveness in produced water treatment. Further testing of ClO_2 is not recommended for this site.

5.5.3 Breakpoint Chlorination Studies

At a chlorine to ammonia-nitrogen ratio of about 7.5:1 almost all of the ammonia was oxidized and the chlorine was reduced in the RO permeate. However, breakpoint chlorination may tend to increase water TDS. This issue must be resolved prior to considering breakpoint chlorination as a viable option for ammonia polishing.

Section 6: Description of Pilot Plant Study

This section describes the equipment, methods and approach used in the pilot plant study. First the unit processes are described, followed by the analytical methods, and the pilot testing approach and schedule.

6.1 Unit Process Descriptions

The following units were selected for pilot testing:

- A 10-30 gpm "Claricone™" clarifier unit from CBI Walker, Plainfield, IL for warm softening of filtered produced water
- A 60 gpm cooling tower from American Cooling Tower Company, Westminster, CA for cooling the softened effluent, and to potentially remove ammonia
- A 10 gpm Reverse Osmosis (RO) unit from Koch Membrane Systems for removing TDS, organics and boron

The schematic of the initial configuration of the pilot plant treatment train is shown in Figure 6-1. A plot plans showing the layout of the various units is shown in Drawing 6-1. Aera Energy LLC with assistance from Kennedy/Jenks developed the piping and instrumentation diagrams (Drawings 6-2 and 6-3) that were used to construct the pilot facilities. An Aera Energy LLC subcontractor (DCCK Engineering) developed the electrical drawings with input on control and alarm strategies provided by Kennedy/Jenks Consultants (Appendix E). Figure 6-2 is a photograph of the pilot plant site during construction.

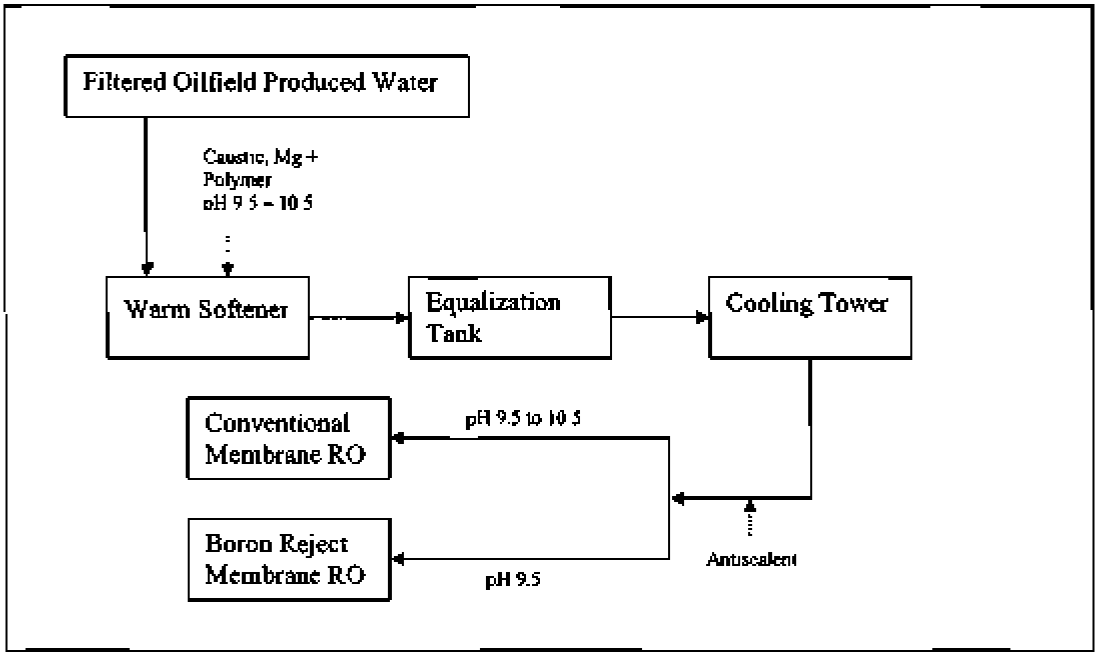
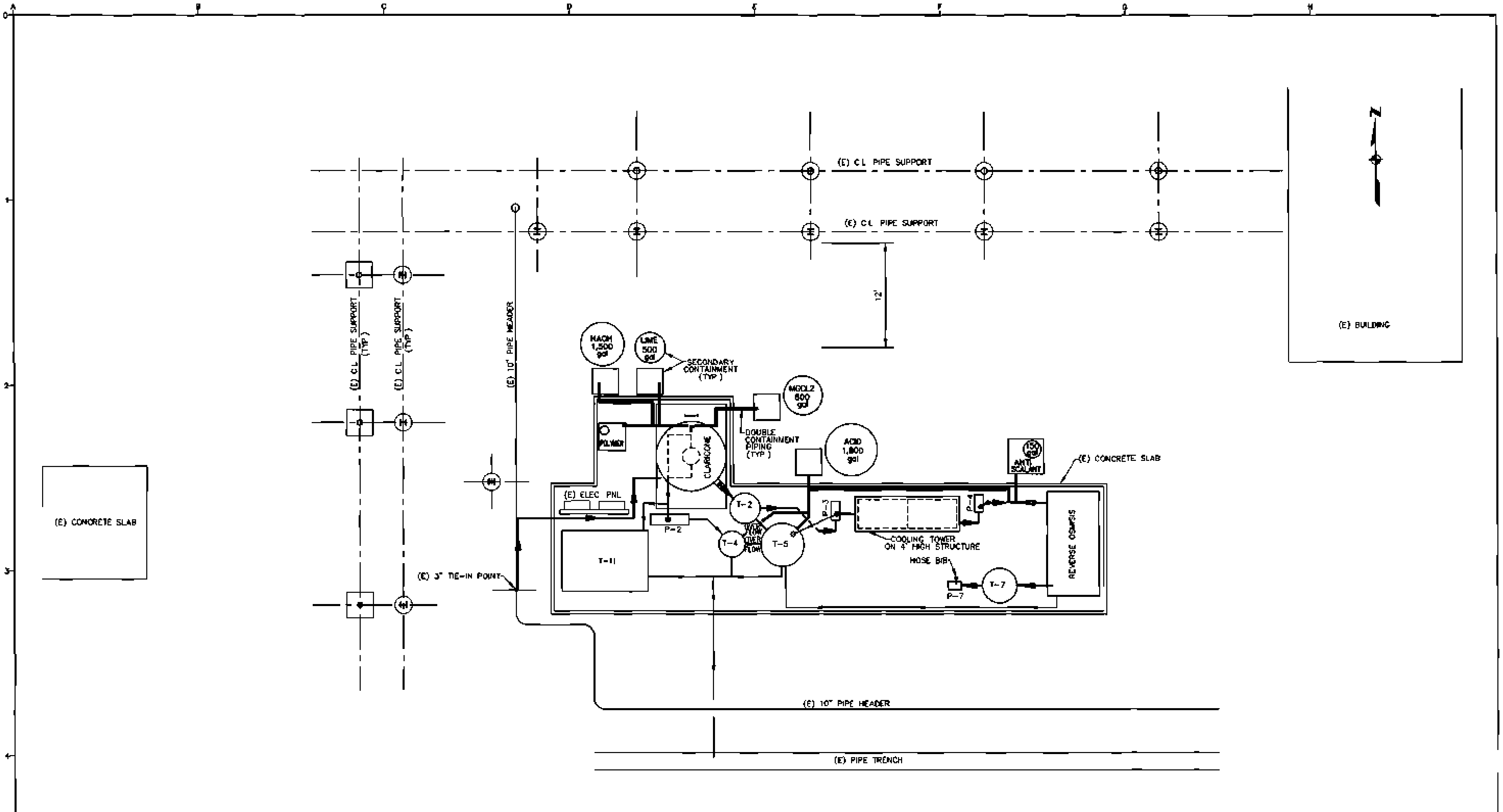


Figure 6-1. General Pilot Plant Schematic



NOTES
1. LOCATION OF EXISTING PIPING, PIPE SUPPORTS, BUILDING, ELECTRICAL, AND PIPE TRENCH ARE SHOWN IN APPROXIMATE LOCATIONS
2. FIELD VERIFY EXISTING LOCATIONS PRIOR TO CONSTRUCTION

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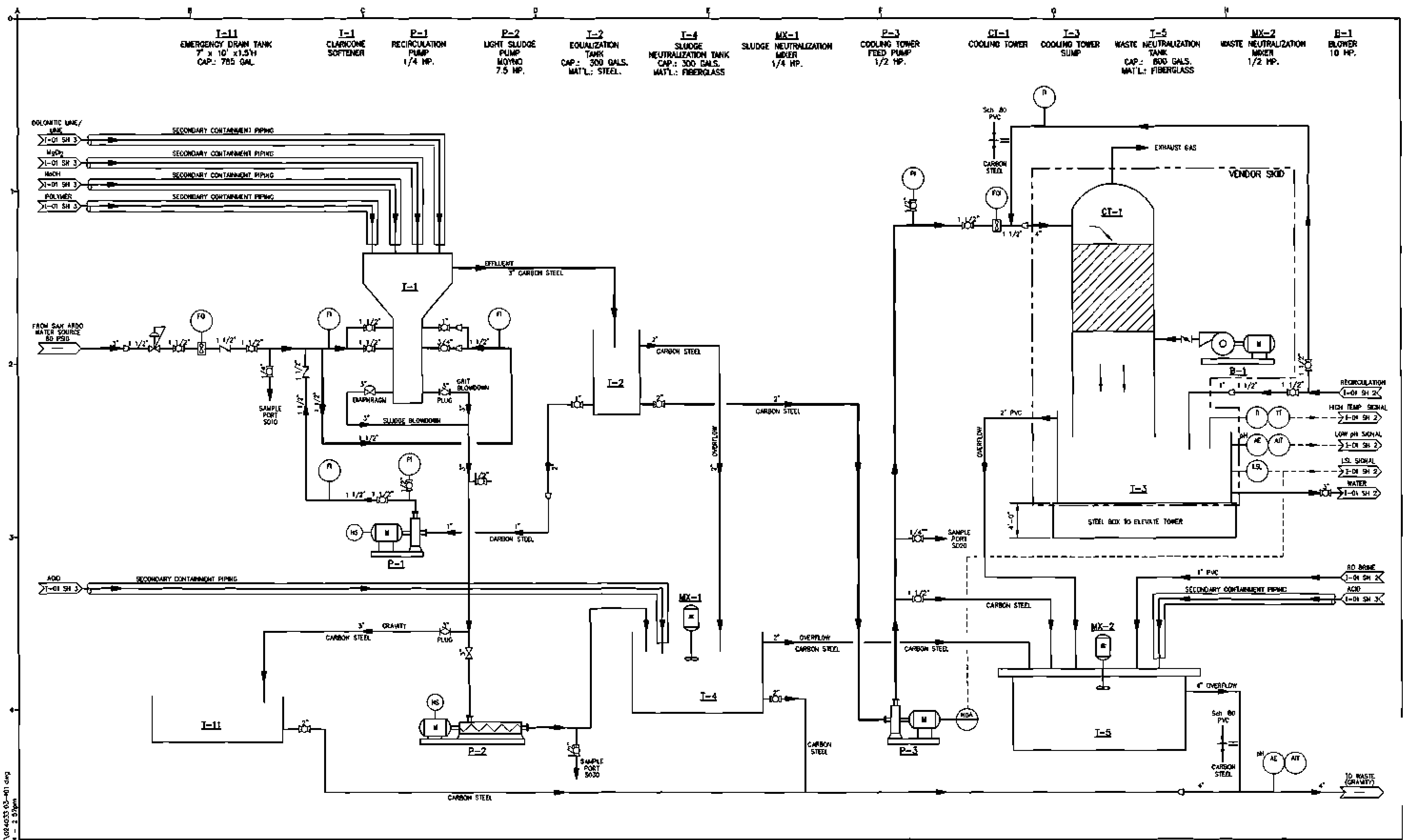
SAN ARDO, CALIFORNIA
BENEFICIAL REUSE OF SAN ARDO PRODUCED WATER

Kennedy/Jenks Consultants
IRVINE, CA

PLOT PLAN
PILOT SYSTEM

FILE NAME 024033.03-M01
JOB NO 024033.03
DATE FEB 2004
SHEET M-01 OF



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BENEFICIAL REUSE OF SAN ARDO PRODUCED WATER

Kennedy/Jenks Consultants

PIPING AND INSTRUMENT DIAGRAM PILOT SYSTEM

FILE NAME 024033.03-I01
JOB NO 024033.03
DATE FEB 2004
SHEET OF
I-01 SH 1

P-4
TRANSFER PUMP
45 GPM @ 25 PSIG
1.5 HP.

SM-1
STATIC MIXER
INLINE

F-1
CARTRIDGE FILTER
5 MICRON
KOCH MEMBRANE SYSTEMS

F-2
CARTRIDGE FILTER
5 MICRON
KOCH MEMBRANE SYSTEMS

P-5
R.O. FEED PUMP
KOCH MEMBRANE SYSTEMS
10 GPM @ 500 PSIG
7.5 HP.

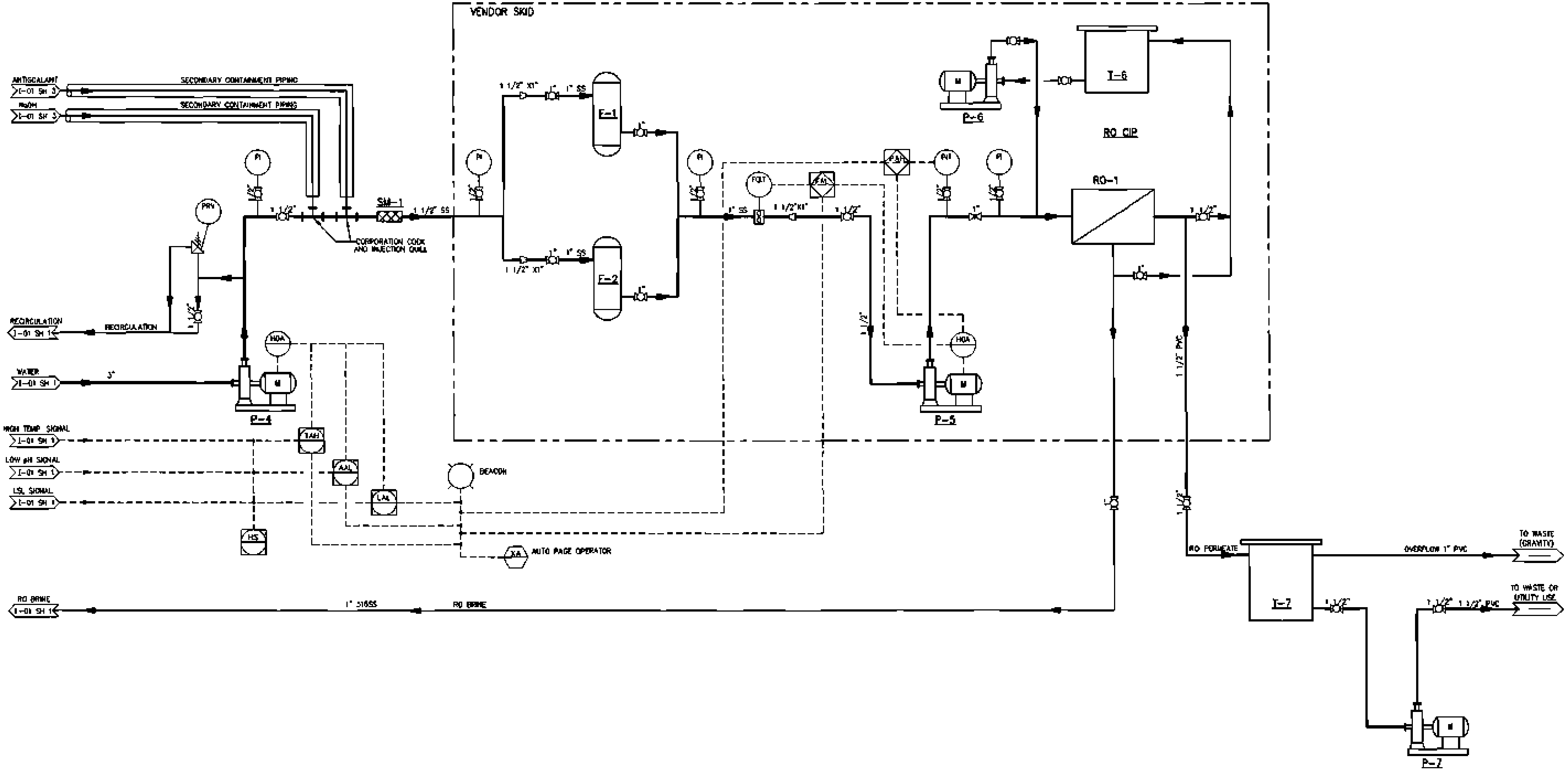
T-6
R.O. CLEANING
TANK
KOCH MEMBRANE SYSTEMS
CAP.: 300 GALS.

RO-1
REVERSE OSMOSIS
SYSTEM
KOCH MEMBRANE SYSTEMS

P-6
R.O. CLEANING PUMP
KOCH MEMBRANE SYSTEMS
20 GPM @ 20 PSIG
1/3 HP.

T-7
R.O. PERMEATE
TANK
CAP.: 500 GAL.

P-7
R.O. PERMEATE
PUMP
8 GPM @ 15 PSIG
1/3 HP.



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SAN ARDO, CALIFORNIA
BENEFICIAL REUSE OF SAN ARDO PRODUCED WATER

Kennedy/Jenks Consultants

PIPING AND INSTRUMENT DIAGRAM
PILOT SYSTEM

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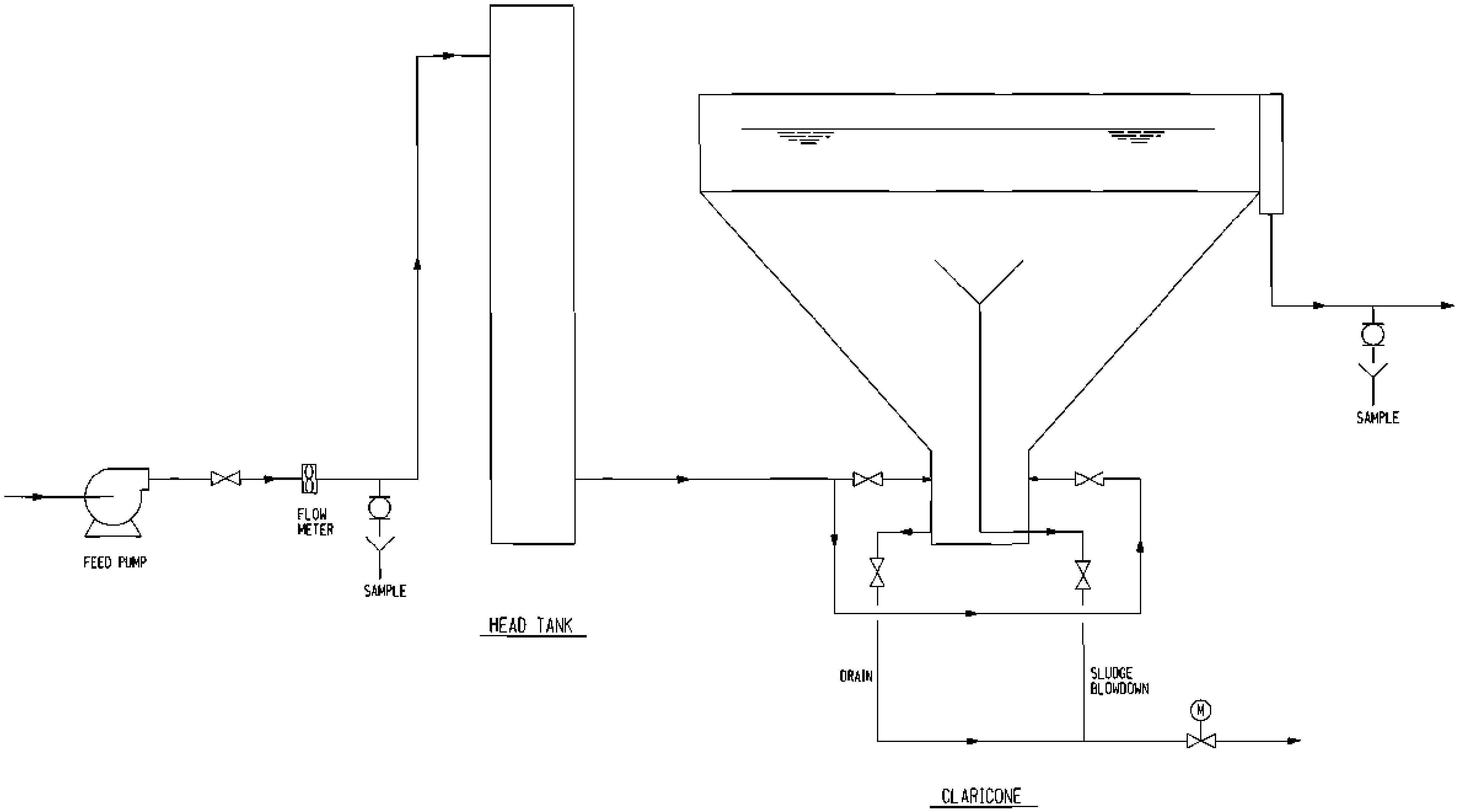
Figure 6-2. Pilot Site During Equipment Installation

6.1.1 Claricone™ for Warm Softening Process

A Claricone™ Clarifier supplied by CBI Walker, Plainfield, IL was selected for this study. Table 6-1 presents the design criteria for this unit. This unit is an up-flow solids-contact clarifier. Figure 6-3 and Drawing 6-4 show a photograph and P&ID of the clarifier unit.

The clarifier consists of a conical steel vessel, with a 2-ft diameter base that expands to 8-ft at the top. Feed water is introduced at the base of the unit. The inlet flow into the conical vessel imparts a helical flow pattern that mixes the feed chemicals and maintains the sludge blanket as the treated water and precipitated solids flow upwards through the unit. Because of the conical design of the vessel, the flow velocity of the water decreases as it moves upwards through the unit. The decreasing velocity helps prevent the smaller precipitated particles from being carried over. The unit is designed to capture solids in the collection funnel located near the center of the unit and remove them via a blowdown valve controlled by a variable timer. The unit also has a grit blowdown line for removing dense solids that collect at the bottom of the unit. The clarified water spills over a weir into a collection box. The Claricone™ unit was installed and operated without the head tank shown in Drawing 6-4.

A 20 % caustic solution was used for hardness removal from San Ardo water. Magnesium chloride (30 %) was added to remove silica as magnesium silicate. Furthermore, 3 ml/l of polymer (EWC 566) was added to aid sludge precipitation.



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PIPING AND INSTRUMENT DIAGRAM

CLARICONE PILOT P&ID

CBI Walker

CUSTOMER'S NO 4P12009
BY DHP CHKD ____ DATE 4/16/80
ENGINEERING SUPERVISOR DNR APPR

SUPPLIER'S / PURCHASER'S NO

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Table 6-1: Claricone™ Process Design Criteria

Design Parameter	Units	Value
Solids Contact Clarifier	-	CBI Walker ClariCone™
Nominal flow rate	GPM	30
Operational flow rate	GPM	10 – 30
Recirculation rate	GPM	0 – 20
Surface Diameter	Ft	8
Base Diameter	Ft	2
Unit Height	Ft	7.67
Water Volume	Gallons	900
Surface Loading Rate	gallons/ft^2/minute	0.6
Hydraulic Retention Time	Minutes	90

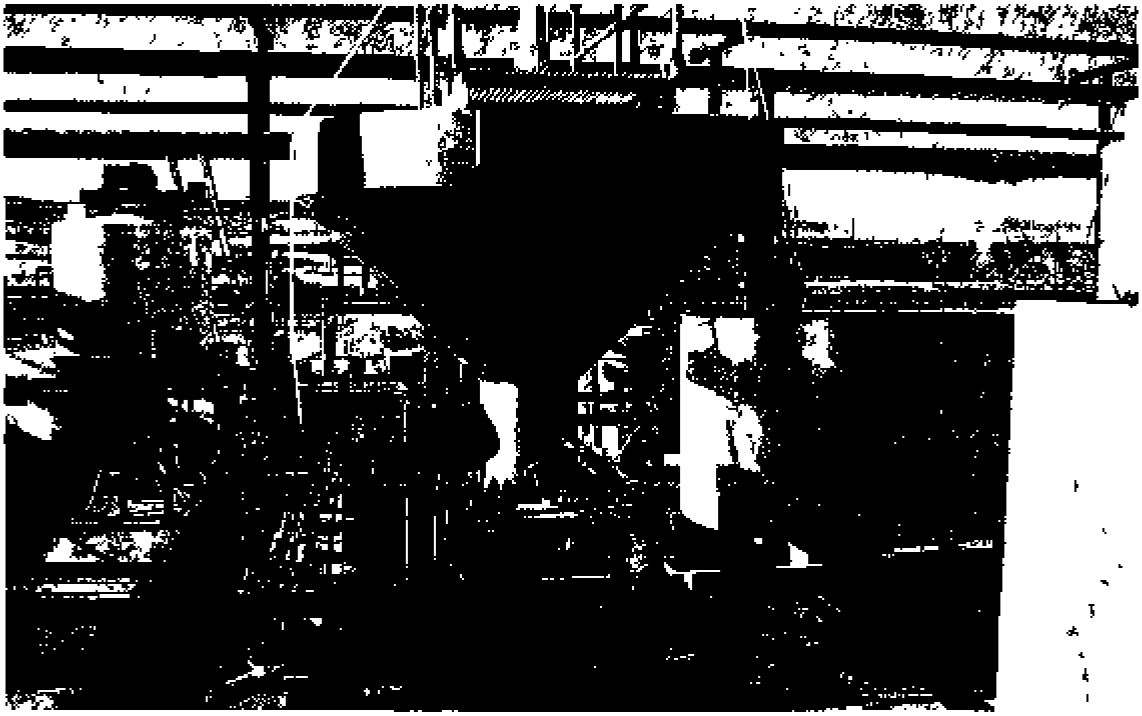


Figure 6-3. Picture of Claricone™ Unit

6.1.2 Cooling Tower

The softened produced water temperature was expected to be between 140 to 185 ° F and had to be cooled to about 105 ° F to protect membrane integrity. In addition to cooling, some ammonia was expected to be removed (air stripped) by the cooling tower. A 60 gpm recirculation mode cooling tower from American Cooling Tower Company, (Westminster, CA), model VXT 120 was installed to lower the temperature of the softened produced water. Table 6-2 presents the design criteria for the cooling tower used in this study.

Table 6.2: Cooling Tower Process Design Criteria

Design Parameter	Units	Value
Cooling Tower Unit	-	American Cooling Tower
Nominal flow rate	GPM	10 – 60
Operational flow rate	GPM	10 – 30
Recirculation rate	GPM	0 – 30
External Dimension (LXWXH)	Ft	12' X 4 X 8' 7"
Packing Material		CPVC
Nominal Flow Temperature	°F	195
Combined Influent Temperature	°F	150
Cooled Effluent Temperature	°F	105
Air Water Ratio		3000:1 to 11,600:1

A chlorinated poly vinyl chloride (CPVC) packing material was used. Individual CPVC blocks of 12"X3"X3" were packed to provide a total contact area of 7452 ft^2 for cooling. A 15 HP fan supplied air for cooling. Due to the anticipated high temperature of the warm softening effluent, the cooling tower was designed to operate in a recirculation mode (Figure 6-4). As per this design, the influent water (30 gpm) at 190 °F would be diluted by 30 gpm recirculation water at 105 ° F. The combined flow of 60 gpm @ 150 ° F will then be cooled to 105 ° F in the cooling tower. Figure 6-6 shows a picture of the cooling tower at the pilot site.

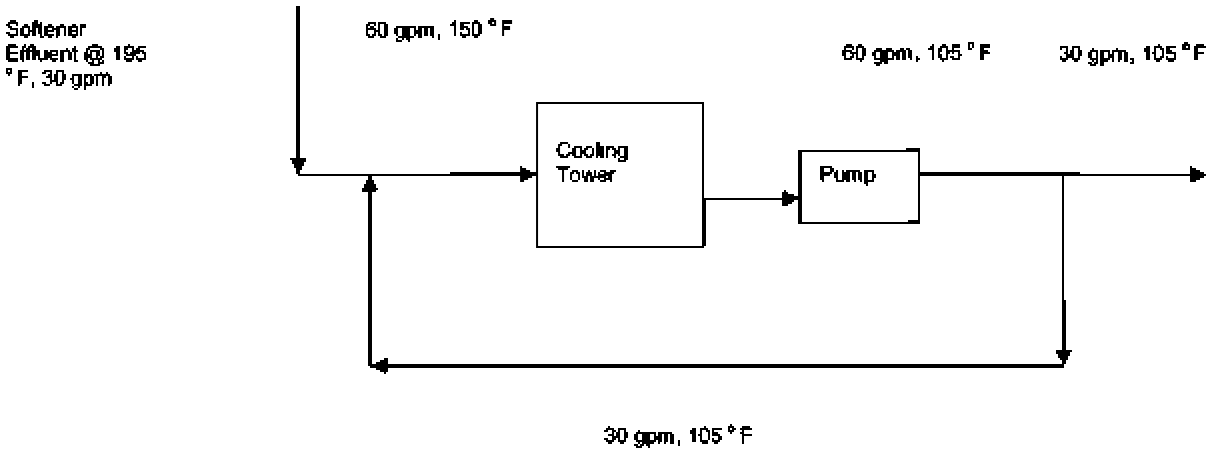


Figure 6-4. Cooing Tower Process Flow Diagram

6.1.3 Reverse Osmosis Unit

The softened cooled produced water was treated by an RO unit (Koch Membrane Systems, Wilmington, MA). The influent temperature of the unit was below 105 °F. The pH of the water was varied from 9.5 to about 11 to facilitate removal of boron in addition to TDS removal The influent water passed through a 5 micron cartridge filter prior to RO treatment The 10 gpm RO pilot unit consisted of an equipment skid with cartridge filter, high pressure pump, membrane housings and control panel

The major components included the following

- Six (6) 4" diameter housings, each capable of holding up to three 4" dia x 40" long spiral wound RO elements
- Eighteen (18) 4" dia x 40" long RO elements
- One (1) steel equipment skid with nominal dimensions of 12' L x 5' W x 7' H
- Two (2) 20" long filter cartridge housing each with a 5 micron nominal rated cartridge filter
- One (1) high pressure pump coupled to a 480 volt, 3 phase, 60 cycle TEFC motor
- Local pH, temperature, conductivity and flow instrumentation
- Local low-pressure, pH out-of-range and high-pressure alarms
- Two (2) chemical metering pumps for acid and/or anti-scalant chemical injection
- One (1) 30 gallon anti-scalant day tank
- Local manually operated valves and skid piping
- A clean-in-place (CIP) unit
- Remote alarm contact

Table 6-3 shows the key process design parameters for the RO unit for the initial testing, and Drawing 6-5 shows the P&ID diagram Although there were 6 membrane housings, the RO unit was configured using a 2X0 array In this configuration, only four of the membrane housings were used for the brackish water membrane For side-by-side comparison between the brackish water and boron rejection seawater membrane trial, a 1X0 array was used In this case only one membrane housing was used for each membrane type Figure 6-5 shows a picture of the RO unit used in this pilot study

Table 6.3: Reverse Osmosis Process Design Criteria for Brackish Water Membrane Trial

Design Parameter	Units	Value
Cartridge Filter		
Number of Housings		2
Number of Cartridge Filters		2
Feed Rate	GPM	10
Filter Rating	µm	5
Size (diameter x length)	inch x inch	2" x 20"
Reverse Osmosis		Koch Membrane Systems
Number of Stages		2
Array		2 X 0
Number of Pressure Vessels		6
Elements per Vessel		3
Membrane Elements		
Number of Elements	-	18
Size (diameter x length)	inch x inch	4 x 40
Permeate Flow Rate	GPM	10
RO Concentrate Flow Rate	GPM	2 5
Percent water recovery	%	75
Feed Pressure	PSIG	350

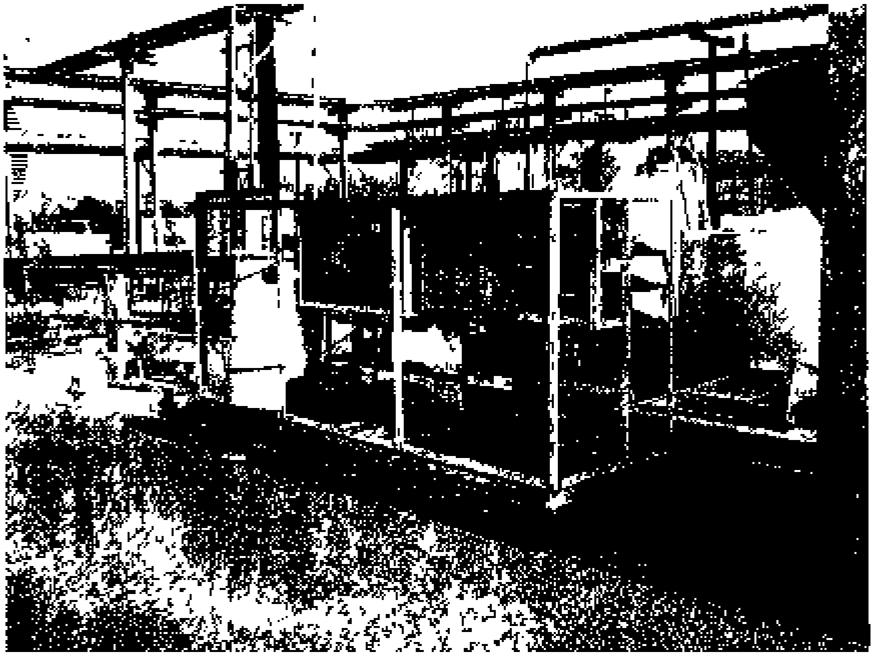


Figure 6-5. Reverse Osmosis Unit (Koch Membrane Systems)

6.2 Unit Process Evaluation Objectives

There were three major unit processes used in this pilot study. The pilot study objectives for each of these major unit processes are described below.

6.2.1 Warm Softening Process

The use of a warm softening process was intended for removal of scale forming constituents such as hardness and silica in the water. The following were the specific objectives of the pilot study:

- Establish the optimal chemical (caustic and magnesium) dose of the warm softening process to meet treated water quality objectives.

- Establish the optimal pH range for operation of the clarifier to treat the brackish produced water specific to the San Ardo, CA oilfield and meet the end water quality objectives. An earlier study (Doran, 1998) at Placerita Canyon oilfield indicated that the optimum pH for removal of hardness and silica by a warm softening process is approximately 9.5. However, for effective removal of ammonia by the cooling tower and boron by the RO, the calculated pH of the softened water had to be above 10.5. Hence, the warm softening unit was operated at a pH range of 9.5 to 11 during the pilot study.

- Evaluate the characteristics of the warm softening process sludge. The sludge must be non-hazardous to facilitate economic disposal and eliminate long-term environmental liability. Several analyses including California Assessment Manual metals (California's method for determining a hazardous wastes), spectral analyses, and percent solids were performed to determine options and associated costs for sludge disposal. During the warm softening operations, some solids carryover problems were observed in the effluent from the clarifier unit. The details of this problem are discussed in later sections. Due to these problems, the effluent from the clarifier unit was allowed to settle in a large (20,000 gallon) settling tank and the settled sludge was collected for this characterization.

6.2.2 Cooling Tower

There were two reasons for having a cooling tower:

- Temperature reduction. The softened produced water temperature was ~140 – 160 ° F and the RO membranes and supporting systems had a maximum temperature tolerance of ≤ 100 ° F.
- Ammonia removal. The final effluent goal for ammonia was 5 mg/l. The pH of the Claricone™ effluent ranged from 9.5 – 11.5 and operational air-to-water ratio was 11,600:1. Since ammonia removal by air stripping was expected under these conditions, characterizing the cooling tower's performance for ammonia removal was an objective.

6.2.3 Reverse Osmosis

The use of reverse osmosis (RO) in the overall treatment scheme was intended to target the removal of dissolved inorganic and organic constituents in the water. The following are the specific objectives for the RO pilot study:

- Establish the optimal pH range for operation of the RO to treat brackish produced San Ardo water and meet treated water quality objectives.
- Evaluate the RO performance to determine the specific flux for the RO elements tested. The specific flux can, in turn, directly be used as a basis to project electrical power requirements for a full-scale facility at San Ardo.
- Monitor and estimate the fouling potential of San Ardo water on the RO membranes to determine the cleaning regimen and frequency requirements.
- Compare the performance of brackish water RO elements versus RO elements designed specifically for use on high boron seawater. This objective was incorporated into the study during the latter stage of pilot testing when such high boron seawater membranes were made available for use by the membrane vendor.

6.3 Pilot Plant Operations

After startup and shake down of individual units, the pilot plant was ready to generate operational data. However, changes were required as a result of poor Claricone™ effluent water quality. As a result the study was divided into different operation phases that are summarized in Table 6-4. Below is an explanation for these changes.

Table 6.4: Summary of Pilot Plant Unit Processes Operations

Case	Units on-line	Objectives	Approach	Dates of Operation
1	Claricone™	Optimize silica and hardness removal	Fixed Mg Addition and vary target pH; Fixed pH with caustic and vary Mg feed	Jul - Oct 04
2	Claricone™, holidng tanks, cooling tower	Determine reduction of temperature and ammonia	Operated cooling tower at 15 GPM and collect a total of 5 sets of data and samples to determine performance	Feb 05
3	Claricone™, holding tanks, RO	Characterize brackish water membrane	Operate RO in 2X1 array until several CIP are performed	Oct 04 - Feb 05.

Case	Units on-line	Objectives	Approach	Dates of Operation
4	Claricone™, holding tanks, RO	Side-by-side comparison of brackish water membrane and boron rejection membrane	Reconfigure RO to two single array units. Install brackish water membranes in one side and boron rejection membrane on the other.	Feb - Mar 05

6.3.1 Background

Initially, the Claricone™ clarifier and the cooling tower were operated to ensure proper turbidity and temperature to protect the RO from early failure. Due to high solids in the clarifier effluent, two 20,000 holding tanks were added to assist in protecting the RO membranes from early fouling. After installing the holding tanks and operating the Claricone™ clarifier and cooling tower in series, it was determined that the cooling tower was breaking up the floc, which remained suspension even after 24 hours of settling. The resultant turbidity was too high to treat this water by RO. As a result, the cooling tower was taken off-line as described in Table 6-4, cases 3 and 4.

6.3.2 Case 1, Claricone™

During the construction for adding the two holding tanks, field work concentrated on developing operating conditions for this unit process to maximize removal of hardness and silica.

6.3.3 Case 2, Claricone™, Holding Tanks and Cooling Tower

To obtain data to determine the performance of the cooling tower, the Claricone™ clarifier was operated in series with the holding tanks and cooling tower at pH 10-11 (Table 6-4, Case 2). This configuration was operated for a week to characterize the performance of the cooling tower with respect to temperature and ammonia removal.

6.3.4 Case 3, Claricone™, Holding Tanks and Brackish Water RO

These studies were performed using 12 elements (four housings) in a 2X0 array system. The intent of these studies was to establish target operating parameters suitable for a full-scale process to meet the treated water quality goals described in Section 2. Ideally, the pilot RO unit would have been operated 24 hours a day, 7 days a week for the entire period. However, problems with solids settling and removal in the upstream warm softening process prevented such continuous operation. Therefore, the unit was generally operated ~8 hours a day, 5 days a week to allow monitoring by Kennedy/Jenks onsite staff. Data from the pilot RO operation was evaluated on a cumulative run time basis.

These operating parameters include:

- RO Recovery (ratio of permeate flow rate to RO water feed flow expressed as a percentage). The target recovery for an RO system dictates the required power, chemicals, cleaning costs and the capital cost to construct the system. Typical recoveries for brackish water RO systems fall within 50% to 75%. The field evaluation targeted 67% recovery. A feed rate of 7.5 gpm was maintained. The feed pressure was adjusted to yield permeate and reject stream flow rates of 5 and 2.5 gpm, respectively. KOCHTREAT® MAX an inorganic scale inhibitor/antifoulant provided by Koch Membrane System (KMS), was added to the RO feed water during all test runs at a rate of 5.4 mg dry powder/L feed water to reduce organic and inorganic fouling.

- Operating pH of the Feedwater. Boron rejection by the brackish water RO membranes is highly dependent on feedwater pH. Previous pilot investigations (Doran, 1998) indicated that a pH between 10.5 and 11 was needed to ionize the boron so that it would be removed by the brackish water membranes. However, the optimum pH for hardness and silica removal in the warm softening unit is about 9.5. The field evaluation of RO membranes targeted an operating pH in this range.

- Allowable Run Time. During operation of an RO system various foulants gradually accumulate on membrane surfaces, leading to progressively increasing operating pressure to maintain constant recovery. Typically, the end of an operating run is reached when the specific flux for the membrane system declines by 15 to 25% from the specific flux at the start of the operating run. The pilot test evaluated the allowable run time based on this pressure increase criteria.

- Membrane Cleaning Requirements and Frequency. Membrane cleanings are conducted following the end of an operating run and generally entail the use of a low pH cleaning solution to remove inorganic scale and/or a high pH cleaning solution to remove organic foulants. The field evaluation investigated the type of cleaning regimen needed to address the foulants specific to San Ardo water.

  Following the end of the test run, the RO unit was put through a clean-in-place (CIP) process, which entailed the following sequence of steps:

  - Cleaning RO membranes with a low pH cleaning solution (KOCHKLEEN® 100) (0.2-0.3%) for 30 minutes in order to remove inorganic contaminants scale on the membrane surface. The system was then flushed with RO permeate for 15 minutes and the membranes were allowed to relax for nearly two hours.
  - Return of the RO unit to service at the target recovery established prior to the low pH cleaning. The pressure recovery achieved was observed.
  - Cleaning RO membranes with a high pH cleaning solution (KOCHKLEEN® KLD III) for 30 minutes to dissolve organic foulant from the membrane, followed by flushing with RO permeate for 15 minutes.
  - Return of the RO unit to service at the target recovery established prior to the high pH cleaning. Observe any additional pressure recovery achieved.
  - Restore operation of the RO unit to the conditions targeted at the start of the pilot RO test run.

6.3.5 Case 4, Claricone™, Holding Tanks Side-by-Side Brackish Water and High Boron Rejection Seawater RO Membranes

This portion of the pilot test sought to compare the performance of brackish water membrane elements to equivalently sized high boron rejection seawater membrane elements exposed to the same water quality and operating conditions. Performance data supplied by Hydranautics for their high boron rejection membranes in seawater applications suggested that these elements could potentially be used to meet the end water quality goals for San Ardo at a lower feedwater pH. If successful, these membranes would reduce caustic demand and result in a significant O&M cost reduction for a full-scale system. However, several tradeoffs do exist that could potentially outweigh the benefits of operating at a lower feedwater pH. These include:

- Potential Increased Operating Pressure. Seawater membranes may require higher operating pressure to achieve the same recovery as a brackish water membrane under the same conditions. Higher operating pressures would result in greater energy usage and increase electrical O&M costs for a full-scale system.

- Potential Decreased Run Times. Seawater membranes may be susceptible to fouling at a quicker rate than brackish water membranes. An increased fouling rate would result in shorter run times between required cleanings and increase the cleaning O&M cost for a full-scale system.
- Potential Shorter Membrane Life. Seawater membranes may more susceptible to permanent fouling than brackish water membranes, which could potentially reduce the useful life of the membrane elements. Such a decrease in membrane life would increase the replacement frequency and associated O&M cost for a full-scale system.

The pilot test to evaluate the two membrane types was conducted from 18 February 2005 through 3 March 2005. Time limitations in the overall pilot schedule prevented a longer evaluation period. At the conclusion of the test run, CIP were performed on the membranes to evaluate fouling/scaling characteristics.

6.4 Summary of Pilot Sampling and Data Collection

A sampling plan, summarized in Tables 6-5 and 6-6, was formulated to provide guidance for the operation of the process train. The sampling plan was intended to provide information to assist in making operational decisions. It was not intended to provide rigorous scientific data to defend or develop theoretical mechanisms of performance or removal of unit processes within the treatment train.

Table 6.5: Summary of Field Data and Sampling Program

Water Parameters	Warm Softener Influent	Warm Softener Effluent	Warm Softener Sludge	Cooling Tower Effluent	RO Influent	RO Permeate	RO Concentrate
Field Readings							
Flow Rate	✓	✓			✓	✓	✓
Total Flow Rate		✓			✓		
Flow Calibration		✓				✓	✓
Pressure	✓				✓	✓	✓
Temperature	✓	✓		✓	✓	✓	
Field Analyses							
pH	✓	✓		✓	✓	✓	✓
Conductivity	✓	✓			✓	✓	✓
Turbidity	✓	✓			✓	✓	
Silt Density Index					✓		
Alkalinity	✓	✓			✓	✓	✓
Total Hardness	✓	✓				✓	✓
Calcium Hardness	✓	✓				✓	✓
UV	✓	✓				✓	
SiO_2	✓	✓				✓	✓

Table 6.6: Summary of Laboratory Analytical Program

Water Parameters	Influent Produced Water	Warm Softener Effluent	Warm Softener Sludge	Cooling Tower Effluent	RO Influent	RO Permeate	RO Concentrate
Gen. Minerals/Gen. Physical[1]	✓	✓				✓	
pH			✓	✓	✓		✓
TDS					W		✓
Alkalinity			✓				✓
Boron	✓	✓	✓			✓	✓
Silica	✓	✓				✓	✓
Anions[2]	✓					✓	
Cations[3]	✓		✓			✓	
NH_3				✓		✓	
Metals[4]	✓	✓	✓			✓	✓
Iron & Manganese			✓				
Heterotophic Plate Count						✓	
Biochemical Oxygen Demand						✓	
Total Organic Carbon	✓	W		✓		✓	✓
Base/Neutral/Acid Extractable	✓			✓		✓	
Volatile Organic Compounds	✓			✓		✓	
Trihalomethane Formation Potential	✓					✓	
Haloacetic Acids	✓					✓	
Toxicity	✓					✓	
% Solids			✓				
California Assessment Manual Metals			✓				
CTR[5]						✓	

Notes:
1. pH, alkalinity, TDS, TSS, Total Hardness, Turbidity, Ammonia, Conductivity
2. Chloride, sulfate, nitrate, bromide
3. Calcium, magnesium, sodium, potassium
4. Iron, manganese, barium, strontium
5. California Toxic Rule Constituents.

6.5 Summary of Analytical Methods

The field analyses were performed by Kennedy/Jenks staff. The testing methods are summarized in Table 6-7. The laboratory analyses were performed by Zymax Envirotechnology, Inc. (San Luis Obispo, CA), Truesdail Laboratories, Inc. (Irvine, CA), Zalco Laboratories, Inc (Bakersfield, CA) or Toxscan Laboratories (Watsonville, CA). The methods and the laboratories used for each analysis are summarized in Table 6-8. All laboratories are approved by the California Department of Health Services to perform all the assigned analyses. The approval requires that each laboratory maintain an extensive quality assurance and quality control system to ensure the reliability of the reportable laboratory findings.

Table 6.7: Field Analytical Methods

Parameter	Method/Description
pH	Standard Methods 4500 H+/Meter
Temp (°F)	Standard Methods 2550 B/Meter
Turbidity (NTU)	Standard Methods 2130/Meter
Conductivity (µmho)	Standard Methods 2510 B/Meter
UV Absorbance, . 254 nm	Shimadzu UV-1601 Spectrophotometric
Alkalinity (mg/L as $CaCO_3$)	Hach Method 8203/Titration
Total Hardness (mg/L as $CaCO_3$)	Hach Method 8226/Titration
Ca (mg/L as $CaCO_3$)	Hach Method 8222/Titration
SiO_2	Hach Method 8185/Colorimetric, 420 nm

Table 6-8: Summary of Laboratory Analytical Methods

Parameter	Method/Description	Laboratory
pH	Standard Methods 4500 H+/Meter	Zymax
Temp (°F)	Standard Methods 2550 B/Meter	Zymax
Alkalinity (mg/L as CaCO3)	Standard Methods 2320/Titration	Zymax
Total Hardness (mg/L as CaCO3)	USEPA Method 200.7/Calculated, Ca and Mg from ICP-AES	Zymax/Zalco
Calcium (mg/L as CaCO3)	USEPA Method 200.7/ICP-AES	Zymax
Magnesium (mg/L as CaCO3)	USEPA Method 200.7/ICP-AES	Zymax
Boron	USEPA Method 200.7/ICP-AES	Zymax
Iron	USEPA Method 200.7/ICP-AES	Zymax
Silica	USEPA Method 200.7/ICP-AES	Zymax/Zalco
Potassium	USEPA Method 200.7/ICP-AES	Zymax
Sodium	USEPA Method 200.7/ICP-AES	Zymax
Barium	USEPA Method 200.7/ICP-AES	Zymax
Strontium	USEPA Method 200.7/ICP-AES	Zymax
Chloride	USEPA Method 300.0/Ion Chromatography (IC)	Zymax
Sulfate	USEPA Method 300.0/IC	Zymax
Bromide	USEPA Method 300.0/IC	Zymax
Nitrate-N	USEPA Method 300.0/IC	Zymax
Total Organic Carbon (TOC)	USEPA Method 415.1	Zymax
Ammonia-N	4500 NH3 D/Selective Ion Probe	Zymax
Total Suspended Solids (TSS)	Standard Methods 2540 D/Gravimetric	Zymax
Total Dissolved Solids (TDS)	Standard Methods 2540 C/Gravimetric	Zymax
% Sludge Solids and Spectral Analyses	USEPA Methods 3050 B/Sample digestion with Aqua Regia/ and USEPA 6010 B	Zymax
Base Neutral Acid Extractables	USEPA Method 8270/GC-MS	Zymax
Purgeable Organics (Volatiles)	USEPA Method 624/GC-MS	Zymax
BOD	USEPA Method 405.1/Probe	Truesdail
COD	USEPA Method 410.4/Spectrophotometric	Truesdail
CAM Metals for Solids	USEPA Methods 7.3H2S, 7.3CN, 418.1, 1010, 1311A, 6010A, 7061A, 7471A, 7741A, and 9045. CA Dept. of Fish and Game LC50	Zymax
Metals for CTR analyses (Sb,Be,Cd,Cu,Pb,Hg,Mo,Se,Tl,Ag)	Standard method 200.8/245.1 for Hg	Toxscan

Section 7: Pilot Plant Results and Discussion

This section is organized in the same manner as Section 6,*i.e.*, by individual treatment units. The discussion focuses on the performance of the units to meet the water quality goals and ensuing implications rather than a theoretically based explanation of results. The section discusses the removal of organic and inorganic compounds in the produced water, the quality of sludge from the softening process, the RO concentrate quality, as well as the operational findings of importance by unit process. The raw data is presented in Appendix B.

7.1 Warm Softening Unit

The Claricone™ warm softening unit was operated under various caustic and magnesium feed conditions to remove silica and hardness from San Ardo produced water. The typical water quality characteristics for San Ardo produced water are shown in Table 7-1. Placerita Canyon water quality is also presented for comparison. The hardness and alkalinity levels in San Ardo produced water is lower (~70 & 25%, respectively) than those in Placerita Canyon water. This suggested that the San Ardo water might require a lower amount of caustic for softening. However, the magnesium concentration of the San Ardo water (~ 5 mg/l) is significantly lower than that of Placerita Canyon water (~ 75 mg/l). Hence, the San Ardo water may require a higher dose of magnesium for silica precipitation.

Table 7.1: Typical Water Quality Characteristics of San Ardo and Placerita Canyon Produced Waters

Parameter (mg/l unless otherwise noted)	Placerita Canyon	San Ardo
Alkalinity	482	367
Aluminum	-	0.2
Ammonia - Nitrogen	15	31.1
Barium	1.5	0.41
Bicarbonate	-	448
Boron	20	26.8
Calcium	260	111
Chloride	3,180	4050
Fluoride	-	1.8
Hardness, Total (mg/l as $CaCO_3$)	1,100	303
Iodide		3.1
Iron	0.16	0.17
Magnesium	97	6.07
Manganese	-	0.105
Nitrate	-	4
Oil and Grease	-	46.2
pH (units)	7.02	7.54
Potassium	75	61.6

Parameter (mg/l unless otherwise noted)	Placerita Canyon	San Ardo
Silica	206	227
Sodium	1,650	2,540
Sulfate	82	63
Sulfide	-	12
TDS	6,000	7,540
Temperature (° F)	152	190
TPH	-	1.9
Turbidity (NTU)	-	4.3
TOC	99	80

7.1.1 Silica Removal in the Warm Softener

Figure 7-1 shows the silica levels in the treated water when adding 500 mg/l of caustic and varying amounts of magnesium. At a dosing rate of 60 mg/l magnesium, the effluent pH was 10, and silica level was about 100 mg/l (~ 50% removal). A silica level of ~60 mg/l was achieved at 100 mg/l magnesium dose. Figure 7-2 shows the silica levels in the treated water when the caustic dosing was increased to 600 mg/l. Silica removal in the softener improved by increasing the caustic dose to 600 mg/. The effluent silica levels were 65, 40 and 20 mg/l at magnesium dosing rates of 75, 100 and 150 mg/l, respectively. Figures 7-3 & 7-4 compare effluent pH and silica levels when adding 500 and 600 mg/l caustic. While caustic addition tends to increase the effluent pH, magnesium chloride reduced the effluent pH. For the same magnesium dosing, silica removal increased with increase in caustic addition. The difference was more pronounced at 100 mg/l magnesium dosing (~ 50%) than at 75 mg/l (~15%).

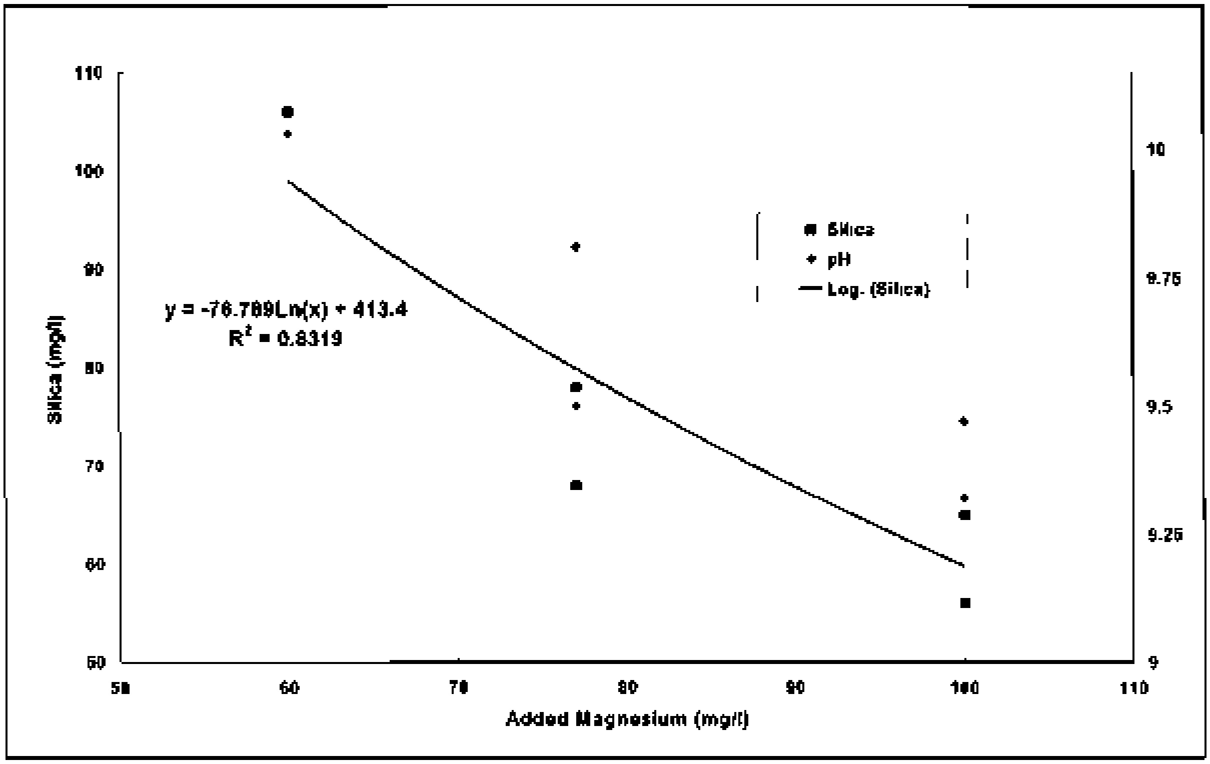


Figure 7-1. Warm Softening Effluent Silica and pH Levels at 500 mg/l Caustic as a Function of Varying Magnesium Concentrations

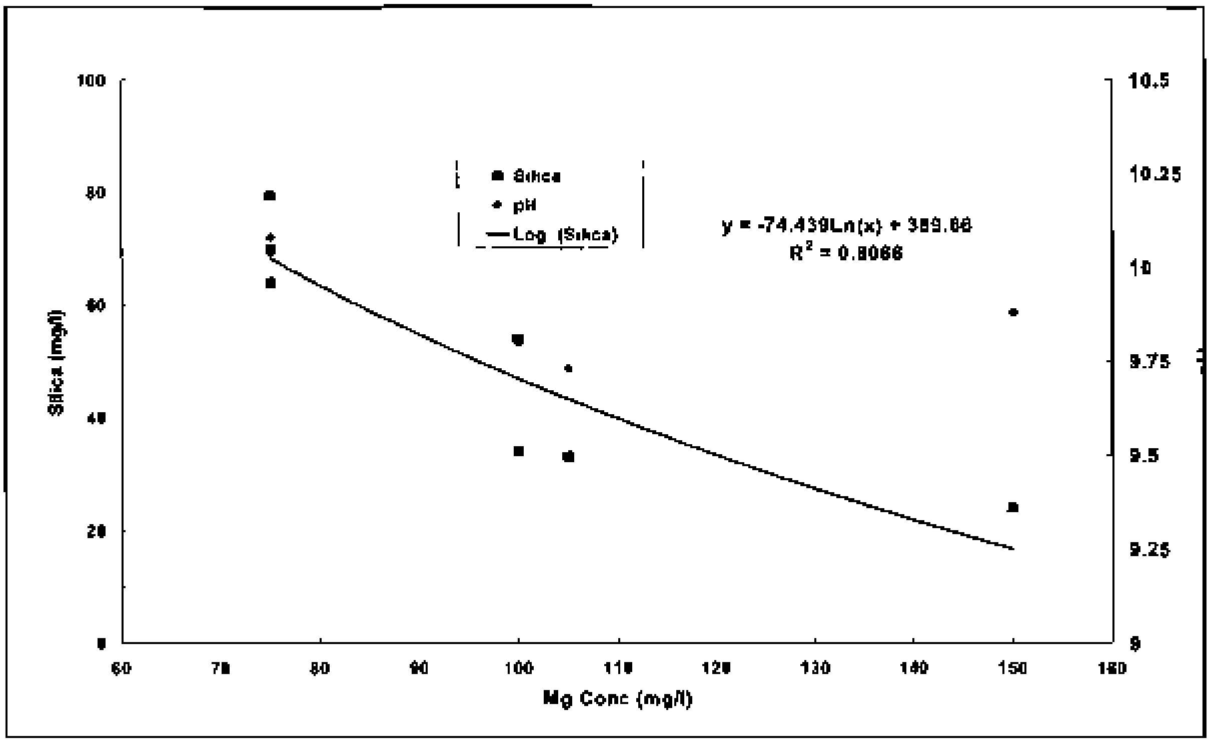


Figure 7-2. Warm Softening Effluent Silica and pH Levels at 600 mg/l Caustic as a Function of Varying Magnesium Concentrations

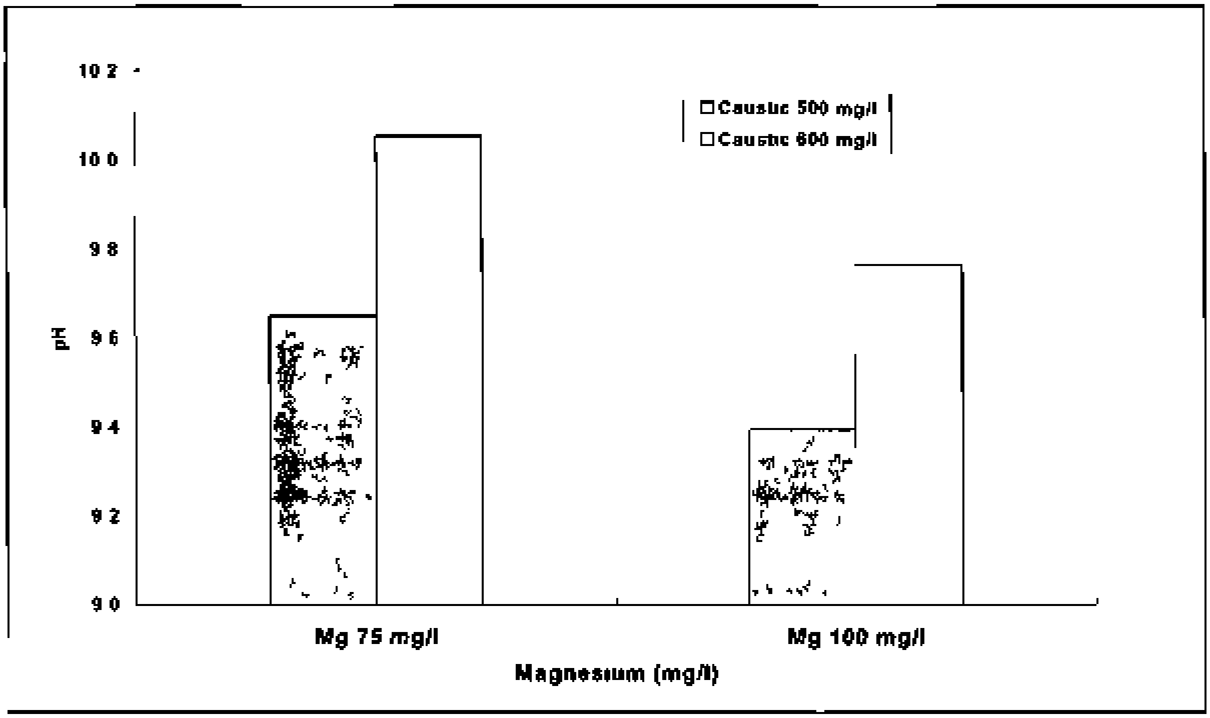


Figure 7-3. Effluent pH at Two Caustic and Two Magnesium Feed Rates

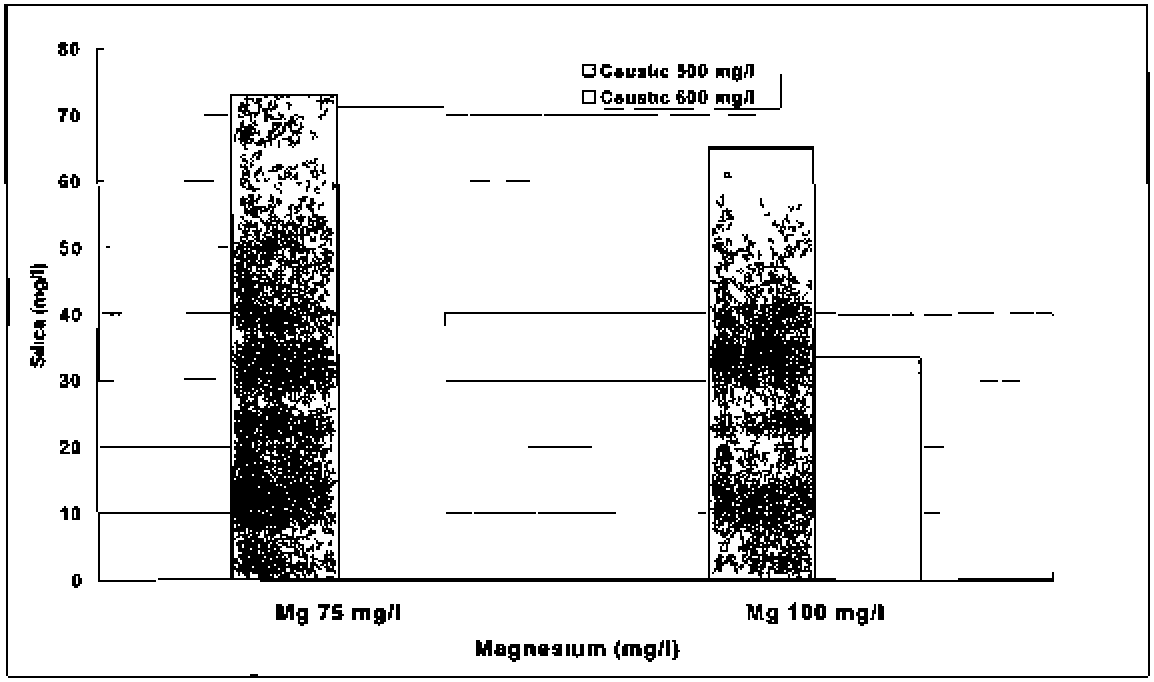


Figure 7-4. Effluent Silica at Two Caustic and Two Magnesium Feed Rates

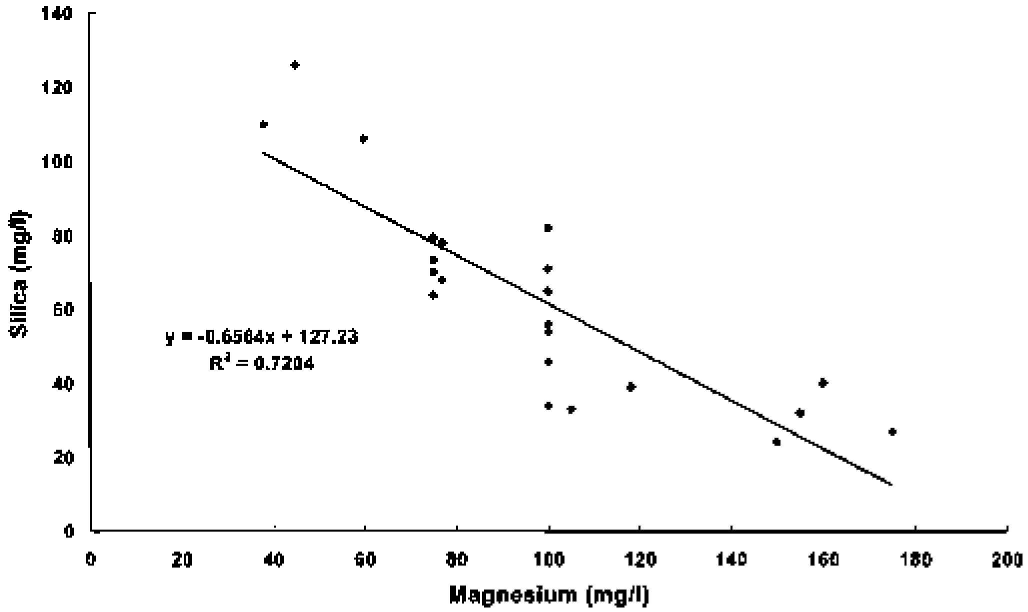


Figure 7-5. Effluent Silica Concentrations as a Function Magnesium Dosing Concentrations

Figure 7-5 further illustrates the relationship between magnesium dosing and effluent silica levels during treatment of San Ardo produced water. In general, an increase in magnesium concentration resulted in a decrease in effluent silica level. The silica goal of 60 mg/l was achieved at magnesium dose of 100 mg/l or higher. However, a wide range of silica concentration for a given magnesium dosing (e.g. 100 mg/l) indicated the role of other parameters (pH, caustic dosing) in silica removal efficiency.

Figure 7-6 shows the relationship between the pH and effluent silica levels. Unlike all the earlier data that represent the silica levels of Claricone™ effluent samples, Figure 7.6 shows silica levels in the settled water from the 20,000 gallon settling tank downstream of the Claricone™ unit. In general, the silica levels in the softened water increased with an increase in pH. Mujeriego, et al., (1976) reported that maximum silica precipitation by magnesium addition occurs at the pH corresponding to the average pKa values for the first and second dissociation constants (pK_1 and pK_2) of orthosilicic acid. The $pK_{1\&2}$ values vary with water temperature during precipitation. In the current pilot study, the average temperature of the softened water in the settling tank was about 140 °F. At this temperature, the pH optimum ($(pK_1+pK_2)/2$) for silica removal is calculated to be 9.8. Above this calculated pH, silica levels increased as predicted.

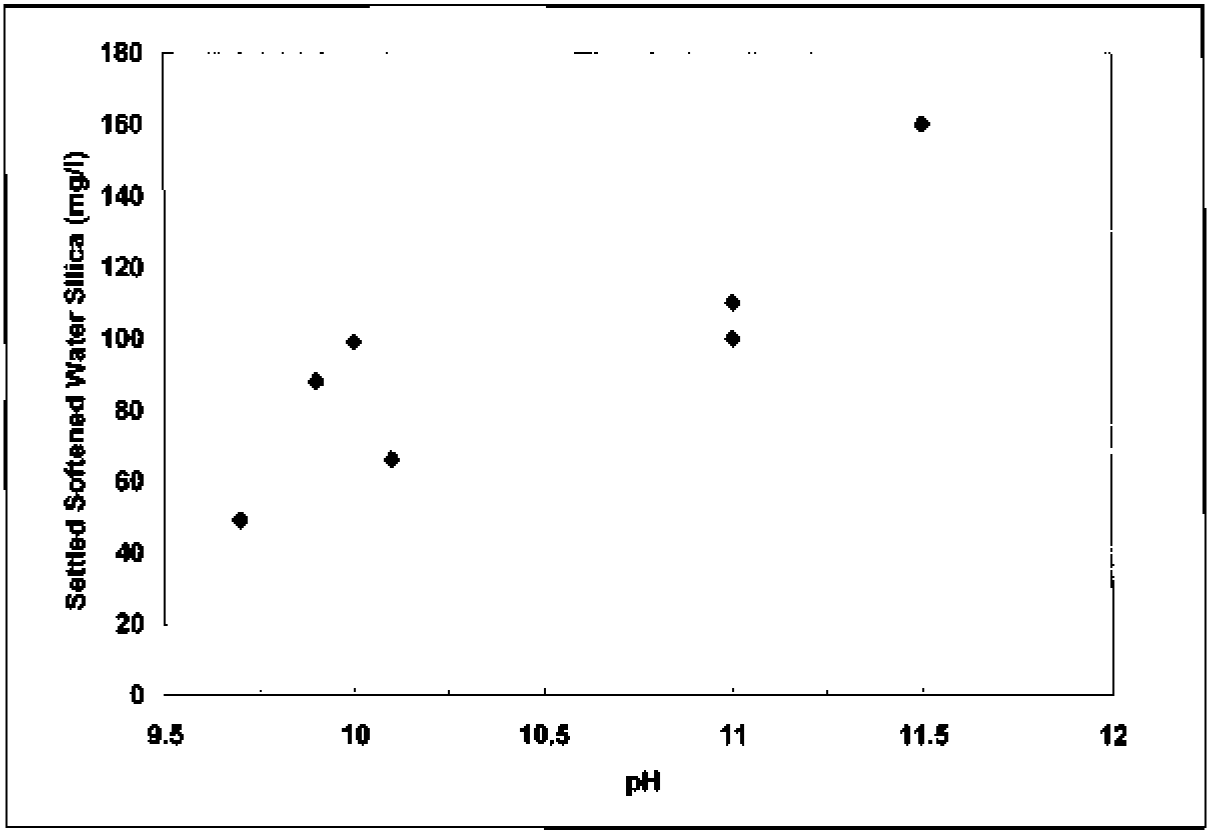


Figure 7-6. Silica Levels in Softened Settled Water at Various pH Levels

7.1.2 Hardness Removal

The warm softening process effluent hardness concentration is a function of caustic, magnesium dose and the resulting pH. Select samples were analyzed during the pilot study to verify hardness levels achieved in the bench scale evaluations.

Figure 7-7 shows the effluent hardness as a function of pH. The residual hardness of the clarifier effluent was below 10 mg/l when the effluent pH was between 9.3 and 10.5. Effluent pH was less than 9.3 (pKa of carbonate) at low caustic (<400 mg/l) or at high magnesium dosing rates (> 125 mg/l). The residual hardness was higher than the hardness goal (10 mg/l as $CaCO_3$) under these conditions. Also, effluent pH higher than 10.5 occurred at high caustic (e.g. 700 – 800 mg/l) and low magnesium (0 – 70 mg/l) dosing rates. The effluent hardness was higher than the treatment goal under these conditions, probably due to ineffective silica removal at the low magnesium dosing (Figure 7-6). A high residual hardness level (26 mg/l as $CaCO_3$) was observed in one sample at pH 9.6. It was later observed that the magnesium pump was clogged that day and hence, little or no magnesium was delivered to the clarifier.

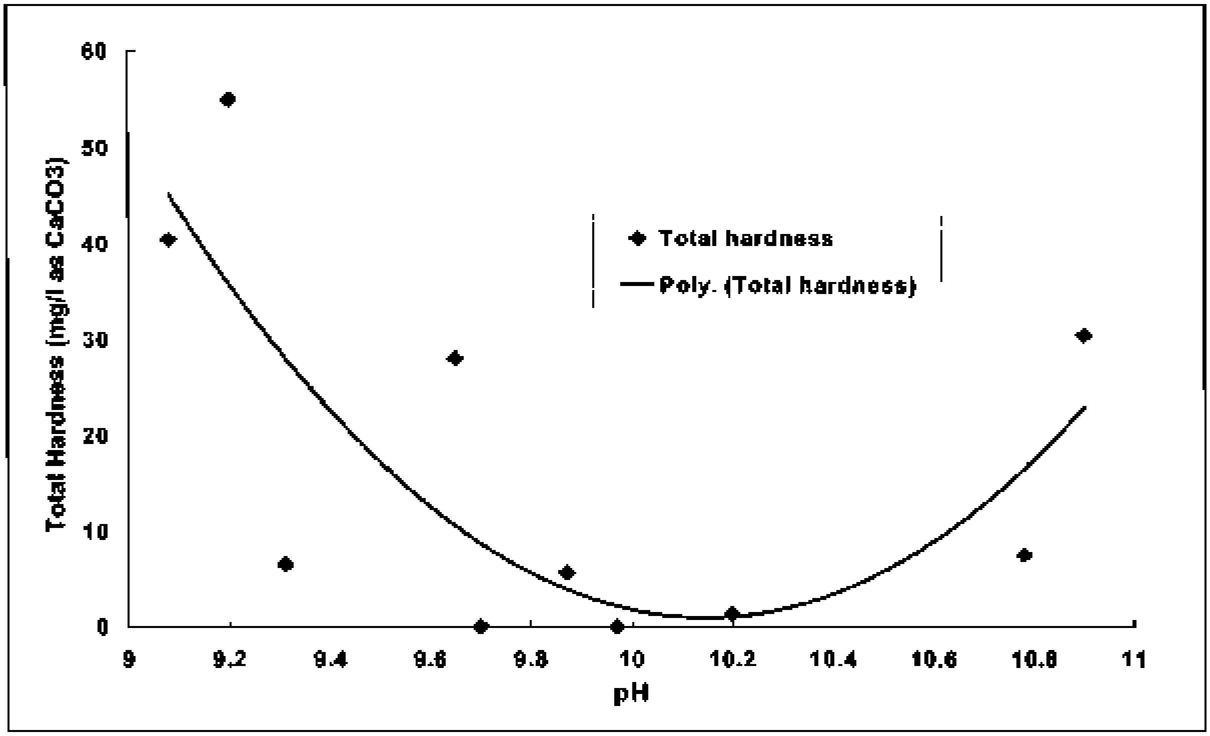


Figure 7-7. Clarifier Effluent Hardness Concentrations as a Function of Treated Water pH

7.1.3 Warm Softening Sludge

Warm softening sludge samples were analyzed for elemental and mineral composition by spectral analyses. Furthermore, a California Assessment Manual (CAM) metals composition of the samples was also analyzed to evaluate potential California hazardous characteristics of the sludge. Analysis of the solids indicated that the sludge primarily consisted of calcium carbonate, magnesium hydroxide, and magnesium silicate (Tables 7-2 and 7-3). Sodium and boron levels in the sludge were high, which may restrict the beneficial use of the sludge as a soil amendment.

Table 7.2 Elemental Composition of Warm Softening Sludge

Parameter (mg/l)	*Sample #1 (% weight)*	*Sample#2 (% weight)*
Calcium	4.1	3.5
Magnesium	6.4	4.95
Sodium	7.8	8.3
Potassium	0.11	0.11
Boron	9.9	12
Silica	3	2.6
Iron	0.2	0.06
Bromide	0.04	0.035
Strontium	0.1	0.08
Carbonate	60	60
Chlorine	7.8	7.7
Sulfur	0.12	0.09

Table 7.3: Chemical Composition of Warm Softening Sludge

Parameter (mg/L)	*Sample #1 (% weight)*	*Sample#2 (% weight)*
CaO	16.05	16.04
Na_2O	3.27	6.63
MgO	15.24	12.9
Al_2O_3	0.17	0.18
SiO_2	19	20.42
P_2O_6	0.006	0.009
K_2O	<0.04	0.06
TiO_2	0.006	0.009
MnO_2	0.015	0.012
Fe_2O	0.46	0.35
SrO	0.31	0.31
SO_3	0.49	0.46
Loss in ignition	50.81	47.65

7.1.3.1 Hazardous Waste Determination

Analyses of the sludge indicated that it would not be considered a hazardous waste. Table 7-4 is a comparison of the threshold concentration and the concentration found in one sample of the warm softening sludge and provides information that makes the sludge a non-hazardous waste. All of the CAM metals, except barium, were below the methods detection limit in the sludge samples tested. Barium levels in the samples were also significantly below the regulatory level for the TTLC test. These data indicate that the sludge generated from the warm softening process during the pilot study is not hazardous. Similar results were obtained during analyses of warm softening sludge in the DOE Placerita Canyon pilot study (Doran, 1998).

Table 7.4: Summary of Sludge and Hazardous Waste Criteria

Substance	**San Ardo Sludge**		**California Hazardous Waste Criteria**
	Wet Weight (mg/Kg)	***Dry Weight mg/Kg***	***Total Threshold Limit Conc. TTLC (mg/Kg)***
Antimony and/or antimony compounds	<5	<5	500
Arsenic and/or arsenic compounds	<1	<1	500
Barium and/or barium compounds (excluding barite)	7.7	295	10,000
Beryllium and/or beryllium compounds	<0.5	<0.5	75
Cadmium and/or cadmium compounds	<1	<1	100
Chromium and/or Chromium (III) compounds	<1	<1	2,500
Cobalt and/or cobalt compounds	<1	<1	8,000
Copper and/or copper compounds	<0.5	<0.5	2,500
Lead and/or lead compounds	<1	<1	1,000
Mercury and/or mercury compounds	<0.1	<0.1	20
Molybdenum and/or molybdenum compounds	<1	<1	3,500
Nickel and/or nickel compounds	<1	<1	2,000
Selenium and/or selenium compounds	<5	<5	100
Silver and/or silver compounds	<1	<1	500
Thallium and/or thallium compounds	<5	<5	700
Vanadium and/or vanadium compounds	<1	<1	2,400
Zinc and/or zinc compounds	<1	<1	5,000

7.2 Cooling Tower Operation

The high pH and high air to water ratios used in the pilot trials were expected to remove ammonia by air stripping. During the pilot study, due to some concerns with solids carryover, the warm softening effluent was settled in an equalization tank prior to cooling tower operations. As a result, the influent water temperatures to the cooling tower were lower (58–105 °F) than the designed inlet temperature (~150 °F). Table 7-5 summarizes the operating conditions and results from the cooling tower studies. Approximately 63 and 44 % of ammonia were removed in the cooling tower at influent pH of 10.8 (104.6 °F) and 10.3 (58 °F), respectively.

Table 7.5: Cooling Tower Operation and Results

Parameter	Units	Operating Condition 1	Operating Condition 2
Water flow rate	gpm	15	15
Air flow rate	cfm	23,100	23,100
Air: Water ratio	vol: vol	11,600:1	11,600:1
Influent water temperature	°F	58.0	104.6
Effluent water temperature	°F	53.4	65.6
Average temperature reduction	°F	4.2	39.0
Average air temperature (wet bulb)	°F	42.9	45.2
Influent Ph	Std units	10.3	10.8
Influent ammonia-N	mg/l	12	17
Effluent ammonia-N	mg/l	6.6	6.3
Ammonia-N removal	%	44	64

7.3 Reverse Osmosis

7.3.1 Pilot Studies Using Brackish Water RO Membrane

Most of the pilot evaluations were performed using the Koch Membrane System (KMS) RO unit fitted with the conventional brackish water membrane (Fluid Systems) at pH 9.5 to 11 to remove TDS, boron, TOC, silica and ammonia from the softened, cooled San Ardo produced water. Because of high turbidities of the unsettled Claricone™ softened water, water from the holding tanks was used as feed water for the RO studies.

7.3.1.1 TDS Removal

RO is the main unit process that addresses TDS removal from San Ardo produced water. Chemical addition in the warm softening process increased the TDS of the produced water slightly. A TDS goal of 400 mg/l was set for the RO process. The TDS removal in the RO unit at various pH is shown in Figure 7-8.

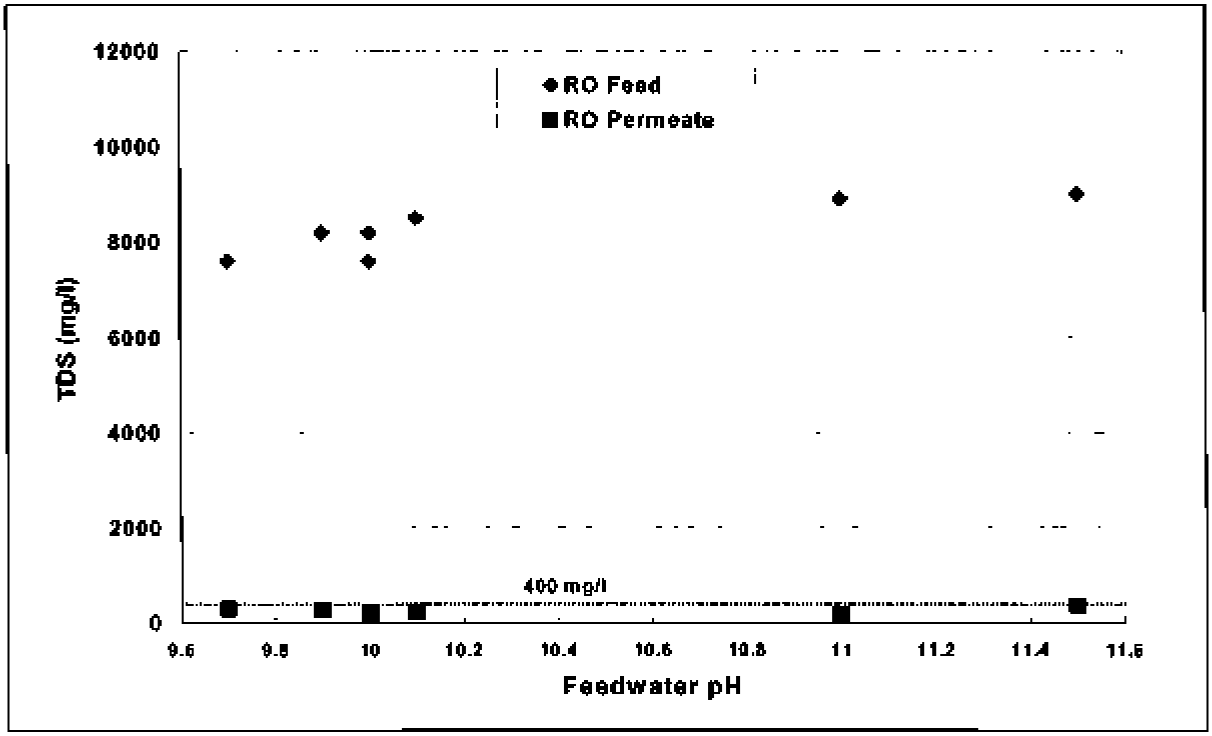


Figure 7-8. TDS Levels in RO Influent and Permeate at Various pH Levels

The TDS of the RO feed water varied from 7,500 to 9,000 mg/l (Figure 6). The average TDS of the permeate was 215 mg/L. The pH of the RO feed did not significantly impact the permeate TDS. Post treatment operations such as stabilization of permeate for corrosion control, calcium addition for Sodium Absorption Ratio (SAR) compliance and final disinfection, if needed, will slightly increase the treated water TDS prior to its intended end use. The validity of the measured TDS and various dissolved ion concentrations were verified by ion balance evaluation. Table 7-6 shows the average concentrations of various ions measured in the RO effluent.

Table 7.6: Summary of Average Cation, Anions, and Other Parameters of Interest in RO Effluent

Cations	*Average (mg/L)*	*Anions*	*Average (mg/L)*	*Other Parameters of Interest*	*Average (mg/L)*
Na	90	Alkalinity*	106	TOC	<1
K	1.2	Cl	82	SiO_2	0.76
Ca	0	BO_3 (B^{+5})	13.98		
Mg	0				
TDS by Addition	91.2		152		0.76

*Alkalinity is as $CaCO_3$

The major cation in the permeate was sodium, and the major anions were chloride, bicarbonate, and boron. Ammonia nitrogen concentration (4.8-13 mg/l) was not included in the evaluation, since ammonia tends to evaporate when performing a TDS measurement. The alkalinity for TDS balance estimates was adjusted by assuming that ~50% of the BO_3

titrates as alkalinity. The estimated TDS by addition using these adjustments is 211.66 mg/L which is within 10 percent of the average gravimetric TDS (215 mg/l), indicating very good closure.

The milliequivalents (meq) thus calculated for the cation and anion are 3.95 meq/L and 3.73 meq/L, respectively which are close to acceptable limits according to Standard Methods (1992). The TDS by addition and the meq/L balance are quality assurance checks on reported average values. Both of these checks indicate that these estimates are consistent.

7.3.1.2 Boron Removal

Figure 7-9 summarizes the removal of boron by the RO processes. An increase in the feed water pH decreased the boron concentration in the permeate. The influent boron levels varied from 20 to 25 mg/l during the pilot study. The boron goal of <1 mg/l in the permeate was not achieved when the pH of the RO feed was 10.2 or lower. This trend, in general, is consistent with the speciation chemistry of boron. In the pH range at which the pilot was operated, an increase in pH increases the fraction of the ionic boron species ($B(OH)_4^-$) which is amenable for removal by the brackish water RO membrane.

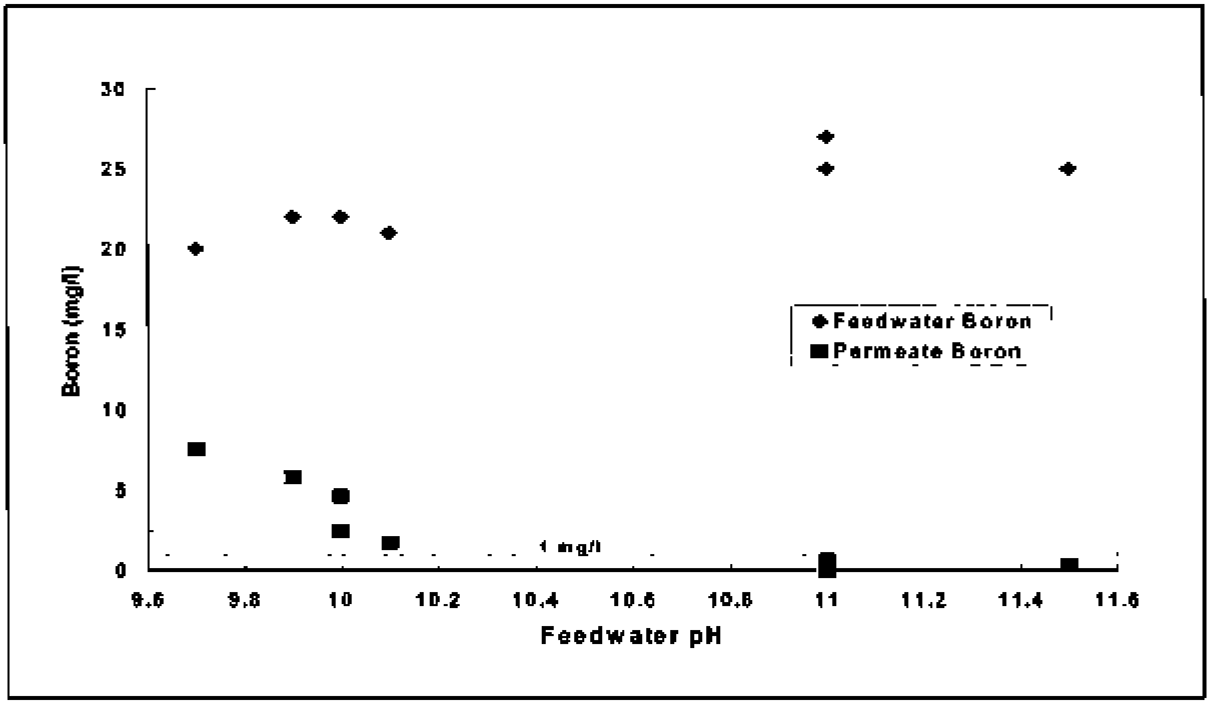


Figure 7-9. Boron Levels in RO Influent and Permeate at Various Influent pH Conditions

7.3.1.3 Ammonia Removal

Figures 7-10 and 7-11 provide a summary of ammonia levels during the pilot treatment process.

The influent ammonia concentration to the RO varied from 6 to 13 mg/l ammonia as N. Approximately 10 to 15% of the ammonia was removed by the membranes at pH 9.6 to 10.2. No ammonia was removed at pH 11 by the RO process. These trends are consistent with ammonia speciation chemistry. At pH above 9.2, at which the pilot was operated, a significant fraction of the ammonia remains in the unionized NH_3 form which is not conducive for removal by a RO process. At pH 9.5 to 10, only about 20% of ammonia remains in the ionized NH_4^+ form which is amenable for removal by RO. As the pH increases to near 11, less than 10 percent of the ammonia is ionized.

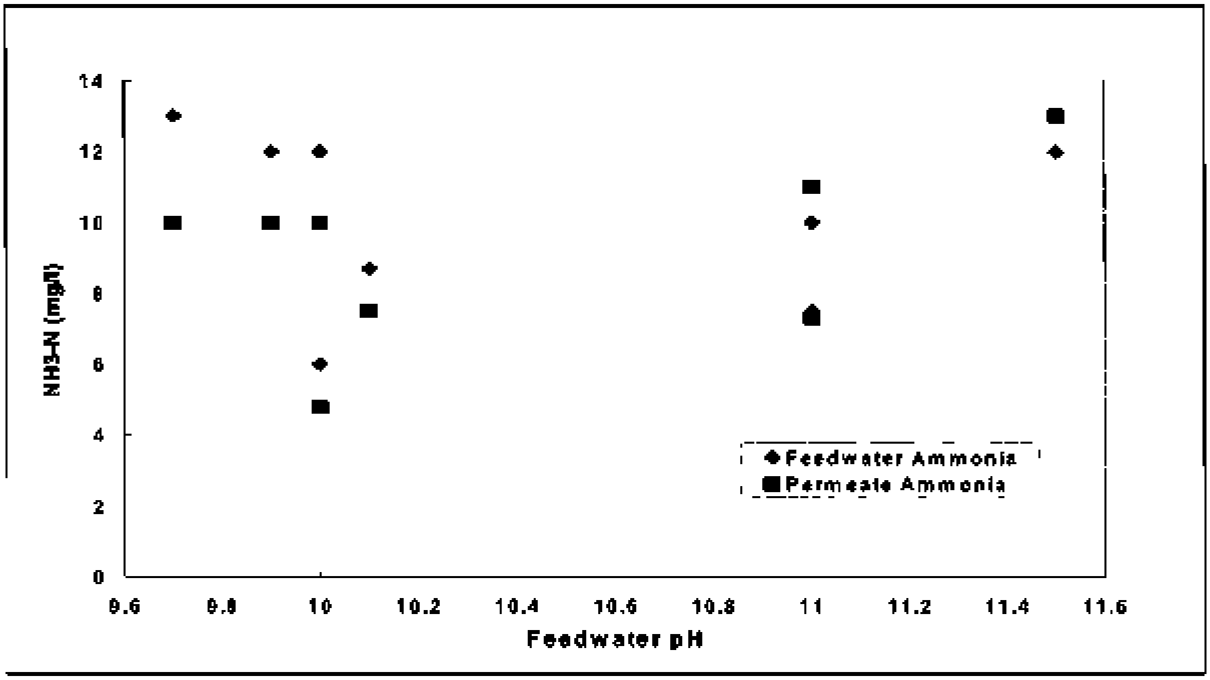
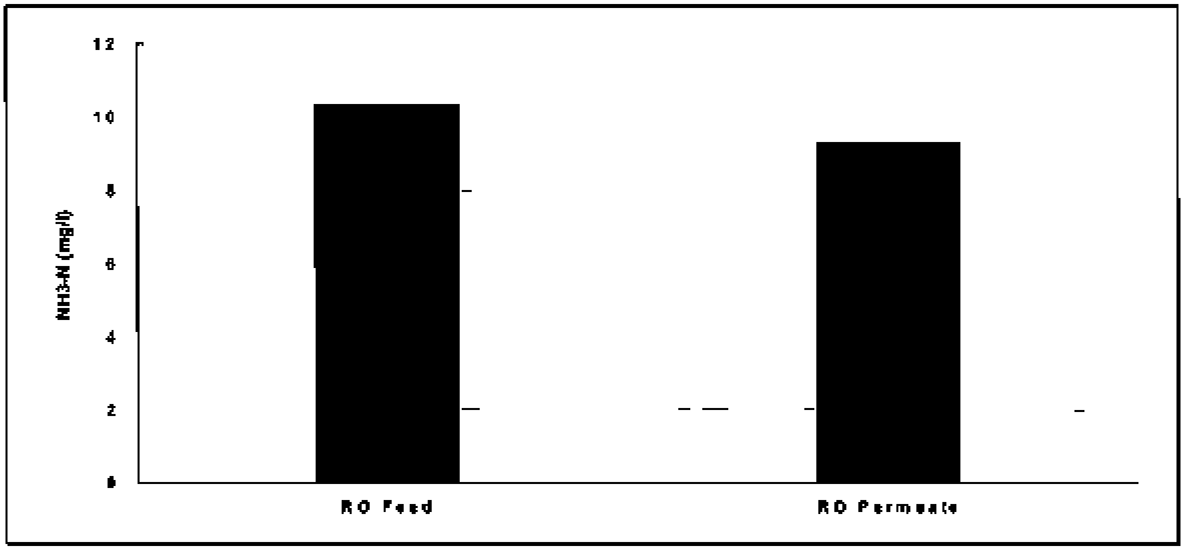


Figure 7-10. Ammonia Levels in RO Influent and Permeate at Various Influent pH Conditions



7.3.1.4 Removal of Organic Compounds

Organic removal in the RO process was evaluated by TOC levels in the feed, permeate and concentrate streams. Figure 7-12 shows the TOC levels in RO influent and permeate. The TOC of the RO feed water varied from 60 to 80 mg/l throughout the pilot study. The permeate TOC was below the detection limit (3 or 1 mg/l) in all samples. The TOC levels in concentrate varied from 200 to 290 mg/l. Mass balance indicated that the estimated mass of TOC in the concentrate varied from 90 to 130% of the feed water. This suggested that most of the organic compounds from the feed water remained in the concentrate stream rather than fouling the membrane

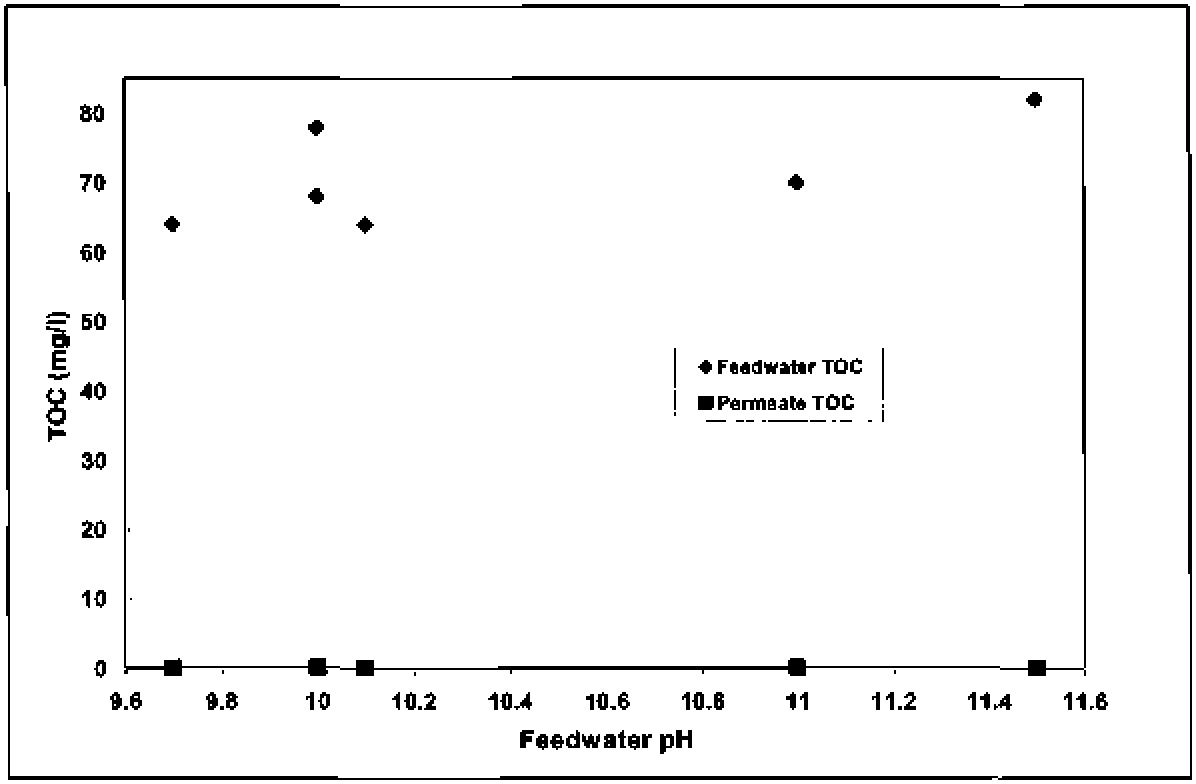


Figure 7-12. TOC Levels in RO Influent and Permeate at Various Influent pH Conditions

7.3.1.5 Silica Removal in RO Treatment

Figure 7-13 shows silica levels in the RO feed and permeate streams during the pilot treatment process. In general, the influent silica level (from the settling tank) increased with an increase in the pH. The silica levels in RO permeate varied from 0.4 to 1.4 mg/l, with the levels <1 in most cases. Influent water pH did not significantly impact the treated water silica levels. Mass balance indicated that the estimated mass of silica in the concentrate varied from 80 to 115% of the feed water. This suggested that most of the silica from the feed water remained in the concentrate stream during the pilot study.

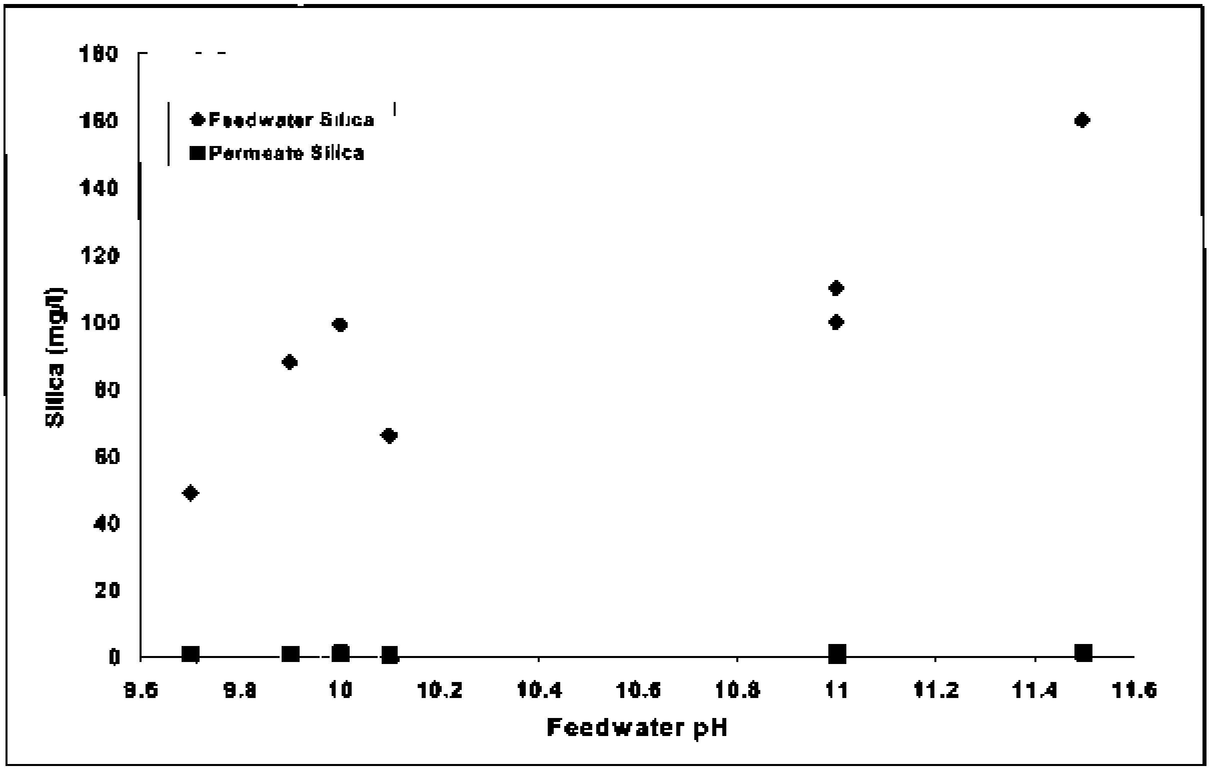


Figure 7-13. Silica Levels in RO Influent and Permeate at Various Influent pH Conditions

7.3.1.6 THM Formation Potential of RO Permeate

Using the RO permeate, this test was performed to evaluate the potential for formation of carcinogenic trihalomethane compounds upon chlorination for disinfection. Approximately 5 mg/l of chlorine in excess of that required to achieve break point chlorination of the permeate was added and allowed to react for about 7 days. The bench scale test for breakpoint chlorination indicated that approximately 7.5 parts of chlorine is required to remove each part of ammonia-N in the RO permeate. The RO permeate used in this study had an ammonia concentration of about 12 mg/l. Hence, approximately 95 mg/l of chlorine was added to the sample. After seven days the samples were analyzed for various trihalomethane constituents. Table 7-7 shows the results from this study.

Table 7.7: Concentration of THM Constituents in RO Permeate

Constituent	Conc. in Chlorine Treated Permeate (µg/l)
Bromodichloromethane	7.5
Bromoform	14
Chloroform	2
Dibromochloromethane	16
Total THM	40

Bromoform and dibromochloroethane were the predominant THM constituents in the sample analyzed. The total THMFP of 40 µg/l was significantly lower than the EPA MCL of 80 µg/l for drinking water supplies. This suggested that the RO treated San Ardo produced water is not likely to exceed the THM MCLs.

7.3.1.7 RO Concentrate

The concentrate stream was approximately 33 percent of the treated flow. Table 7.8 presents the major anions and cations for the reject stream. The estimated TDS by addition of these constituents is 26,893 mg/l, which is within 2. 7 percent of the measured average gravimetric TDS (27,666 mg/l) . Assuming the alkalinity is as carbonate/borate as previously described, the milliequivalents (meq) for the anions and cation are 513 meq/L and 406 meq/L, respectively. The average TDS of 27,666 mg/L is approximately four times the TDS of currently injected produced water. However, when comparing the measured dissolved ions in the RO concentrate with the produced water currently injected at the San Ardo field, the only potential problem that can be identified is the high pH. The pH of the concentrate can be appropriately adjusted by acid or carbon dioxide addition, prior to disposal by deep well injection.

Table 7.8: Summary of Average Cation, Anions, and Other Parameters of Interest in RO Concentrate

Cations	Average (mg/l)	Anions	Average (mg/l)	Other Parameters of Interest	Average (mg/l)
Sodium	11,700	Alkalinity*	2,550	TOC	254
Potassium	210	Chloride	12,700	SiO_2	269
Calcium	0	Bromate (B^{5+})	425		
Magnesium	4				
TDS by Addition	11,914		14,451		528

* - Alkalinity as mg/l $CaCO_3$

7.3.1.8 Membrane Fouling Evaluations

The O&M cost for RO treatment can be significant due to membrane replacement required because of scaling or fouling by produced water constituents. Hence, during this pilot study, the following were performed to characterize the impact of organic and inorganics on the RO membrane:

- Evaluation of transmembrane pressure recovery of the membrane during low and high pH CIP
- Analyses of low and high pH CIP cleaning solutions before and after membrane CIP

Transmembrane Pressure (TMP) Evaluation during CIP Process

A typical RO CIP is a two step process consisting of i) cleaning with an acidic solution designed to remove inorganic scalents (e.g. Ca, Mg, SiO2), followed by ii) cleaning with an alkaline solution designed to remove organic foulants. In this study the impact of organics and inorganics on the membrane was evaluated by operating the RO unit under normal conditions after each step of the cleaning process and measuring the pressure recovery obtained.

Table 7-9 shows the feed pressure required for produced water treatment before, during and after the CIP process. The pressure required to obtain the design yield (67.5%) using a virgin membrane was – 379.5 psi. After about 100 hours of operation, due to an increase in pressure drop across the membrane, the permeate yield reduced to 40%. The corresponding feed pressure was 283 psi. Membrane cleaning using an acidic solution (KOCHKLEEN 100, KMS) was performed at this time to remove inorganic scalents. Subsequently, the membranes were rinsed with clean water and allowed to relax for about two hours (Section 6.3.4). The RO was then operated to treat the produced water (warm softener effluent from equalization tank). The feed pressure required for operation decreased to 222.5 psi. This suggested that a significant fraction of the pressure drop across the membrane was caused by scaling of inorganic materials. The membranes were then cleaned using alkaline solution to remove organic foulants. The feed pressure required for 40% yield, however, did not change significantly after cleaning with the alkaline solution. Approximately 228 psi was still required for operation. This suggested that only a small amount of organic compounds fouled the membrane during treatment of oilfield produced water.

Following the low and high pH cleaning procedure, the pilot RO unit was restored to operating at ~65% yield, similar to that established at the start of the initial test run. Upon restoring these operating conditions, the TMP required to maintain the original yield was higher than the average TMP observed during the initial 20 hours of the test run (Table 7-9). This suggested that some permanent fouling of membrane may have occurred during the produced water treatment.

Table 7.9: RO Transmembrane Pressure Before, During and After CIP

Operation Phase	*Feed Flow (GPM)*	*Yield (%)*	*Transmembrane Pressure (psi)*
Start of Test Run	7.5	67.5	379.5
Operation Prior to CIP	7.6	40.8	283
After Low pH CIP	7.5	40	222.5
After High pH CIP	7.5	40	228
At Design Yield After CIP	5.8	65.5	387

Analyses of CIP solutions

In addition to evaluation of operating feed pressure, acidic and alkaline CIP solutions were collected before and after the cleaning process, and analyzed for inorganic and organic constituents. Table 7-10 shows the concentrations of inorganic (Ca, Mg and SiO_2) and organic (TOC) constituents in the acidic and alkaline cleaning solutions. Calcium, magnesium, silica and hardness level in the acidic solution increased significantly after membrane cleaning. However, the TOC of the alkaline solution did not increase after cleaning; indicating that organic constituents did not significantly foul the membrane during treatment or that the high pH was ineffective in removing membrane bound organics. These findings further supported the previous observation that the majority of the pressure drop across the membrane was due to inorganic scaling.

Table 7.10: Inorganic and Organic Constituents in San Ardo Produced Water Fouling the Brackish Water RO Membrane

Parameter	*Before Cleaning*	*After Cleaning*	*Estimated Conc. from RO Feed*
Low pH Solution			
Calcium (mg/l)	81	110	0.03
Magnesium (mg/l)	33	240	0.24
Silica (mg/l)	53	200	0.17
Hardness (mg/l as $CaCO_3$)	340	1,300	1.13
High pH Solution			
TOC (mg/l)	160	94	-

7.3.1.9 Specific Flux Evaluation

Specific flux is a standard measure of the performance of an RO process and is defined as the membrane flux (permeate flow per square foot of membrane area per day, or gfd) generated per unit net driving pressure (psi) normalized to a reference temperature of 25°C. Once established over the course of an operation condition, the specific flux can provide the following information necessary for the development a full-scale system design:

- Estimation of allowable operating run length based on decline in specific flux over time, which determines membrane cleaning frequency.

- Projection of electrical power usage based on the pressure needed to achieve a given flux and, in turn, the net permeate flow rate for a full-scale process.

The specific flux of the pilot RO unit for the initial test run using the brackish water membranes is shown in Table 7-11, along with average operating conditions for the test run. The average recovery achieved for the test was approximately 67% which yielded an average specific flux of 0.035 gfd/psi. Figure 7-14 shows the specific flux decline through the course of the test run. The data show a high degree of variability in the specific flux ($R^2 = 0.01734$ for best fit line), which is likely due to inconsistent performance of the upstream warm softening process. Based on the exponential best fit curve derived from these data, the estimated allowable run time between membrane cleanings, using the 15% specific flux decline criteria, is 89.6 hours. Increasing the specific flux decline criteria to 25% extends the estimated allowable run time between cleanings to 155.5 hours.

Table 7.11: Summary of Average Operation Conditions During RO Operation Using Brackish Water (Fluid Systems) Membrane

Parameter	*Value*
Membrane Manufacturer	Koch Membrane Systems (KMS)
Model Number	4820XR
No. Elements	12
Total Membrane Area (SF)	936
Array Configuration	2 x 0
Aggregate Run Time (hr)	100.9
Feedwater Flow Rate (gpm)	7.0
Permeate Flow Rate (gpm)	4.5
Concentrate Flow Rate (gpm)	2.5
Recovery (%)	64.5
Feedwater Temperature (°C)	16.9
Temperature Normalized Flux (gfd)	9.3
Trans-Membrane Pressure (TMP, psi)	380.9
Osmotic Pressure (psi)	115.6
Net Driving Pressure (psi)	265.3
Specific Flux (gfd/psi)	0.0352

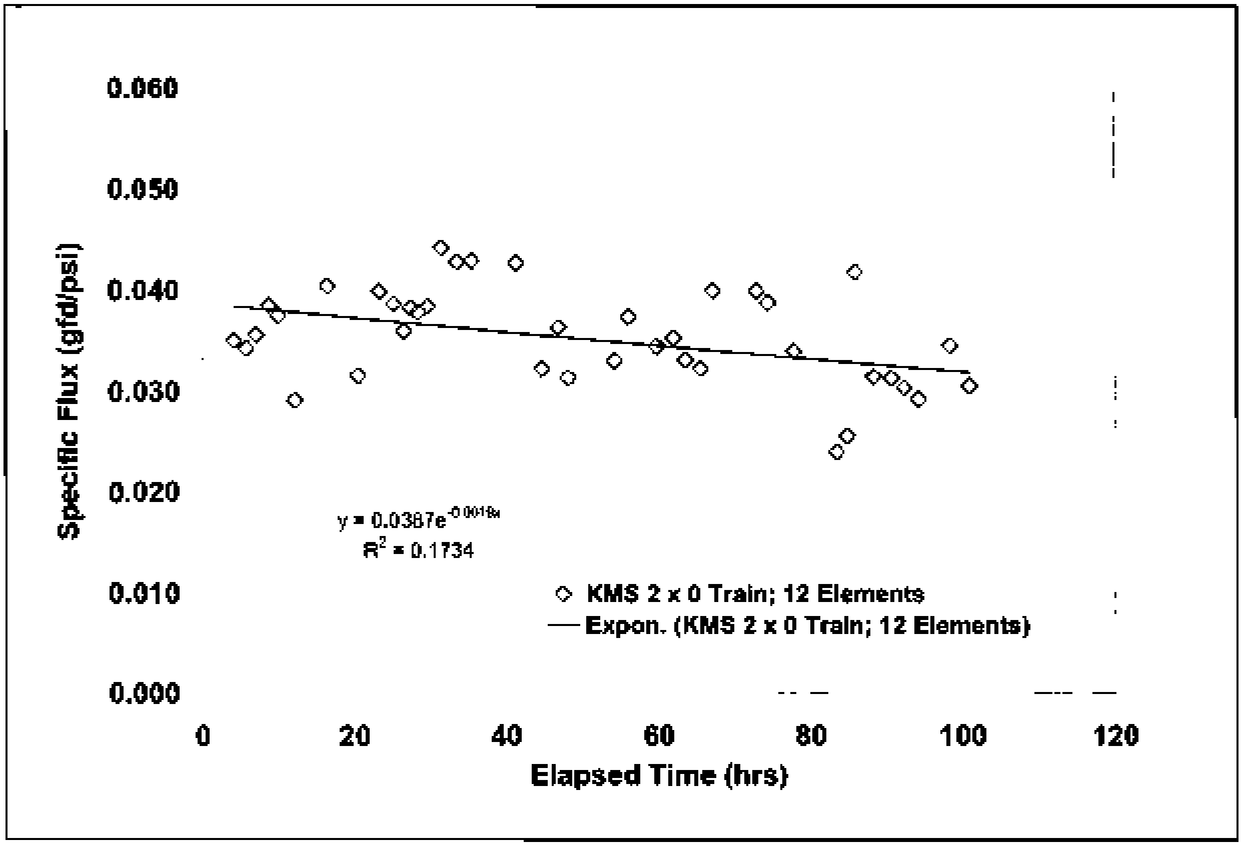


Figure 7-14. Specific Flux of Brackish Water (Fluid Systems) Membrane

7.3.2 Energy Usage Evaluations

The energy required for RO treatment was estimated assuming a single pass array configuration and a design flux of 10 gfd. This design flux is consistent with the findings of the pilot test (9.3 average gfd) and typical design fluxes recommended by the membrane manufacturer. The net driving pressure thus estimated for RO treatment is 284 psi. However, this does not include the additional power required to overcome osmotic pressure across the membrane. Osmotic pressure is a function of the water temperature and the logarithmic average of feed and concentrate stream TDS. Based on a correlation developed by Dow-Filmtec (2006) osmotic pressure required for treatment of San Ardo produced water is about 122.7 psi. Hence, the estimated trans-membrane pressure requirement for RO treatment is about 407 psi. Assuming a pumping efficiency of 67.5% (90% motor efficiency; 75% pump head efficiency) resulted in an estimated power requirement of 1,025 HP or 765 kW. Further, assuming that the system was online 90% of the time, an estimated 6.37 million kW-hr per year of electrical power would be required. The summary of projected operating conditions for a full-scale system using brackish water RO membrane elements and the projected electrical power usage for such a system is indicated in Table 7-12. This estimate, however, does not include energy required for the conveyance of untreated produced water to the system and the transfer of permeate to storage or end-use..

Table 7.12: Projected Energy Use for Systems with Brackish Water RO Membrane Elements

Parameter	Value
Membrane Type	Brackish Water RO
Feedwater Flow Rate (bbl/day)	100,000
Recovery (%)	70%
Feedwater pH	10.5
Feedwater TDS (mg/l)	7,000
Feedwater Temperature (°C)	25
Target Membrane Flux (gfd)	10.0
Average Specific Flux from Data (gfd/psi)	0.0352
Net Driving Pressure (psi)	284.1
Estimated Osmotic Pressure (psi)	122.7
Estimated Required TMP (psi)	406.8
Base Pumping Power Required (HP)	692.1
Average Efficiency for System Pumps	67.5%
Estimated Pumping Power Required (HP)	1,025
Estimated Electrical Energy Required for Pumping (kW)	765
Estimated Annual Energy Use (kW-hr)	6,365,540

7.3.3 Comparison of Brackish Water and Boron Rejection Membrane Performance

The conventional brackish water membrane (Fluidsystems) effectively removed all of the water quality constituents of concern (e.g. TDS, TOC, SiO_2), except boron (and ammonia) at a pH of about 9.5. The pH has to be elevated to above 10.5 to facilitate boron removal.

Recently, a special boron rejection seawater membrane has been developed (SWC4 by Hydranautics) to remove boron more effectively than conventional membranes at all pH levels. To date, most the performance of this membrane has been evaluated for desalination of seawater containing about 5 to 8 mg/l of boron. The estimated boron rejection using this membrane from a water containing 32,000 mg/l TDS and 5 mg/l boron is about 92, 98 and 99% at pH 7, 9.5 and 10.5, respectively (Hydranautics, 2005). However, these membranes have not been evaluated for treatment of brackish waters such as San Ardo produced waters containing higher levels of boron (20 – 25 mg/l).

The performance of this boron rejection membrane at pH of about 9.5 was evaluated. Effective boron rejection at this pH can significantly reduce the cost of chemical addition and other operational issues related to operating the RO at pH 10.5 (or higher) using conventional brackish water membrane systems. The pilot was operated in a 1X0 mode using three four-inch diameter elements. Furthermore, a 1X0 array consisting of three brackish water membrane elements were also operated to obtain a side-by-side performance comparison .

Table 7-13 shows the specifications of the boron rejection membrane and Table 7-14 shows the operating conditions for the study. In summary, each of the membrane systems was operated in parallel for approximately 50 hours. The influent pH was about 9.5. The feed and permeate flow rate were approximately 2.5 and 1.5 gpm (~60% yield). Feed, permeate and concentrate samples were collected and analyzed periodically.

Table 7.13: Specifications of the Boron Rejection Membrane (SWC4)

Parameter	Data
Configuration	Spiral Wound
Membrane Polymer	Composite Polyamide
Nominal Membrane Area	85 ft^2
Maximum Applied Pressure	1000 psi (4") & 1,200 psi (8")
Maximum Feedflow	16 gpm (4"), 75 gpm (8")
Maximum Operating Temp	113 °F
Maximum Feedwater SDI (15 min)	5
Maximum Pressure Drop for Each Element	10 psi

Table 7.14: RO Operation Conditions for the Brackish Water and the Boron Rejection Membranes Evaluation

Parameter	Brackish Water Membrane	Boron Rejection Membrane
Feed water Flow (gpm)	2.65	2.4
Permeate Flow (gpm)	1.65	1.7
Recovery (%)	63	70
Feed Pressure (psi)	460	460
pH	9.5	9.5

Table 7-15 shows the TDS, boron, ammonia; TOC and silica levels in the brackish water and boron rejection membrane permeate. Results indicated that both the membrane systems were able to meet the TDS, silica and TOC goals under operational conditions. The TDS and boron of the boron rejection membrane permeate were significantly lower than in the brackish water membrane permeate. The permeate boron concentration in the boron rejection membrane averaged about 1 mg/l compared with 4.5 mg/l for the brackish water membrane. At the end of the pilot study (~50 hours) the TDS and boron levels increased by two and three fold, respectively, in both membrane systems. The reasons for this increase are not known, however, post-treatment evaluation of the boron rejection membranes indicated that at least one of the elements failed the vacuum test for structural integrity, indicating a physical break in this element.

Table 7.15: Treated Water Quality of Brackish Water and Boron Rejection Membranes

Parameter (mg/l)	Feed Water	Brackish Water Membrane	Boron Specific Membrane
TDS	8500	240	60
Boron	23	4.3	1
TOC	45	1.1	< 1
Ammonia as N	12	6	6.3

7.3.3.1 Transmembrane Pressure Analyses

After about 50 hours of operation the RO permeate conductivity increased significantly for both trains. Furthermore, abnormal recovery and pressure readings were also observed for both trains. These observations suggested that the integrity of one or more of the membrane elements may have been compromised. Consequently, a TMP recovery analysis during the CIP could not be accurately performed to assess any potential differences in fouling characteristics between the two types of membranes. Therefore, in lieu of conducting a TMP recovery analysis, a membrane autopsy was performed on the three boron rejection membranes at Hydranautics' Oceanside, CA facility.

7.3.3.2 Boron Rejection Membrane Autopsy Analyses

All the three elements used in 1X0 array mode were sent to Hydranautics' laboratory. Bubble tests, vacuum tests and a standard re-test for flow were performed on all of the three elements. Subsequently, the element that had the highest amount of fouling (first element in the series) was dissected for scanning electron microscope (SCM) and Energy Dispersive X-ray Microanalysis (EDAX) analyses (Appendix F).

The bubble test data indicated that there were no leaks in any of the membranes. However, in the vacuum test that followed, one of the elements (the downstream element in the series) failed. The reasons for the failure could not be determined. The standard re-test performed to compare the flow rates of the pilot test elements with virgin elements indicated significant reduction in flow in the two membranes that passed the vacuum test. However, the element that failed the vacuum test had higher salt passage than the virgin membrane, and had the highest flow rate and lowest delta P among the three elements tested (Table 7-16). These observations, in general, are in agreement with the increased TDS and boron levels observed during the later part of the pilot study.

Table 7.16: Standard Re-test Performance Data for the Boron Rejection Membrane

Element	Nominal		Re-Test			% Change	
	% Rejection	Flow (gpd)	% Rejection	Flow (gpd)	DeltaP (psi)	Sal Passage	Flow (gpd)
Upstream	99.8	1,150	99.9	871	5.2	- 50	- 24
Middle	99.8	1,150	99.9	945	5.1	- 50	- 18
Downstream	99.8	1,150	99.3	1,003	4.8	+ 246	- 13

After these initial tests, the element that had the lowest flow rate during the re-test (this is the element that was first in the series during the pilot study) was selected for dissection and subsequent SCM and EDAX study. The SCM study indicated that most of the membrane was covered with a thin layer of foulants. EDAX analyses of the foulant layer indicated that the layer primarily consisted of silica, magnesium and iron. A small amount of phosphorus was also found. However, no carbonates or organic constituents were detected in the layer. These results suggested that most of the membrane fouling occurred due to inorganic constituents (silica and magnesium).

7.3.3.3 Evaluation of CIP Solutions

Table 7.17: Inorganic and Organic Constituents in San Ardo Produced Water Fouling the Fluidsystems and SWC4 RO Membranes

Parameter	Brackish Water Membrane		Boron Rejection Membrane	
	Before CIP	After CIP	Before CIP	After CIP
Low pH Solution				
Calcium (mg/l)	81	85	84	92
Magnesium (mg/l)	33	49	33	92
Silica (mg/l)	48	71	58	110
Hardness (mg/l as $CaCO_3$)	340	410	350	610
High pH Solution				
TOC (mg/l)	77	73	79	77

The acidic and alkaline cleaning solutions were collected before and after the CIP, and analyzed for organic and inorganic constituents (Table 7-17). As observed with the brackish water membranes in the earlier trials, most of the membrane fouling occurred due to inorganic scaling. However, fouling on the boron rejection membrane was significantly higher than that on the brackish water membrane. The boron rejection membrane contained 125% more silica and 270 % more magnesium fouling than the brackish water membrane. It is possible that the fouling across the boron rejection membrane was higher due to operation of this membrane at a slightly high recovery (70%) than the brackish water membrane (63%). Further investigation is required to understand the fouling characteristics of this membrane.

7.3.3.4 Specific Flux Evaluation

Table 7-18 summarizes the average operating conditions and estimated flux for the test run using data from the initial 48 hours of operation. Membrane integrity problems were encountered with the boron rejection membrane following the initial 48 hours of operation.

Table 7.18: Summary of Average Operation Conditions During Comparison of Brackish Water and Boron Rejection Membrane for San Ardo Produced Water Treatment

Parameter	Brackish Water Membrane	Boron Rejection Membrane
Membrane Manufacturer	Koch Membrane Systems (KMS)	Hydranautics
Model Number	4820XR	SWC4 – 4040
No. Elements	3	3
Total Membrane Area (SF)	234	255
Array Configuration	1 x 0	1 x 0
Aggregate Run Time (hr)	98.4	48
Feedwater Flow Rate (gpm)	2.7	2.5
Permeate Flow Rate (gpm)	1.6	1.5
Concentrate Flow Rate (gpm)	1.1	1.0
Recovery (%)	59.2	58.7
Feedwater Temperature (°C)	23.8	23.8
Temperature Normalized Flux (gfd)	10.6	9.1
Trans-Membrane Pressure (TMP, psi)	439.2	399.8
Osmotic Pressure (psi)	106.7	74.1
Net Driving Pressure (psi)	332.5	325.7
Specific Flux (gfd/psi)	0.0320	0.0280

Assuming an average recovery for each of about 60% yielded average specific fluxes of 0.0320 gfd/psi and 0.0280 gdf/psi, respectively, for the two membrane systems. Figure 7-15 shows the specific flux decline for each of the membrane trains through the course of the test run. The findings from this chart suggest the following:

- Under similar operating conditions, the boron rejection membrane appears to require more trans-membrane pressure (TMP) to generate the same permeate as the brackish water membrane. At the start of the test run, the specific flux for the brackish water membrane train was 14.8% greater than for the boron rejection membrane train. At the end of the test run, the specific flux difference narrowed to 14.0%, with the brackish water membrane train still outperforming the boron rejection membrane train.
- The allowable run time between membrane cleanings is very similar. Using the 15% specific flux decline criteria, the allowable run times are 15.6 and 15.8 hours for the brackish water membrane train and the boron rejection membrane trains, respectively. Increasing the specific flux decline criteria to 25% extends the run times out to 25.5 and 25.7 hours respectively.

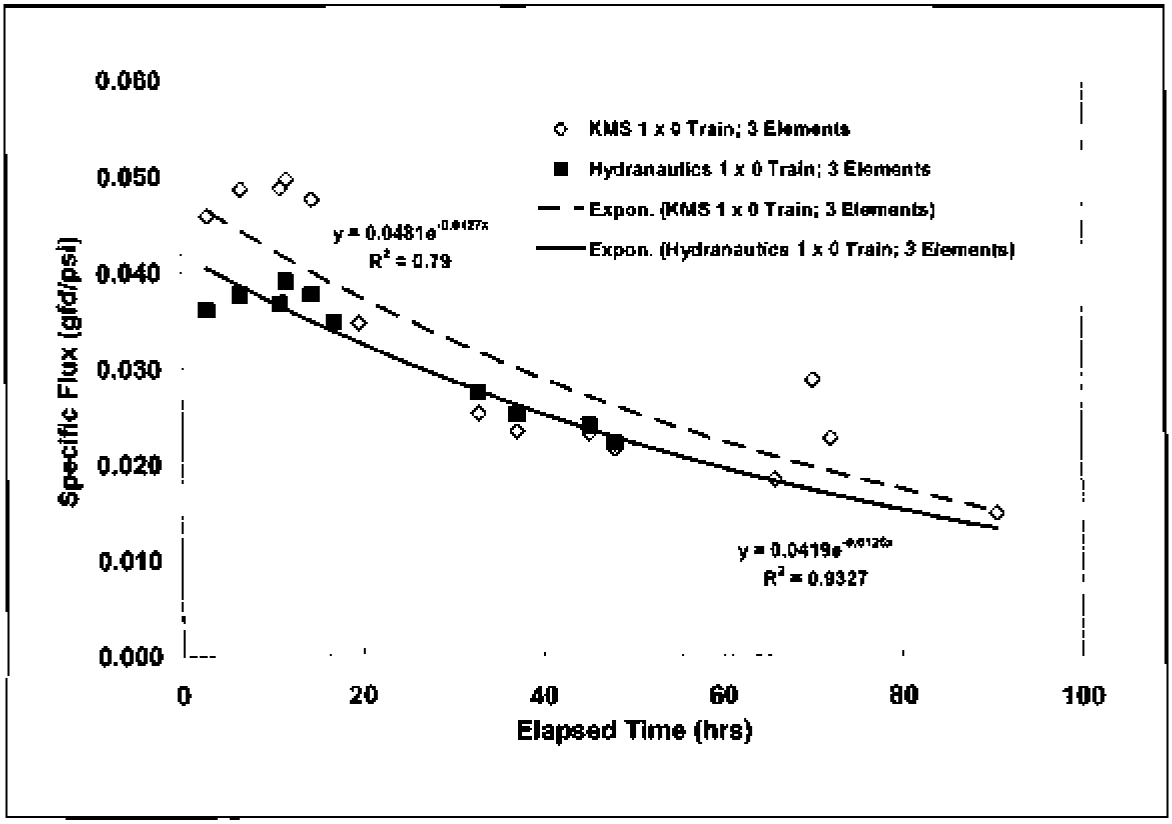


Figure 7-15. Comparison of Specific Flux During Side-By-Side Evaluation of KMS and Hydranautics Reverse Osmosis Elements.

Note that the operating conditions used during the side-by-side comparison studies yielded a significantly shorter RO operation between cleanings (15.6 and 15.8 hours vs. 90 hours), and a lower recovery than the conditions used in earlier tests with the brackish water membrane alone. It is possible that the lower operating pH allowed for higher silica and magnesium precipitation on the membrane surface during the side-by-side study.

7.3.3.5 Energy Usage

As in the previous case, for a full-scale single array system with a design flux of 10 gfd the net driving pressure for the boron rejection membrane system is about 357. psi. The estimated additional osmotic pressure is about 123 psi. Hence, the total trans-membrane pressure estimate for the boron rejection membrane system is about 480 psi. At a pumping efficiency of 67.5% the estimated power requirement is 1,210 HP or 900 kW. If the system were to be operated for 90% of the time, about 7.50 million kW-hr of electrical power would be required per year. Additional energy is required for the conveyance of untreated produced water to the system and the transfer of permeate to storage or end-use. The summary of projected operating conditions and electrical power usage for a full-scale system using high boron rejection membrane elements is shown in Table 7-19.

Table 7.19: Projected Energy Use for Systems with Boron Rejection Membrane Elements

Parameter	Value
Membrane Type	High Boron Rejection Seawater RO
Feedwater Flow Rate (bbl/day)	100,000
Feedwater Ph	9.5
Recovery (%)	70%
Feedwater TDS (mg/l)	7,000
Feedwater Temperature (°C)	25
Target Membrane Flux (gfd)	10.0
Average Specific Flux from Data (gfd/psi)	0.0280
Net Driving Pressure (psi)	357.1
Estimated Osmotic Pressure (psi)	122.7
Estimated Required TMP (psi)	479.8
Base Pumping Power Required (HP)	816.4
Average Efficiency for System Pumps	67.5%
Estimated Pumping Power Required (HP)	1,209
Estimated Electrical Energy Required for Pumping (kW)	902
Estimated Annual Energy Use (kW-hr)	7,508,677

Section 8: Recommended Design Criteria and Estimated Cost

This Section presents the preliminary design criteria and cost estimates for conceptual 70,000 barrel per day San Ardo produced water treatment facility (~50,000 bpd treated water) for potential offsite use. Aera Energy LLC currently generates about 140,000 bpd produced water. However, a design capacity of 70,000 bpd, (50,000 bpd treated water) is selected since Aera Energy LLC, through separate evaluations, determined this to provide the optimum benefit for San Ardo oilfield operations. As discussed in Chapter 2, the water quality criteria for the treated produced water varies with the type of end use selected. As in the pilot studies, in this section a full-scale design and cost estimate is developed using the treatment goals (Table 8-1) adapted from California Central Coast Basin Plan. It should be noted that treatment to the water quality in Table 8-1 does not guarantee the water will meet all required specifications for any specific end use or groundwater recharge. The design criteria are based on the results of the pilot study described in Section 7, augmented by engineering judgment where necessary. Preliminary cost estimates are developed based on information obtained from equipment manufacturers, pilot plant operating experience, recent Kennedy/Jenks water treatment facilities projects, and professional judgment.

Table 8.1: Treatment Goal for Full-Scale Design

Parameter	Treatment Goal
TDS	400 mg/l
Temperature	90 °F
TOC	1 mg/l
Boron	0.5 mg/l
Ammonia Nitrogen	5 mg/l
Silica	40 mg/l
Total Hardness	10 mg/l as $CaCO_3$

8.1 Evaluation of Process Alternatives for San Ardo Produced Water Treatment

The primary water quality goals of the San Ardo produced water treatment facilities are to cool the produced water and remove hardness, silica, TDS, boron, ammonia, and TOC. The pilot plant testing, discussed in Section 7, provided insights into the performance of a number of potential treatment processes and their limitations. This section discusses process alternatives for the key water quality parameters that must be addressed by the treatment facilities.

8.1.1 Hardness and Silica Removal

The inorganic chemistry of the raw produced water suggests that, for the existing produced water temperature (around 160 °F), removal of hardness (primarily calcium) and silica can be optimized at a pH around 9.5. The pilot testing suggests that the addition of about 600 mg/L of NaOH and 100 mg/l of magnesium would achieve this pH and meet hardness and silica goals by removing calcium as calcium carbonate, and magnesium and silica as magnesium silicates, with some magnesium hydroxide precipitation. This operating mode would provide excellent pretreatment for the operation of the downstream reverse osmosis unit. While the warm softening process substantially reduces the hardness constituents and silica, it will slightly increase the total dissolved solids (TDS) in the softened water.

8.1.2 Cooling Using Fin Fan

The ambient produced water temperature of about 160 – 190 °F is ideal for warm softening but would be detrimental to the reverse osmosis process. A cooling tower, designed to lower the produced water temperature from 195 °F to 90 °F was used in the pilot study. However, since the softened effluent from the warm softening unit had to be stored in a settling tank for solids removal, the influent temperature to the cooling tower was always below 105 °F during the pilot study. Furthermore, while a cooling tower could be used for effectively lowering the softened water temperature, use of this unit will involve potential air permitting problems due to possible air emissions of volatile organic chemicals (VOCs) and ammonia.

Another cooling alternative for the treatment of San Ardo produced water is the use of a fin fan heat exchanger. The heat exchanger utilizes fans to drive air at ambient temperature across a series of parallel tubes containing the process water. Attached to the exterior of the tubes are spiral wound metal fins designed to increase available surface area in contact with the passing air. This increased area allows for a greater rate of heat transfer per unit volume of air passing across the tubes. Unlike cooling towers, the use of fin fan cooling will not involve air permitting issues. Also, this unit has been used successfully for lowering produced water temperatures in other studies (Doran, et al., 1998).

8.1.3 TDS Removal

TDS removal would occur after the softening process, where most of the hardness and silica have been removed. Because of low hardness, total inorganic carbon, and silica levels, the RO process can be operated over a wide pH range (pilot tested RO feed pH from 9.5 to 11) to effectively remove TDS. This operating range allows different strategies to be considered for the removal of boron, ammonia, and organics, as discussed below.

8.1.4 Boron Removal

During the pilot study a brackish water membrane at high pH (>10.5) and a boron rejection membrane at relatively low pH (9.5) were effective in removing boron. Although the boron rejection membrane was effective during the 2 week pilot evaluation, more studies are required to evaluate the long term performance of this membrane. To date, full-scale installation of this membrane system has been used primarily for sea water desalination with 5 to 7 mg/l of boron. During the San Ardo pilot study, some structural damage to the membrane occurred, and the RO was operated for less than 50 hours.

Another alternative for boron removal is the use of a boron selective ion exchange process. However, this process is not economical due to resin costs of around $800 - $1,000 per cubic foot.

8.1.5 Ammonia Removal

The pilot RO unit, at the pH range operated (9.5 – 11) did not remove ammonia. Furthermore, ammonia speciation chemistry suggest that acceptable ammonia removal may be achieved only when the RO system is operated at pH lower than 9.0. Thus, there is a fundamental operational conflict in removing both boron and ammonia simultaneously by RO.

Breakpoint chlorination studies using RO permeate indicated that chlorine to ammonia ratio of 7.5:1 is optimum for ammonia removal from the RO permeate. However, addition of chlorine will increase the TDS of the treated water.

Other potential ammonia removal processes include air stripping, ammonium selective ion exchange, biological treatment and wetlands. The air stripping process may involve potential permitting problems with air emissions of produced water constituents. The type of end use identified for the treated produced water and availability of land will dictate the use of biological treatment and wetlands options.

The ammonium selective ion exchange, using clinoptilolite or strong cation resins, appears to be the best choice for San Ardo produced water treatment because it neither increase the TDS nor involves emission of produced water constituents.

8.1.6 Organics Removal

The organics in the produced water were effectively removed by the RO unit during the pilot study. The TOC in the permeate was below the detection limit (1 or 3 mg/l) in most of the samples analyzed. Bench scale studies to evaluate biodegradation of the organics indicated that only about 30% of the organics was biodegradable. Oxidation using chlorine dioxide only partially converted (~ 20%) the non-biodegradable organics to a biodegradable form. Pretreatment using advanced oxidation processes (UV/Ozone) may enhance biodegradation of the organic compounds in the produced water. However, ozone treatment is not a viable option due to the high concentration of bromide (~ 25 mg/l) in the produced water. Also, pretreatment using UV may be energy intensive, and the oxidation byproducts may potentially form carcinogenic THMs during disinfection. In addition, the biological process for organic degradation would increase the microbial concentration, as many as a million bacteria per ml, as shown in other studies (Doran, et al.,1998) and create a potential biofouling problem for the RO membranes. Hence, removal of organics by the RO process appears to be the best option for treatment of San Ardo produced water.

8.2 Design Basis for San Ardo Produced Water Treatment Facilities

The recommended process for the treatment of San Ardo produced water includes warm precipitative softening (at pH 9.5), cooling, equalization storage, booster pumping, multi-media filtration, increase of pH to 10.5 using caustic, cartridge filtration, reverse osmosis, pH adjustment to about 7.5 with sulfuric acid, and ammonium selective ion exchange.

Flow and process schematic diagrams for a proposed 70,000 bpd (2,100 gpm) produced water reclamation facility, illustrating the functional relationship of the various water treatment processes, chemical addition points, sludge handling, wash water recovery and storage facilities are shown in Figure 8-1. Table 8-2 presents the design criteria for various process units. Pumping that may be required for delivery of water to the warm softening unit and pumping required after the ammonia polishing section has not been included.

8.2.1 Warm Precipitative Softening

Warm precipitative softening will be carried out in a 70,000 bpd DensaDeg clarifier. The DensaDeg unit consists of three components; namely, a rapid mix chamber, a reaction tank, and a thickener/clarifier. The rapid mix chamber consists of a 7.5-ft. diameter draft tube in which a turbine mixer provides initial mixing of precipitation chemicals. The rapid mix chamber is inside a 16-ft. x 17.5 ft. deep reaction tank. The retention time at design flow would be 13 minutes. The thickener/clarifier has a 22-ft. diameter, a 17-ft. water depth, and a 24-minute retention time at design flow. The clarified water then exits the clarifier through plate settlers with a loading rate of 308 bpd/sq ft (9 gpm/sq.ft).

The operating temperature is estimated to be 150-170 °F. Chemical additions will include sodium hydroxide to control pH to about 9.5 (average of 600 mg/L), with an anionic polymer (average of 3.5 mg/L) added in both cases to assist with settling of the precipitate. The process will produce approximately 25,300 lb/day of sludge (dry solids (DS), basis) or 1,100 bpd at 7.5 percent DS. The sludge will be dewatered to 20 percent DS with a centrifuge and hauled to a landfill. The filtrate from the centrifuge will be returned to the warm clarifier via the filter washwater tank.

8.2.1.1 Cooling

Six closed system fin fan coolers, each with two 32 HP fans, will be incorporated to reduce the temperature in the clarifier effluent to slightly above ambient air conditions (maximum temperature of 115°F). This will make the water more amenable to reverse osmosis separation, which operates more efficiently at warmer water temperatures.

8.2.1.2 Equalization Storage and Booster Pumping

The cooled water will be routed to an 11,700 barrel equalization tank which will allow the temperature of the softened water to be equalized over the course of the day. Water from the storage tank will be pumped to pressure filters.

8.2.1.3 Filtration

The pumped water will be filtered by polishing multi-media filters consisting of layers of anthracite, sand, and garnet media. There will be four 9-ft diameter pressure filter units in parallel. The filter units will be plumbed so that one unit can be backwashed with the filtrate being generated by the other three units. The spent washwater will be routed to the head end of the DensaDeg so that backwash water is reclaimed.

8.2.1.4 Reverse Osmosis Desalting

The filtered water will be routed to the reverse osmosis (RO) units, which will include pre-cartridge filtration and chemical pretreatment consisting of pH adjustment to 10.5 with NaOH (100 mg/L average dose), scale inhibition (1 mg/L average), and organic fouling control (5 mg/L average). The RO units will be run in a 2x2 array, with 75 percent recovery and a 50 percent (based on feed flow) recycle ratio. The array will consist of 912 (8-in. diameter) thin film RO elements. The membranes will be cleaned in-place every two weeks.

8.2.1.5 Water Stabilization

The pH of the RO permeate will be adjusted to about 7.5 with sulfuric acid (50 mg/L average) so that the water is stable with respect to scaling and suitable for ammonia removal by selective ion exchange.

8.2.1.6 Ammonium Selective Cation Exchange

Ammonia will be removed by selective ion exchange using a strong cation resin, which will be regenerated by a 2% salt solution. The treatment goal will be to reduce the ammonia concentration from 10 mg/L to 4 mg/L.

Three 10-ft diameter *x* 5-ft tall, pressure contactors will be used. Each contactor will be filled with 300 cubic feet of strong cation resin. Two of the three resin contactors will be capable of treating the entire 50,000 bpd permeate flow at a loading of 19 bed volumes per hour.

One contactor will be regenerated each day while the other two are in the operational mode. This will be accomplished by using 10 bed volumes of RO concentrate (adjusted to 2 percent sodium chloride strength, as necessary) followed by rinsing with 30 bed volumes of RO treated water at a rate of 6.5 bed volumes/hr. The regenerant, upon exhaustion, and the first 10 bed volumes of the rinse water will be disposed in the Aera Energy LLC injection facility. The remaining rinse water will be sent to the head works of the treatment plant. Regeneration of each vessel can be accomplished in about six hours.

Table 8.2: Produced Water Treatment Plant Design Criteria

Process Parameter	Units	Value
Plant flow rate: produced water	bpd	70,000
Production flow rate: reclaimed water	bpd	50,000
Overall water recovery	Percent	71.5
WARM PRECIPITATIVE SOFTENING		
Operating pH	std. units	9.5±
DensaDeg Clarifier (1 unit)		
Flow rate	bpd	70,000
Sidewater depth	ft.	17
Reaction Vessel		
Diameter	ft.	16
Volume	barrels	609
Detention time	min.	13
Thickening/clarification		
Diameter	ft.	22
Volume	barrels	1150
Detention time	min.	24
Settling zone surface area	sq.ft.	227
Surface loading rate	bbl/sq.ft.	308
Chemical Systems		
Sodium hydroxide (50% solution)		
Dosage, avg.	mg/L	550
Use, avg.	lb/day	13,450
Storage Tanks		
Number	-	3
Chemical concentration	lb/bbl	269
Capacity, ea.	bbl	286
Supply, at avg. dose	days	17

Magnesium Chloride (27% solution)		
Dosage, avg.	mg Magnesium/L	100
Use, avg.	lb/day	2,445
Storage tank		
Chemical concentration	lb/gal	0.83
Capacity	bbl	286
Supply, at avg. dose	days	7
Anionic Polymer		
Dosage, avg.	mg/L	3.5
Use, avg.	lb/day	86
Storage Tote		
Concentration	lb/bbl	350
Capacity (2)	bbl	6.5
Sludge volume	*bpd*	*1,100*
Percent solids	%	7.6
Sludge Filter Press		
Type	-	Centrifuge
Capacity	dry lb/hr	1000
Feed Solids Content	%	60
Main Drive	HP	50
COOLING		
Cooling Heat Exchangers		
Type	-	fin fan
Inlet water temperature	°F	170
Outlet water temperature	°F	100
Total Cooling capacity	tons of cooling	4,200
Design air temperature (95th percentile)	°F	90
Number of heat exchangers	-	6
Unit size	ft x ft	13 x 40
Number of fans per unit	-	2
Fan Motor size, each	HP	40
EQUALIZATION STORAGE		
No. of Tanks	No	2
Volume	bbl	5800
Depth	ft.	17
Diameter	ft.	50
BOOSTER PUMPING (2 pumps)		
Pumping capacity, each	bpd	70,000
Discharge pressure	psig	100
Supply, at avg. dose	53 days	

PRESSURE FILTRATION		
Number of units	-	4
Diameter	ft.	9
Surface loading rate	bpd/sq.ft.	275
Media Depths		
0.85-0.95 mm anthracite	inches	18
No. 20 sand	inches	8
No.30 - No.40 garnet	inches	4
Support Gravel depths		
No.4 quartz	inches	3
1/4-in.x 1/8-in. quartz	inches	3
1/2-in.x 1/4-in. quartz	-	Bottom fill
Polymer System		
Dosage, avg.	mg/L	3.5
Use, avg.	lb/day	86
Storage Tote		
Concentration	lb/bbl	360
Capacity	bbl	6.5
Supply, at avg. dose	days	27
Washwater recovery system		
Equalization tank	bbl	1,500
Return pumps (2) capacity, each	bpd	2, 180
CARTRIDGE FILTRATION		**Auto Bag Filters**
Number of bags	-	18
Nominal sized particle removed	µm	5
Capacity per bag	bpd	3,900
REVERSE OSMOSIS		
Operating RO feed pH	std. units	10.5±
Flow rates		
feed flow rate	bpd	70,000
recycle flow rate	bpd	35,000
permeate flow rate	bpd	50,000
reject flow rate	bpd	20,000
Elements		
Number	-	912
Array scheme	-	2x2
Effective surface area, each	sq.ft.	400
Flux rate	bpd/sq.ft.	0.19
Chemical Systems		
Sodium hydroxide (50% solution)		
Dosage, avg.	mg/L	100
Use, avg.	lb/day	2445
Storage Tanks	Not required*	-
Scale Inhibitor		
Dosage, avg.	mg/L	1.0
Use, avg./max.	lb/day	24
Storage tank		
Concentration	lb/bbl	378
Capacity	bbl	1.3
Supply, at avg. dose	days	20
Antifoulant		
Dosage, avg.	mg/L	5.0
Use, avg.	lb/day	122
Storage Tank (2)	bbl	1.3
Concentration	lb/bbl	378
Capacity		

RO MEMBRANE CLEANING SOLUTIONS		
Dosage, avg.	bbl sol'n: bbl water	1:40
Use, avg./max. (per cleaning)	bbl.	12
Storage Tanks (2)		
Capacity, ea.	bbl	55
pH ADJUSTMENT		N.A.
Sulfuric Acid (93 %)		
Dosage, avg.	mg/L	50
Use, avg.	lb/day	873
Storage Tank		
Concentration (93%)	lb/bbl	588
Capacity	bbl	119
Supply, at avg. dose	days	80
AMMONIA SELECTIVE EXCHANGE		
Number of contactors	-	3
Contactor type	-	Pressure
Contactor diameter	ft	10
Contactor length	ft	5
Ion Exchange Medium	-	Strong Cation Exchange
Medium size		-
Medium depth	ft	4.0
Surface loading rate	bpd/sq.ft.	318
Volume loading rate	BV/hr	19
Empty Bed Contact Time	minutes	1
Run length	hours	24
Regenerant salt solution	percent	2
Regenerant volume (40 BVs)	bbl.	1,100

8.3 PRELIMINARY COST ESTIMATES

Preliminary capital, annual operations and maintenance, and unit treatment cost estimates were prepared based on experience gained with the pilot plant operations, budgetary cost input from equipment manufacturers, cost estimating information from recent Kennedy/Jenks projects and professional judgment.

The preliminary design criteria and dimensions of treatment process units, chemical feeding and storage facilities, storage tanks, and booster pumping are shown in Table 8-2. It is assumed that the area required for construction of full-scale facility (~ 4 acres) is available in the project location. A 5,400 sq.ft. building is proposed to house the RO system and sludge handling facilities, and to provide office and laboratory space.

The costs are in 1st quarter 2006 dollars. Table 8-3 summarizes the cost factors used in the conceptual treatment facility.

Table 8.3: Cost Factors and Assigned Values

Parameter	*Value*	*Unit*
Dollar	1^{st} Qtr 2006	index year
Interest rate	7	% per annum
Capital recovery period	20	years
Capital		
Electrical and instrumentation	15	% of process train costs
Site work	10	% of process train costs
Contractor's overhead and profit	12	% of direct construction cost
Mobilization and bonding	2	% of direct construction cost
Contingency	10	% of direct construction cost
Indirect construction costs	38	% of construction "bid" cost
O&M		
Sodium hydroxide	0.25	$ per lb
Magnesium chloride	0 61	$ per lb.
Polymer	2 40	$ per lb
RO antiscalant	2 23	$ per lb
RO antifoulant	3 22	$ per lb
RO chemical cleaning solution	3 57	$ per lb
Sulfuric acid	0.046	$ per lb
Electricity	0.10	$ per kW-hr
Labor rate	32	$ per hr
Replacement RO membrane elements	550	$ per element (24 month life)
Misc maintenance materials	1	% of process train costs
Sludge disposal	28	$ per ton wet
Brine disposal	11	¢ per barrel
Contingencies	10	% of direct annual O&M

8.3.1 Construction and Total Capital Costs

Capital cost estimates include both the actual construction ("bid") costs and the indirect costs associated with implementing the project. Capital cost include costs related to purchase and installation of process and residuals handling equipment, site preparation, building and structural work, and other construction costs a contractor includes in a "bid cost" for a treatment facility such as mobilization and bonding, overhead and profit, and contingencies to account for uncertainties and unforeseen expenses. Indirect capital cost include such expenses as engineering design and construction management, financial, legal, and administrative services, interest during construction, utility connection fees, environmental impact reports and permits. These costs have been estimated at 38 percent of the construction "bid" costs in this report. The capital cost estimates assume a level site and are believed to have an accuracy of approximately -15 to +30 percent.

Table 8-4 summarizes the capital cost estimate for the conceptual 70,000 bpd produced water treatment facility that would reclaim approximately 50,000 bpd (2,000 acre ft/yr) of water. The estimated construction "bid" cost is $12.5 million, with indirect capital cost of $4.8 million, for a total project capital cost of $17.3 million. The unit construction and total capital costs are $179/bpd and $247/bpd produced water treated, respectively. Note the capital cost estimates given above are only for the treatment facility as shown in Figure 8.1; additional capital required for equipment upstream and downstream of the treatment facility is not included. Significant additional capital expenditures for trace oil removal and filtration upstream of the treatment process as well as expenditures for post-treatment storage and handling of the treated water are excluded from these figures.

Table 8.4: Total Project Capital Cost Estimate for 70,000 Barrel Per Day

Cost Component		*Cost ($1,000s)**
1	Direct Process Costs	
	Warm lime softening + Sludge Thickening	2,300
	Cooling	590
	Equalized storage	270
	Booster pumping	285
	Granular media filtration	1,000
	Reverse Osmosis	2,500
	Stabilization (pH adj)	20
	Ammonium selective ion exchange	390
Subtotal		**7,480**
2	Treatment Building	690
3	Process + Building Subtotal	8,200
4	Other Direct Construction	
	Electrical + Instrumentation @ 15% of Item 1 Subtotal	1,100
	Site work @ 10% of Item 3 Subtotal	820
5.	Direct Construction Subtotal	10,000
6	Contractor Markups	
	Contractor's overhead & profit @12% of Item 5 Subtotal	1,200
	Mobilization @ 2% of Item 5 Subtotal	200
	Contingency @ 10% of Item 5 subtotal	1,000
7.	Total Construction Cost Estimate (Bid Cost)	12, 500
8.	Indirect Capital Cost Estimate @ 38% of bid cost	4, 800
9	Total Capital Cost Estimate	17,300
10.	Unit Construction Costs	
	$/bpd produced water treated	180
	$/bpd water reclaimed	250
11	Unit Total Capital Costs	
	$/bpd produced water treated	250
	$/bpd water reclaimed	350

*Values rounded to two significant figures or nearest $100,000.

8.3.2 Annual Operations and Maintenance (O&M) Cost

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.

Table 8-5 summarizes the estimated annual O&M cost. Total annual O&M cost is estimated to be $6.5 million, which is equivalent to 26 ¢/bbl of produced water treated. The O&M cost consists of $2.6 million/yr for chemicals, $0.98 million/yr for energy, $0.65 million/yr for labor, $0.30 million/yr for maintenance materials, $1.4 million for residuals management, and $0.57 million/yr for contingencies.

The O&M cost is dominated by the costs for chemicals and residuals disposal. The chemicals and residuals management costs represent 62 percent of the O&M cost. The energy cost (14%) and labor cost (10%) are the other major O&M cost constituents. The largest cost reduction benefit for San Ardo produced water treatment will come from reducing chemical costs or finding a beneficial use for the sludge. For example, the use of waste caustic from refinery/industrial facilities might further reduce the caustic cost.

Table 8.5: Annual and Unit Treatment Costs

Cost Component		*Cost ($1000s/yr)**
1. Chemicals		
Sodium hydroxide		1,480
Magnesium chloride		560
Polymers		91
Antiscalant		24
Antifoulant		164
RO cleaning solution		240
Sulfuric acid		17
	Subtotal	**2,576**
2. Electricity		
Warm softening		106
Cooling		292
Booster pump		124
Reverse osmosis		447
pH		1
	Subtotal	**970**
3. Labor		
Operations		655
	Subtotal	**655**
4. Maintenance Materials		
RO membranes		250
Other materials		53
	Subtotal	**303**
5. Residuals Disposal		

Sludge		590
RO concentrate		803
	Subtotal	**1,393**
6. Direct Annual O&M		5,925
7. Contingency @10% of Item 6		588
8. Total Annual O&M		6,515
9. Unit Annual O&M Cost		
¢ / bbl produced water treated		24
¢ / bbl water reclaimed		34

8.4 Unit Treatment Costs From Water Utility Perspective

If the treated water were to be used for an offsite use, Water Utilities that procure the water often evaluate the total treatment cost which is the sum of the annual O&M cost and amortized capital cost per acre-foot of water treated. Accordingly, amortized capital cost for this project was estimated using a 20 year loan period, at an annual interest rate of 7 percent, which is a typical scenario for municipal projects that are financed through bonds.

The total annual cost thus estimated for the 70,000 bpd (3 MGD) facility is $8.15 Million (Table 8-6). The unit treatment cost estimate is approximately 46 ¢/bbl ($3,600/acre-ft or $11/1000 gallons) of water reclaimed. The annual amortized capital payment is about 20 percent of the total annual cost. This suggests that potential savings should be investigated in O&M expenses, as discussed previously.

Table 8.6: Summary of Water Reclaimed and Unit Treatment Costs

Parameter	*Cost*
Produced Water Treated	
bbls/day	70,000
acre ft/yr	3,300
Water reclaimed	
bbls/day	50,000
acre-ft/year	2, 360
Overall Water Recovery	71.5
Total Capital Cost($1,000s)	17,290
Annual O&M Cost ($1,000s/yr)	6,515
Annual amortized capital costs ($1,000s/yr)	1,630
Total annual costs ($1,000s/yr)	8,150
Unit treatment costs	
¢/bbl. produced water treated	32
¢/ bbl. reclaimed	46
$/acre-ft. reclaimed	3,470

8.5 Sensitivity Analysis of Key O&M Cost Components

In order to evaluate the potential to minimize the O&M cost for treating San Ardo produced water, a sensitivity analysis was performed using the following changes from the base case cost assumptions:

- Changing the labor rate from $32/hour to $28/hour
- Changing the electric rate from $0.10/kw-hr to $0.08/kw-hr
- Changing the dewatered sludge concentration from 20 percent to 50 percent
- Changing the NaOH cost from $0.25/lb. to $0.15/lb
- Combined impact of making all four changes simultaneously (best case)

Table 8-7 compares the impact of these constituents on San Ardo produced water treatment. The cost of caustic has the biggest impact on annual O&M costs (~2.5 ¢/bbl. of produced water treated). Increasing the dewatered sludge concentration to 50 percent solids reduces annual O&M costs of produced water by about 1.5 ¢/bbl of produced water treated. The labor and electric rate changes have a smaller impact on annual O&M costs, of about 0.3 and 0.8 ¢/bbl, respectively.

Table 8.7: Annual O&M Cost Comparison

Cost Component	***Base Case***	***Labor ($28/hr)***	***Electricity (8¢/kWH)***	***Sludge (50%)***	***NaOH (15 ¢/lb)***	***Cumulative Case***
Annual O&M Costs	**$1,000s**	**$1,000s**	**$1,000s**	**$1,000s**	**$1,000s**	**$1,000s**
Unit treatment cost	***¢/bbl***	***¢/bbl.***	***¢/bbl.***	***¢/bbl.***	***¢/bbl***	***¢/bbl.***
1. Warm softening	3,316	3,292	3,293	2,927	2,664	2,228
	13	*12.9*	*12.9*	*11.5*	*10.4*	*8.7*
2. Fin Fan Cooler	416	405	353	416	416	342
	1.6	*1.6*	*1.4*	*1.6*	*1.6*	*1.3*
2. Equalized Storage	29	25	29	29	29	25
	0.1	*0.1*	*0.1*	*0.1*	*0.1*	*0.1*
3. Booster Pumping	190	184	163	190	190	156
	0.7	*0.7*	*0.6*	*0.7*	*0.7*	*0.6*
4. Pressure Filters	113	103	113	113	113	103
	0.4	*0.4*	*0.4*	*0.4*	*0.4*	*0.4*
5. Reverse Osmosis	2,347	2,321	2,249	2,347	2,347	2,223
	9.2	*9.1*	*8.8*	*9.2*	*9.2*	*8.7*
6. Stabilization	46	44	46	46	46	44
(pH Adjustment)	*0.2*	*0.2*	*0.2*	*0.2*	*0.2*	*0.2*
7. Ammonium Ion	65	58	63	65	65	57
Exchange	*0.25*	*0.2*	*0.2*	*0.25*	*0.25*	*0.2*
Annual O&M	**6,521**	**6,432**	**6,309**	**6,132**	**5,869**	**5,178**
	25.5	***25.2***	***24.7***	***24.0***	***23.0***	***20.3***

Section 9: Technology Transfer Activities

The objective of this task is to publicize the findings of this DOE funded project so that others can adopt the technology. Table 9-1 shows the list of project presentations and papers. A total of eight presentations were proposed in the initial scope of work. Abstracts were submitted to eleven conferences (or meetings), and presentations were eventually made in nine conferences (or meetings). The abstracts and manuscripts from these presentations are included in Appendix B.

Table 9.1: Summary of Technology Transfer Activities.

No	Conference/Meeting	Industry Focus	Presentation Title	Date/Comments
1	Santa Maria Section Society of Petroleum Engineers Section Meeting, Santa Maria, CA	Oil Industry	Treatment and Possible Reuse of San Ardo Produced Water	June 2005
2	Bakersfield Section Society of Petroleum Engineers Section Meeting, Bakersfield, CA	Oil Industry	Treatment and Possible Reuse of San Ardo Produced Water	July 2005
3	20th Annual WateReuse Symposium, Denver, CO	Water Industry	Evaluating the Potential for Beneficial Use of Oilfield Produced Water for Agricultural Irrigation in San Ardo, CA	September, 2005
4	West Coast Petroleum Technology Transfer Council Meeting, Valencia, CA	Oil Industry	Treatment and Possible Reuse of San Ardo Produced Water	September, 2005
5	Channel Counties Water Utilities Association, Ventura, CA	Water Industry	Treatment and Possible Reuse of San Ardo Produced Water	October, 2005
6	12th Annual International Petroleum Environment Conference, Houston, TX	Oil Industry	Overview of Regulations for Potential Beneficial Use of Oilfield Produced Waters in California	November, 2005
7	Denver Section Society of Petroleum Engineers Section Meeting, Denver, CO	Oil Industry	Treatment and Possible Reuse of San Ardo Produced Water	December 2005
8	San Joaquin Valley Geological Society Meeting, San Joaquin, CA	Oil Industry	Investigating the Potential for Treatment And Beneficial Reuse of San Ardo Produced Water	January 2006
9	American Water Works Association, California – Nevada Spring Conference, Burlingame, CA	Water Industry	Pilot Study for Desalination of Oilfield Produced Water Containing High Levels of Boron and Ammonia	April, 2006. Abstract was submitted but not accepted for presentation.
10	Society of Petroleum Engineers, Annual Technical Conference and Exhibition (ATCE06), San Antonio, TX	Oil Industry	Pilot Study Results to Evaluate Membrane Treatment Optimization for Potential Oilfield Produced Water Reuse in San Ardo, CA	November, 2006. Abstract was submitted but not accepted for presentation.
11	Water Environment Federation Annual Conference (WEFTEC06), Dallas, TX	Water Industry	Evaluation of Potential Beneficial Reuse of San Ardo Produced Water	October, 2006.

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List of Acronyms and Abbreviations

A/C	Authority to Construct
AF	acre-foot
AFY	acre-foot per year
AG	Agricultural Water Supply
AWWA	American Water Works Association
bpd	barrels per day
bbl	barrel
BOD	biochemical oxygen demand
BV	bed volume
Ca^{+2}	Calcium
$CaCO_3$	calcium carbonate
$Ca(OH)_2$	calcium hydroxide
CAM	California Assessment Manual
CCRWQCB	Central Coast Regional Water Quality Board
CDFG	California Department of Fish and Game
CDNR	California Department of Natural Resources
CDOGGR	California Division of Oil, Gas, and Geothermal Resources
CEQA	California Environmental Quality Act
CFR	Code of Federal Regulations
cfs	cubic feet per second
CIP	clean-in-place
ClO_2	chlorine dioxide
COE	Corps of Engineers
CPVC	chlorinated polyvinyl chloride
CSIP	Castroville Seawater Intrusion Project
CTR	California Toxics Rule
CUPA	Certified Unified Program Agency
CWA	Clean Water Act
CWRCB	California Water Resources Control Board
CWC	California Water Code
DBPs	disinfection by-products
DOE	Department of Energy
DS	dry solids
DSD	Division of Safety and Dams
DTSC	California Department of Toxic Substance Control
DWR	Division of Water Rights
EDAX	energy dispersive X-ray microanalysis
EDR	electrodialysis reversal
EIR	Environmental Impact Report
ENR	Engineering News Report
F	degrees Fahrenheit
gfd	gallon flux per day
GIS	Geographical Information System
gpm	gallons per minute
hp	Horsepower
H&SC	Health and Safety Code
IND	Industrial Water Supply
IPEC	International Petroleum Environment Conference

KMS	Koch Membrane System
kWhr	Kilowatthour
MBR	Membrane Bio Reactor
MBUAPCD	Monterey Bay Unified Air Pollution Control District
MCAPCB	Monterey County Air Pollution Control Board
MCL	Maximum Contaminant Level
MCWRA	Monterey County Water Resources Agency
MED	multiple effect distillation
meq/l	milliequivalents/liter
Mg	Magnesium
MGD	million gallons per day
mg/l	milligram per liter
ml	Milliliter
mM	Millimole
MSF	multi-stage flash distillation
MUN	Municipal And Domestic Water Supply
Na_2CO_3	sodium carbonate
NaOH	sodium hydroxide
NH_3	Ammonia
NH_3-N	ammonia nitrogen
NPDES	National Pollution Discharge Elimination System
NTR	National Toxics Rule
NTU	nephelometric turbidity unit
O&M	operation and maintenance
P&ID	process and instrumentation diagram
P/O	Permit to Operate
ppm	parts per million
psi	pounds force per Square Inch
QAQC	Quality Assurance/Quality Control
RO	reverse osmosis
rpm	rotations per minute
SAP	Sampling and Analyses Plan
SCM	scanning electron microscope
SDI	silt density index
SiO_2	Silica
SPE	Society of Petroleum Engineers
sq.ft	square feet
SVWP	Salinas Valley Water Project
TDS	total dissolved salts
THM	Trihalomethane
THMFP	trihalomethane Formation Potential
TMP	transmembrane pressure
TOC	total organic carbon
TTLC	total threshold limit concentration
USEPA	United State Environmental Protection Agency
USFWS	United States Fish & Wildlife Services
USGS	United States Geological Survey
VOC	volatile organic compounds
WDRs	Waste Discharge Requirements
WEF	Water Environment Federation
yr	Year

Appendix A: Pilot Study Work Plans

Kennedy/Jenks Consultants

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949-261-2134 (Fax)

Work Plan
San Ardo Oilfield
San Ardo, California

For

Cooperative Agreement No: DE-FC26-02NT15463

Recovery of More Oil-in-Place at Lower Production Costs while Creating a Beneficial Water Resource

17 October 2003

Prepared for

Aera Energy LLC
10000 Ming Avenue
Bakersfield, CA 93389

K/J Project No. 024033.00

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Section 1: Introduction

This work plan is intended to provide information for the pilot system to treat produced water from Aera Energy LLC's San Ardo Oilfield. This work plan provides a description of the pilot system, the intended objectives of testing, target operating conditions to be evaluated, the anticipated test schedule, and information pertaining to installation and demobilization of the pilot system.

1.1 Background

Aera Energy LLC leases and operates an oil production field in the region in and around San Ardo, California. The oil production process there entails steam flooding the geologic formation to reduce the viscosity of the crude oil so that it can be pumped to the surface. As is the case for many mature oil production well fields, the liquid pumped from the formation contains a large amount of water (produced water) with the crude oil. In many instances, up to 15 barrels of produced water can be produced for every barrel of oil. Once brought to the surface, the oil is recovered and the produced water is pumped back into the formation through the use of deep well injection.

Such on-field injection may increase the produced water to oil ratio and reservoir pressure resulting in higher oil production costs. A potential alternative to the current operating practice would entail treatment of the water so that it could be put to beneficial reuse. Reducing Class II injection through beneficial reuse of treated produced water can optimize oil production and increase recoverable reserves in an oilfield. Recognizing that these potential benefits to water reuse exist, Aera Energy LLC has agreed to participate in a pilot investigation with Kennedy/Jenks Consultants (Kennedy/Jenks) along with funding from the U.S Department of Energy (DOE) to determine if pursuing treatment on a full-scale basis is warranted.

This pilot investigation will look into the treatment of the produced water through the following three-stage process:

- Warm precipitative clarification to remove hardness, carbonate alkalinity, and silica;
- Cooling through the use of a cooling tower to remove excess heat energy and to possibly strip ammonia; and
- Reverse osmosis (RO) to remove boron, ammonia, total organic carbon (TOC), and total dissolved solids (TDS).

Kennedy/Jenks has previously investigated this treatment process at other oil fields and viewed it to be the most suitable process to evaluate treatment of the produced water at San Ardo.

1.2 Objectives

The pilot investigation at San Ardo will seek to meet the following objectives:

- Determine the optimum range of operating conditions in the precipitative clarification process to remove hardness, carbonate alkalinity, and silica.

- Determine the best chemical additive(s) for use in the precipitative clarification process.
- Estimate the sludge generation rate for the precipitative clarification process and develop a characterization of the sludge.
- Determine the capacity of the cooling tower to remove ammonia via air stripping
- Determine the optimum range of operating conditions in the RO process to remove boron, ammonia, and TOC.
- Estimate the cleaning requirements and lifespan of the RO membranes.
- Determine the chemical consumption rates for the RO process for both operation and cleaning.
- Determine the impact of environmental factors on the entire process through the operating period (estimated to be 8 months over a 9 month period).
- Based on the findings of the pilot test, develop planning level estimates of the capital and operations and maintenance (O&M) costs for a full-scale facility at San Ardo. These estimates will include cost scenarios for treatment to meet California Department of Health Services (DHS) requirements for groundwater recharge as well as treatment to meet California Regional Water Quality Control Board (RWQCB) requirements for irrigation use.

1.3 Pilot Schedule

The pilot program will be performed in two Phases (IIA and IIB), each over a period of four months. It is anticipated that Phase 2A study will be performed from January '04 to April '04. The data from this study will be evaluated in May '04 and used to refine the work plan for Phase 2B study. Phase 2B will be performed from June 04 to September 04.

1.4 Organization of the Work Plan

Section 1 of the work plan provides the background, objectives of the pilot study. Section 2 provides the details of pilot system, components and operating conditions. Section 3 provides installation and demobilization schedule and Aera Energy LLC and Kennedy/Jenks roles and responsibilities. Section 4 provides details of test schedule, system operations, equipment calibration and adjustment.

Section 2: Pilot System and Components

The pilot system will treat a 30 gpm stream of produced water taken from one of the pipelines that currently returns produced water from the San Ardo field to the existing deep well injection process. The system will consist of 3 main treatment components, with each component designed to remove specific constituents from the produced water. They include a warm precipitative softening unit, followed by a cooling tower, and finally an RO process. Figure 2-1 shows a schematic process flow diagram for the pilot study. The produced water is first introduced to the precipitative softener unit at approximately 190°F. This unit will remove primarily hardness (calcium and magnesium), alkalinity (as carbonate), and silica, and will function secondarily to remove some of the boron in the water. The cooling tower is intended to reduce the temperature from the 190°F range to less than 115°F to protect the RO membranes. The cooling tower will also be evaluated for potential removal of the ammonia and carbon dioxide present in the water via air stripping. The RO unit will remove the bulk of the dissolved solids (TDS), organic compounds, residual hydrocarbons, and boron from the water.

This section provides details on each of the treatment components of the pilot system including a description of each unit and how it functions, its treatment mechanism(s), the normal operating conditions for the unit, and information on any ancillary systems associated with the unit.

2.1 Precipitative Softening

Precipitative softening is a process designed primarily to remove hardness (calcium and magnesium), carbonate alkalinity, and silica. It functions on the principle that these constituents can be precipitated out as insoluble salts. The process generally consists of two steps, with the first involving raising the pH of the feed water through the addition of either caustic soda (sodium hydroxide) or dolomitic lime (lime). Once the pH is raised, the hardness and alkalinity constituents precipitate mainly as calcium carbonate, magnesium hydroxide, and magnesium carbonate. Silica is simultaneously removed from the feed water through precipitation as magnesium silicate and through silica adsorption onto precipitated magnesium hydroxide. The second step in the process involves separating the solids from the treated water. Separation is typically accomplished through the use of an upflow clarification step, in which the water and solids are introduced to the bottom of the clarification vessel and flow upwards at a relatively low loading rate. Because of their mass, the solids slowly settle to the bottom as the treated water flows over a weir at the top of the unit. The solids, which form a sludge as they settle, are removed from the unit through a periodic or continuous blowdown. A polymer is typically added to increase the weight percent of solids in the blowdown sludge.

2.1.1 Unit Description

The unit to be used in the pilot test is a ClariCone precipitative softening unit, manufactured by CBI Walker, Plainfield, IL. It consists of a conical steel vessel, with a 2-ft diameter base that expands to 8-ft at the top. The total height of the unit is 12-ft, 8-in, and it occupies a footprint of 7.5-ft by 12-ft. Figures 2-2 and 2-3 show the plan and elevation views of the unit. The feed water is introduced at the base of the unit at up to a flow rate of 30 gpm. Caustic, lime, and/or polymer are also introduced at this location. After a short mixing, the treated water and precipitated solids begin flowing upwards through the unit. Because of the conical design of the vessel, the upflow velocity of the water decreases as it moves upwards through the unit. The decreasing velocity helps prevent the smaller precipitated particles from being carried over to the cooling tower. The solids are captured in the collection funnels located near the center of the unit and are removed via continuous blowdown. The clarified water spills over a weir into a collection box, which then conveys the water to the cooling tower.

2.1.2 Operating Conditions

The ClariCone unit is designed to handle the feed water at temperatures up to 190°F at atmospheric pressure. It is designed to treat a continuous feed water flow rate of 30 gpm supplied by a separate feed pump.

2.1.3 Chemical Feeds

Four chemicals will be used in the warm softening process to remove hardness, alkalinity, and silica. They are:

- Caustic soda (sodium hydroxide). Technical grade caustic is the cleanest chemical that can be used for this process. The higher cost of caustic soda over hydrated lime, and the increase in sodium levels in the softened water may pose limitations on the potential use of this chemical for warm softening.

- Lime. This chemical is often preferred over caustic soda because it is less expensive and supplements the magnesium concentration to assist in the silica removal. Due to its lower solubility, hydrated lime is often used as a slurry in the treatment process. The chemical will be supplied as slurry by the vendor. Although less expensive than caustic, use of lime requires substantially more operator attention than caustic because it is prone to frequent plugging and clogging in conveyance and chemical feed systems.

- Magnesium. This chemical is used in conjunction with either caustic soda or hydrated lime to increase the precipitation of silica as magnesium silicate. This chemical will be added directly as magnesium chloride solution or through the use of dolomitic lime, depending on cost and availability.

- Anionic polymer. This chemical will be added to increase the settleability of the sludge solids. Jar tests may be performed as needed to determine the optimum dosing rate range.

The chemicals will be stored separately in a storage container and will have individual metering pumps and feed systems. Caustic soda, lime and magnesium chloride storage and feed systems will be housed in secondary containment.

2.1.4 Solids Management

The solids generated in the process will consist mostly of calcium carbonate, magnesium carbonate, and magnesium hydroxide with smaller quantities of magnesium silicate, calcium sulfate, and borate salts. Based on this makeup, the solids from the process are not anticipated to be classified as a hazardous material. The solids will be separated from the water as a sludge in a blowdown stream and are anticipated to be anywhere from 2 percent to 20 percent solids by weight, depending on the chemicals added at the front end of the unit. The sludge blowdown will be captured in a watertight mud tank. Once in the tank, the sludge will be allowed stand so that the solids can further settle from the water. The excess water will be decanted from the mud tank and returned to the San Ardo produced water conveyance system. The settled solids will be removed for offsite disposal.

2.2 Cooling Tower

It is anticipated that the temperature of the softened water from the clarifier will be about 190°F. Cooling this water below 115°F is essential to protect the RO membranes. Cooling could be achieved through the use of either a heat exchanger or cooling tower. The cooling tower option was chosen for the pilot system due to the potential to strip the ammonia from the water.

2.2.1 Unit Description

The cooling process consists of two components: an equalization tank that captures the effluent from the precipitative softener, followed by the cooling tower. The equalization tank is a 6,500 gallon tank with a fixed overflow nozzle and a suction discharge at the base of the tank. The overflow drains the excess flow volume from the precipitative softener to the pilot system waste line. This configuration allows the tank to maintain a fixed water level and a fixed amount of total dynamic head for the feed pump to the cooling tower.

The cooling tower to be used in the pilot system is a 55-inch diameter by 111-inch tall single-pass unit. It is a countercurrent design with an approximate 56-inch depth of packing material and provides up to 25 tons of cooling. Effluent from the precipitative softener is fed to the cooling tower through a 2-½ -inch inlet at the base of the unit. Air to cool the water is provided through a ¾ HP blower. The cooled water, collected in a sump, is pumped to the membrane treatment process via a 2 ½-inch outlet at the base of the cooling tower. Schematics of the cooling tower will be included upon receipt from the vendor.

2.2.2 Operating Conditions

The equalization tank is expected to capture a 30 gpm effluent stream from the precipitative softener. 25 gpm is expected to flow through the cooling tower, with the 5 gpm balance to spill into the overflow line. The cooling tower is designed to reduce the water temperature from 190°F to 115°F at a flow rate of up to 50 gpm. Since the unit is oversized, it should be able to achieve the same temperature reduction for the anticipated 25 gpm stream.

2.3 Reverse Osmosis (RO)

RO functions on the principle that water can be separated from colloidal material and/or dissolved constituents by forcing the water through a semi-permeable membrane. In a typical operation, the untreated water is introduced on the feed side of the membrane where it is subjected to high pressure. Once the pressure of the feed water is increased beyond the osmotic pressure of the membrane, water will begin to pass or "filter" through leaving behind the colloidal material and/or dissolved constituents. The materials originally present in the feed are then left to concentrate in the remaining water on the feed side of the membrane. The water that passes through the membrane, or permeate, is collected as treated water. The water remaining on the feed side of the membrane, containing the now concentrated colloidal and dissolved constituents, is disposed of as brine.

This pilot system will utilize RO membranes as the primary treatment mechanism to remove boron, ammonia, organic compounds and TDS. Other membrane types, such as nanofiltration or ultrafiltration membranes, may also potentially be evaluated depending on the findings from the initial test runs with RO.

2.3.1 Unit Description

The pilot RO unit to be used in the pilot will be a VINTAGE™ V series system (VC06) from US Filter. The system consists of a 5 micron cartridge filter, six 4"X40" brackish water spiral bound membrane housed in six pressure vessels arranged in a five stage (2:1:1:1:1) array, a submersible pump, and a recycle line to return a portion of the reject stream into the incoming feed. The dimensions of RO unit are 72"(H)X38"(W)X34"(L). The unit requires a 480V power supply. The membranes to be used will be Fluid Systems XR "extra high rejection" polyamide membranes. Table 2-1 provides the design criteria for the system. Figure 2-3 shows the schematic and process flow diagram for the RO process.

2.3.2 Operating Conditions

The RO unit will be operated with 75 percent water recovery. At a feed rate of 10 gpm, the RO unit will produce about 7.5 gpm of permeate and 2.5 gpm of RO concentrate (brine). The flux rate would be about 25 gpd/sf of membrane area. The feed water pressure at the suction side of the booster pump must be between 15 and 25 psig. The unit will be operated approximately at a feed pressure of about 320 psig.

2.3.3 Chemical Feeds

PreTreat Plus 0100, an inorganic scale inhibitor/antifoulant manufactured by King Lee Technologies, will be added to the RO feed water during all test runs at a rate of 1 mg dry powder/L feed water to reduce the prospect for inorganic fouling. During pH < 9.6 and all following trials, Protec RO, an organic antifoulant manufactured by King Lee Technologies, will also be added to the RO feed water at a rate of 5 mg dry powder/L feed water to minimize potential residual oil fouling. Cleaning will be performed using DIAMITE AFT manufactured by King Lee Technologies when either a pressure drop of 20 percent is observed between stages or a 20 percent pressure increase is observed across the membrane at the inlet to the first stage. Ninety gallons of cleaner will be made by diluting 1 part concentrated cleaning solution to 40 parts water. For each cleaning, the solution will be circulated through the RO unit at 20 gpm and 60 psi for 1 hour.

2.3.4 Clean In Place

USFilter CIP-30 Clean-in-place system (CIP) will be used for cleaning the RO unit. This unit consists of a solution tank (90 gallons), centrifugal recirculation pump (30 gpm, 70 psig, 5 HP) and a filter housing. The overall dimensions of the unit are 72"(L)X41"(W)X41"(H). During the cleaning cycle, the RO unit will be taken offline and the valving reconfigured so that the CIP system can pump cleaning solution through the RO in a closed recirculation loop.

TABLE 2-1
Design Parameters for RO Process During Phase 2A Study
Aera Energy LLC-DOE Produced Water Pilot Study

Design Parameter	Units	Value
Cartridge Filter		
Number of Units		1
Feed Rate	Gpm	10
Filter Rating	µM	5
Size (diameter x length)	Inch x inch	2.5" x 10"
RO		USFilter Membrane Systems
Number of Stages		5
Number of Vessels		6
Elements per Vessel		1
Membrane Elements		Fluid Systems XR
Number of Elements	-	6
Size (diameter x length)	inch x inch	4 x 40
Effective Surface Area	Sf/Element	72
Flux Rate	gpd/sf	15.7
Permeate Flow Rate	Gpm	7.5
RO Concentrate Flow Rate	Gpm	2.5
Percent water recovery	%	75
Feed Pressure	Psi	350

Cleaning will be performed using DIAMITE AFT manufactured by King Lee Technologies when either a pressure drop of 20 percent is observed between stages or a 20 percent pressure increase is observed across the membrane at the inlet to the first stage. In addition, the RO unit will be purged through a cleaning cycle prior to changing test conditions. Ninety gallons of cleaner will be made by diluting 1 part concentrated cleaning solution to 40 parts water. For each cleaning, the solution will be circulated through the RO unit at 7 gpm and 60 psi for 1 hour.

Section 3: Installation and Demobilization

Installation is anticipated to take two to four weeks, depending on the arrival of vendor rented equipment, availability of contract construction personnel, and availability of facilities/equipment supplied by Aera Energy LLC. Delineation of responsibilities during installation is as follows:

- Aera Energy LLC will provide utilities (potable water as available, power, disposal facilities for sludge and spent chemicals, etc), large storage tankage for chemicals, and secondary containment for chemical storage.
- Aera Energy LLC will supply contract personnel and construction equipment for system construction.
- Aera Energy LLC will supply all piping, meters, gauges, valves, and associated fitting necessary for construction of the pilot system.
- Kennedy/Jenks will supply construction oversight.
- Kennedy/Jenks will supply chemical feed equipment, chemical storage tanks not available through Aera Energy LLC, and chemicals.
- Kennedy/Jenks will subcontract equipment vendors for rental of pilot units.

Demobilization is anticipated to take two weeks. Delineation of responsibilities during demobilization is as follows:

- Aera Energy LLC will supply contract personnel and construction equipment for system disassembly.
- Aera Energy LLC will dispose of all residual materials from the pilot system (pipes, fittings, etc.)
- Kennedy/Jenks will coordinate disposal of all residual chemicals at the end of the pilot test.
- Kennedy/Jenks will supply field oversight during demobilization activities.
- Kennedy/Jenks will coordinate with vendors for return shipping of rental pilot units.

Section 4: Test Schedule and System Operations

4.1 Test Schedule

The pilot investigation is scheduled to run for a 9-month test period during which a number of operating conditions will be evaluated. Because the later stages of testing will depend on the findings of the initial test runs, the pilot investigation has been divided into two phases (2A & 2B). The first phase (2A) will run for four months and is intended to establish the optimum baseline conditions for the various chemicals that are to be evaluated. Table 4-1 summarizes the test conditions during the initial four-month operating period.

TABLE 4-1
Phase 2A Tests
Aera Energy LLC-DOE Produced Water Pilot Study

Week	Precipitative Clarifier Chemical(s) Added	Target Effluent pH	Reverse Osmosis Target Feed pH
1	Caustic Soda	9.7	9.7
2	Caustic Soda	9.7	9.7
3	Caustic Soda	9.7	9.7
4	Caustic Soda Magnesium Chloride	9.7	9.7
5	Caustic Soda Magnesium Chloride	9.7	9.7
6	Caustic Soda Magnesium Chloride	9.7	9.7
7	Caustic Soda Magnesium Chloride	9.7	10.75
8	Caustic Soda Magnesium Chloride	9.7	10.75
9	Caustic Soda Magnesium Chloride	9.7	11
10	Caustic Soda Magnesium Chloride	9.7	11
11	Dolomitic lime	9.7	9.7
12	Dolomitic lime	9.7	9.7
13	Dolomitic lime	9.7	9.7
14	Dolomitic lime	9.7	9.7
15	Dolomitic lime	9.7	9.7
16	Dolomitic lime	9.7	9.7

The scope and schedule of Phase 2B will be defined based on the results from Phase 2A study. However, the tentative scope of the work and schedule (Table 4-2) during this phase are provided below:

- Evaluation of a biocatalyst/surfactant system developed by Advanced Biocatalytics Corporation, Irvine, CA for the cleaning of RO membrane to enhance membrane life. The catalyst may be added continuously or at the end of each cycle.
- Evaluation of a membrane developed by Osmonics (DS-3) to compare with the performance of USFilter XR membrane. This duraslick thin film element is designed to treat high fouling brackish waters. Membrane life and effectiveness of treating oil field produced water of this membrane will be compared with those of the USFilter DX membrane.
- Evaluation of warm precipitation using spent caustic from refinery operations using bench scale studies

TABLE 4-2
Phase 2B Tests
Aera Energy LLC-DOE Produced Water Pilot Study

Week	Precipitative Clarifier Chemical(s) Added	Target Clarifier Effluent pH	Reverse Osmosis Target Feed pH	Comments
1	Caustic Soda	9.7	9.7	Continuous Biocatalyst Feed
2	Caustic Soda	9.7	9.7	Continuous Biocatalyst Feed
3	Caustic Soda	9.7	9.7	Continuous Biocatalyst Feed
4	Caustic Soda	9.7	9.7	Biocatalyst cleaning at the end
5	Caustic Soda	9.7	9.7	Biocatalyst cleaning at the end
6	Caustic Soda	9.7	9.7	Biocatalyst cleaning at the end
7	Caustic Soda	9.7	9.7	Osmonics DS-3 Membrane[1]
8	Caustic Soda	9.7	9.7	Osmonics DS-3 Membrane
9	Caustic Soda	9.7	9.7	Osmonics DS-3 Membrane
10	Dolomitic lime	9.7	9.7	Osmonics DS-3 Membrane
11	Dolomitic lime	9.7	9.7	Osmonics DS-3 Membrane
12	Dolomitic lime	9.7	11	Osmonics DS-3 Membrane
13	Dolomitic lime	9.7	11	Osmonics DS-3 Membrane
14	Dolomitic lime	9.7	11	Osmonics DS-3 Membrane
15	Dolomitic lime	9.7	11	Osmonics DS-3 Membrane
16	Dolomitic lime	9.7	11	Osmonics DS-3 Membrane

4.2 System Monitoring

The Kennedy/Jenks staff will operate the pilot treatment units during business week days. During the evenings and on weekends, when there is no demonstration staff at the site, Aera staff will respond to any alarms and shut the plant down. Demonstration plant staff will fix the problems and restart the plant the following weekday except on Friday. If it is a Friday, the plant will be restarted the following Monday for routine operations.. Operators will use log sheets to record pilot plant operating data. Kennedy/Jenks staff will also perform field water quality analyses and collect samples for outside laboratory analyses, consistent with the Sampling and Analysis Plan.

4.2.1 Warm Softening Process

Log sheets will be set up to record produced water flow rate to the clarifier, effluent recirculation flow rate, and net operating flow rate through each of the unit inlets. We will monitor these parameters, adjust the flow meters to the target rate as necessary, and record the results every 3 hours until we get operating history on the unit. We will also record the frequency and duration of the automatic sludge blowdown. We should also make a visual inspection of the unit and the sludge blanket from the bridge at least twice a day.

4.2.2 Cooling Tower

Log sheets will be set up to record flow rates to the influent and temperature at the influent and effluent of the cooling tower. Operating staff should monitor and record the readings every three hours.

4.2.3 RO Process

Log sheets will be set up to record flow rates (RO feed, permeate, and RO concentrate), pressures (cartridge filter feed, post cartridge filter, boosted RO feed, permeate – as provided by vendor). Staff should monitor these instruments and record these values once every 3-hours. Staff should also record temperature, pH, and electrical conductivity from the meters provided on the units at least daily.

4.2.4 Chemical Feed Systems

The operators need to determine the chemical feed rate for each chemical fed to each process unit so that the chemical dosage being used is documented. During the each monitoring round performed by the operator, data on the chemical feed rate (ml/min) to each process unit will be recorded on the log sheet. Additionally, the chemical feeds will be adjusted if the dosing rate is observed to have drifted from the dosing target.

4.3 Equipment Calibration/Adjustment

The pilot plant is not automated and most of the treatment processes will require periodic adjustment or calibration of key flow rates, operating pressures, chemical feed rates, and residuals production rates. Each of these items for each process unit is addressed below.

4.3.1 Pressure/Flow Rate Adjustment

The sections below address the requirements to adjust the pressure and flow for each treatment processes in the pilot system.

4.3.1.1 Warm Softening Process

Produced water from the walnut shell filter is discharged to a 6,500 gallon storage tank, which supplies the feed for the warm softening process. The produced water is pumped from the tank to the clarifier unit with a centrifugal pump. The pump is controlled via start/stop pushbuttons mounted locally on panel adjacent to the pump. Flow from the tank to the clarifier unit is controlled with a 2" butterfly valve located just downstream of the pump and a 0 – 50 gpm rotameter. Downstream of the valve and rotameter, the produced water feed is combined with a recirculation stream that reintroduces treated effluent from the process back to the influent of the unit. A separate centrifugal pump is used to recirculate the treated effluent back to the influent and is controlled with locally mounted on/off pushbuttons. The recirculation flow is controlled through the use of a 1" ball valve and a 0 – 20 gpm rotameter, both located on the discharge line of the recirculation pump. The combined influent is introduced at the base of the clarifier unit through two pairs of tangentially oriented inlet pipes (four total). Flow through each pipe is controlled with a ball valve. A 0 – 30 gpm rotameter is located upstream of each pair of inlet pipes to indicate the flow.

To adjust the flow into the clarifier unit, the produced water feed is first set. Then, the recirculation flow rate is adjusted. Once these flows are set, the combined influent is balanced between the two pairs of inlet pipes at the base of the clarifier unit. The clarifier unit does not operate under pressure (water level controlled by an overflow weir) and, consequently, does not have any controls for pressure.

4.3.1.2 RO Unit

In the RO operating configuration, the feed water is supplied to an RO booster pump that, in turn, increases the pressure to the level required for the membrane process to achieve the desired recovery. As part of such a configuration, the operating criteria specified by the RO vendor must be maintained. These include the following:

- Raw Water Supply Pressure – The pressure on the suction side to the RO booster pump must be maintained between 15 and 50 psig. A pressure gauge for this purpose is located just upstream of the RO booster pump.
- RO Feed Water Temperature – The total feed temperature to the RO must not exceed 113°F.
- RO Feed Water Temperature - The total feed flow must be maintained approximately at 10 gpm. Flow meters for the permeate and concentrate lines are used to determine the total flow through the unit.

While maintaining these operating requirements, the RO unit must also be maintained at the target recovery for the pilot test period. The following valves are used to balance these three operating parameters:

- Concentrate Control Valve – This valve is located on the concentrate line of the RO skid and is used to set the recovery of the unit.
- Influent Water Throttling Valve – This gate valve is located on discharge pipe from the warm softening unit. It is intended to provide control over the total flow output from the softener.
- Softened Water Bleed-off Valve – This gate valve controls the volume of water from softener unit that is allowed to discharge directly to the waste discharge line as excess flow. This valve is used to help control the feed pressure to the RO unit on the suction side of the RO booster pump.

- RO Booster Pump Throttling Valve – This gate valve is located immediately downstream of the RO booster pump and is used to control the membrane feed pressure and total feed water flow through the RO unit.

Adjustments to any of these valves may impact the feed pressure to the RO booster pump, the total feed flow to the RO unit, and the recovery to shift. Therefore, adjustments to maintain the RO at the desired operating conditions will generally require balancing of all four valves.

4.3.2 Chemical Feed Systems

This section lists the chemical feeds and the chemical feed pump types used for each treatment process. Note that Section 4.3.3 immediately following this section provides the procedure to adjust the chemical feed rates.

- Reverse Osmosis:
    - Antiscalant (King Lee Pretreat Plus 0100) – diaphragm metering pump.
    - Antifoulant (King Lee Protec RO) - diaphragm metering pump.
    - Cleaning Solution (King Lee DIAMITE AFT) – USFilter CIP30 with centrifugal pump.
- Warm Softener:
    - Dolomitic Lime (45 percent hydroxide) – progressive cavity metering pump.
    - Caustic Soda (20 percent sodium hydroxide) – diaphragm metering pump.
    - Magnesium Chloride (27 percent solution) – diaphragm metering pump.
    - Chemtreat P-813E, (King Lee - a 35 percent by weight anionic polyacryamide polymer) - diaphragm metering pump

4.3.3 Chemical Feed System Adjustment

All chemical feed systems except the CIP are manually controlled and utilize calibration columns to make adjustments to the chemical dosing rates. The following is the procedure used to perform a chemical feed system calibration for any of the systems listed in Section 4.3.2:

1. Open the valve at the base of the calibration column while the chemical feed system is in operation. The column is located on the suction side of the chemical feed pump at an elevation near the base of the chemical storage tank. The static head provided by the chemical level in the tank will allow the column to fill.
2. Once the column fills above the "0 ml" mark, close the valve on the suction line that allows the chemical feed pump to draw chemical from the storage tank. The pump will begin drawing chemical from the calibration column.

3. When the liquid level in the column drops to the "0 ml" mark, observe the volume of chemical drawn down in 60 seconds. This is the actual dosing rate. Time is monitored with a stopwatch.

4. Open the valve on the pump suction line allowing the chemical feed pump to draw from the storage tank. Close the valve at the base of the calibration column. The chemical feed pump is now reconfigured for normal dosing operation.

5. If chemical is not being dosed at the target level, adjust the local speed and stroke controls (diaphragm metering pumps) or the local speed the speed control (peristaltic pumps). Repeat steps 1 – 4 until the target dosing rate is achieved.

4.3.4 Residuals

The unit processes will generate residual streams as part of their normal operation. They include the following:

- Warm Softening Process – Residuals from this process will include sludge, consisting mostly of calcium carbonate, calcium hydroxide, magnesium hydroxide, and magnesium carbonate. These materials are anticipated to be removed from the clarifier unit via a blowdown line as a 10 to 20 percent solids sludge stream. Sludge blowdowns will be controlled through a timer and a motorized valve. Sludge blowdowns will initially be set for 20 second durations at 90 minute intervals, per recommendations from the equipment manufacturer. The blowdown durations and frequencies will be adjusted as needed based on the findings of each test run.

- RO Process – The RO unit will be operated with 75 percent water recovery. At a feed rate of 10 gpm, the unit will generate a reject stream of 2.5 gpm. The reject stream will have a TDS of about 24,000 mg/l and a temperature of about 110°F. A portion of the reject stream will be recirculated to the feed water stream to the RO process. The remaining flow will be discharged back into Aera Energy LLC produced water disposal system. The recirculation and waste stream flows are controlled by two ¾" throttling valves.

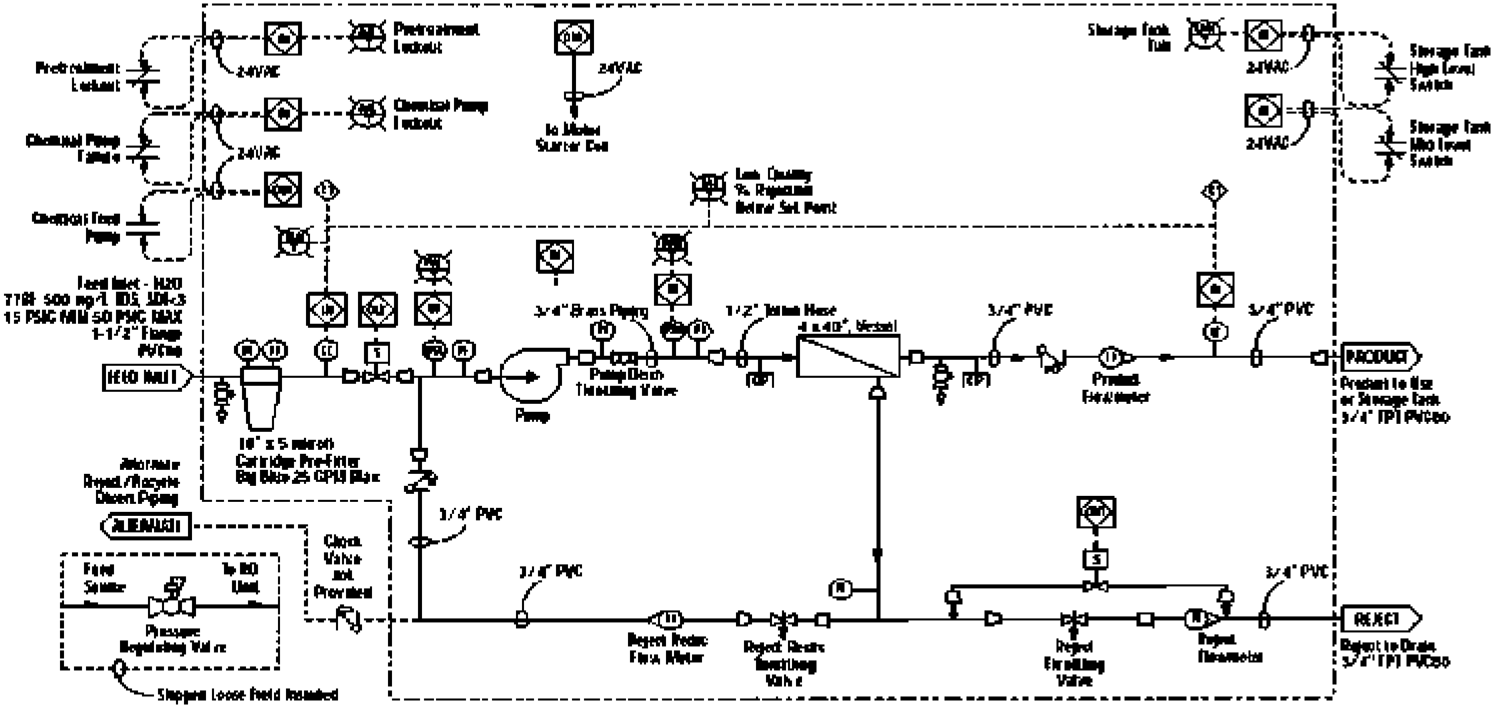

Figure 2-4. USFilter VANTAGE™ RO Process Flow Diagram

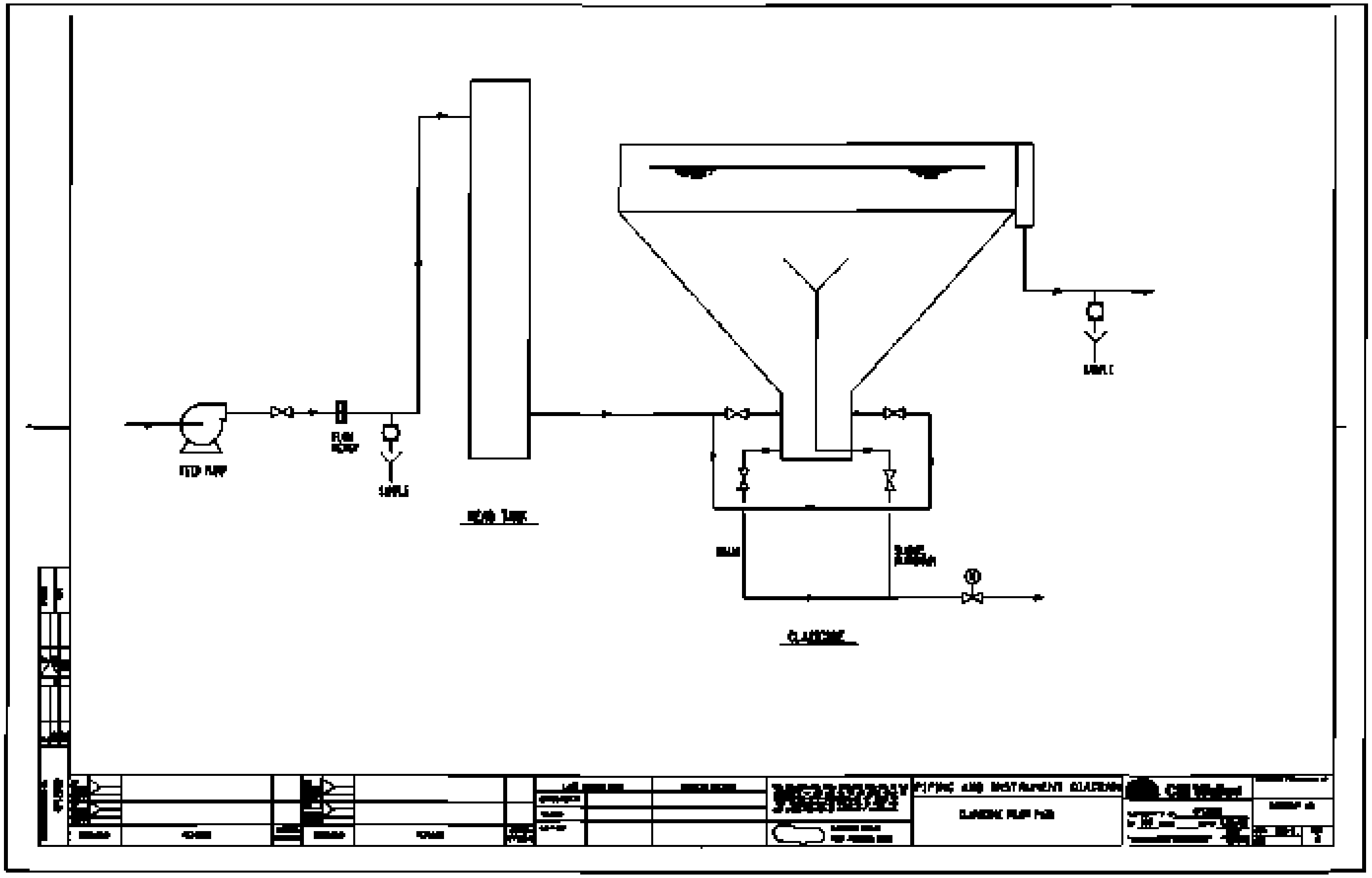

Figure 2-2. Elevation View of the CBI Walker Caricone Pilot Unit

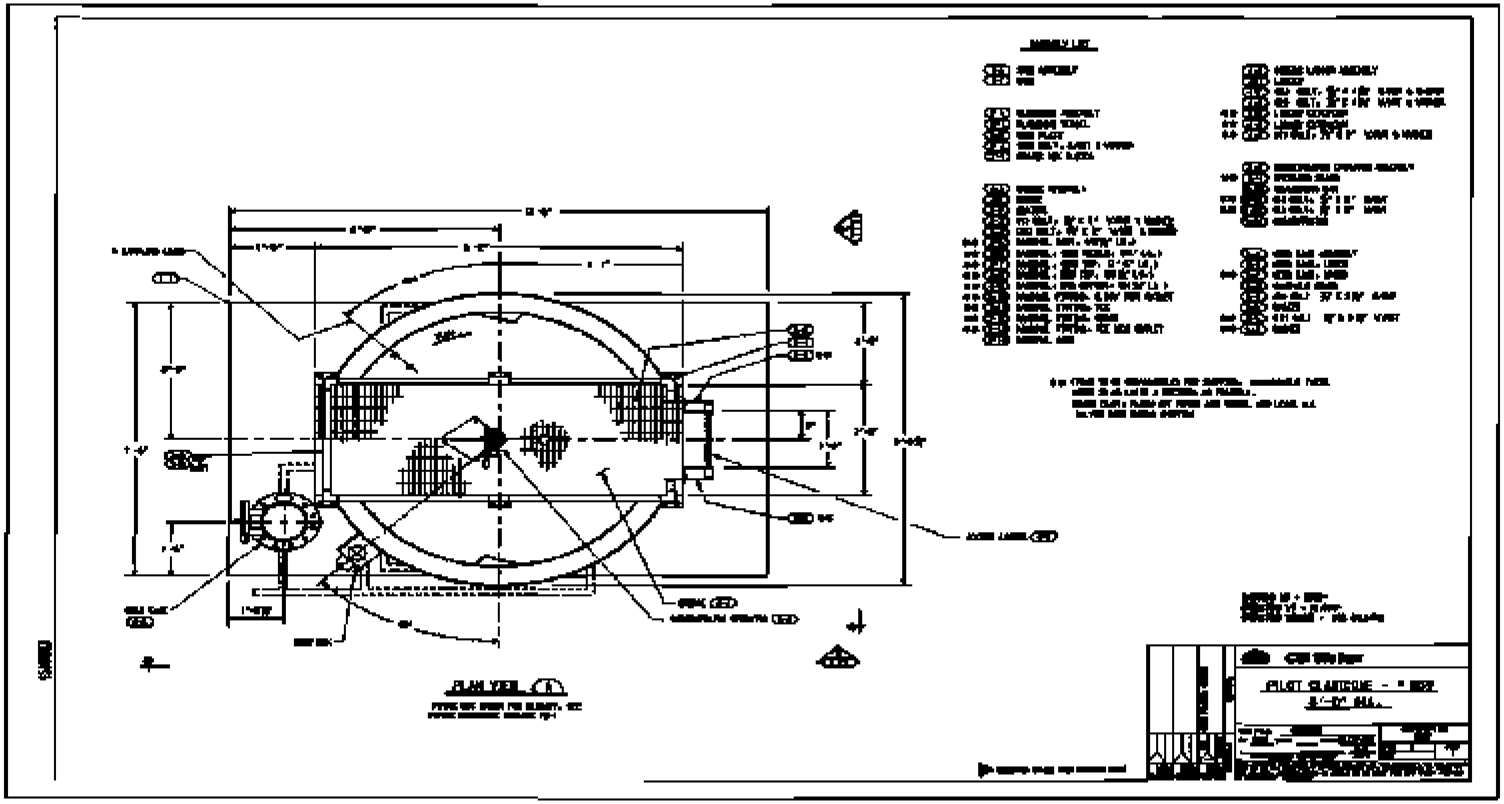

Figure 2-3. Plan view of the CBI walker ClariCone Unit

Hazardous Substance Plan

Project Title:

Recovery of More Oil-in-Place at Lower Production Costs While Creating a Beneficial Water Resource

COOPERATIVE AGREEMENT
INSTRUMENT NO.: DE-FC26-02NT15463

November 19, 2002

RECIPIENT: **Aera Energy LLC**
10000 Ming Avenue
P.O. Box 1164
Bakersfield, CA 93389-1164

This plan identifies each hazardous substance as defined under 40 CFR 261, subpart D anticipated to be purchased, utilized or generated in the performance of this Cooperative Agreement.

There are no hazardous substances anticipated to be purchased, utilized or generated in the performance of this Cooperative Agreement as defined under 40 CFR 261 subpart D.

Information Type	**Information**
Description of Substance/Chemical	None
EPA Hazardous Waste Number	None
EPA Hazard Code	None
Anticipated Quantity to be purchased, utilized or generated	None
Anticipated Hazardous Waste Transporter	None
Anticipated Hazardous Waste Disposal Facility	None
Participant and Location	Not Applicable
Anticipated Treatment Method	None

Kennedy/Jenks Consultants

2151 Michelson Drive, Suite 100
Irvine, California 92612-1311
949-261-1577
949-261-2134 (Fax)

Draft Site Health and Safety Plan
Aera Demonstration Plant
San Ardo Oilfield, San Ardo, California

4 June 2003

Appendix A

Prepared for

Aera Energy LLC
66893 Sargent Canyon Road
San Ardo, Ca 93450

K/J Project No. 000000.00

Table of Contents

Table of Contents (cont'd)

List of Tables

Site Health and Safety Plan Summary

Site Name: Aera Demonstration Plant

Address: San Ardo Oilfield

Site Telephone: To Be Determined

Project Start Date: To Be Determined

K/J Job Number: 034

Site Safety Officer (SSO): Sunny Huang

Project Manager: Larry Leong

Type of Investigation:

Sampling Investigation:
- ☐ Hand Auger
- ☐ Drilling
- ☐ Trenching
- ☐ Well Installation
- ☐ Soil Sampling
- ☐ Groundwater Sampling
- ☒ Other: Treatment Plant Operation

Site Remediation:
- ☐ Excavation
- ☐ Treatment System Installation
- ☐ UST Removal

☐ Site Walk-through

☐ Other: ____________

Potential Hazards:

☐ Organics
☐ Inorganics
☐ Metals ☐ Acids
☐ Solvents ☒ Bases
☐ Pesticides ☐ Fire/Explosion
☐ Other: ____________

Personal Protective Equipment:

☐ Level C
☒ Level D

Section 1: Introduction

This Site Health and Safety Plan establishes general health and safety protocols for Kennedy/Jenks Consultants (Kennedy/Jenks) personnel at the Aera Energy Produced Water Pilot Study Treatment Plan located at the San Ardo Oilfield, Monterey County, California. As needed, addenda containing activity-specific health and safety protocols will be prepared and attached to this Site Health and Safety Plan prior to the initiation of each additional field activity. The Site Health and Safety Plan and activity-specific addenda, as a minimum, contain the following information:

- Names of key personnel and alternates responsible for site health and safety and appointment of a Site Safety Officer.
- A health and safety risk evaluation for each site task and operation.
- Personal protective equipment to be used by employees for each site task and operations being conducted.
- Medical surveillance requirements.
- Frequency and types of air monitoring, personal monitoring and environmental sampling techniques and instrumentation to be used. Methods of maintenance and calibration of monitoring and sampling equipment to be used.
- Site control measures.
- Decontamination procedures.
- Site's standard operating procedures.
- An Emergency Response Plan that addresses effective site response to emergencies.

For informational purposes only, this plan may be provided to subcontractors of Kennedy/Jenks involved in activities at the Site, interested regulatory agencies, or others. However, entities and personnel other than Kennedy/Jenks shall be solely responsible for their own health and safety and shall independently assess onsite conditions and develop their own health and safety protocols. Entities or personnel that anticipate using health and safety measures which are less stringent than Kennedy/Jenks' measures should immediately contact the Kennedy/Jenks Site Safety Officer (SSO).

Kennedy/Jenks has developed a corporate health and safety program (Kennedy/Jenks Consultants, Industrial Services Group, Corporate Health and Safety Program, June 1991). The corporate program complies with current health and safety regulations, including OSHA 29 CFR 1910.120, Hazardous Waste Operations and Emergency Response, and CalOSHA Standards (8 CCR 5192). Many of the protocols of the corporate program are conducted on a routine basis (general training, respirator fit testing, general medical record keeping, etc.) and are not repeated herein. The corporate program is available to Kennedy/Jenks employees. Questions regarding the corporate program are referred to the Kennedy/Jenks Regional Safety Supervisor.

A copy of the Site Health and Safety Plan along with any addenda containing activity specific health and safety information will be kept in a conspicuous location at all times while work is being conducted at the site.

Section 2: Key Health and Safety Personnel

The Kennedy/Jenks SSO is Sunny Huang. In the absence of the SSO during field activities, a member of the site operators team will be designated as the Kennedy/Jenks Field Site Safety Officer (FSSO). The SSO or FSSO is responsible for the following.

- Observing field activities for compliance with this Site Health and Safety Plan, applicable addenda, and Kennedy/Jenks' Corporate Health and Safety Program.
- Maintaining the onsite medical surveillance, if required, and emergency medical treatment programs, and assisting in onsite emergencies.
- Modifying health and safety protocols or terminating field work when unsafe work conditions exist.
- Familiarizing personnel with health and safety protocols.
- Observing that field personnel wear appropriate personal protective equipment.
- Evaluating potential hazards.
- Recording the occurrence of any site injury or illness.

If unsafe conditions are encountered, if illness or injury occurs, or if the level of protection needs to be changed, the SSO or FSSO will consult in a timely manner with the Project Manager, Larry Leong, or the Corporate Industrial Hygienist, Bert Drews.

Section 3: Site Description and History

Kennedy/Jenks Consultants will conduct a pilot study at the San Ardo Oilfield to assess treatment technologies for produced water from the oil production process. The goal of this project is to evaluate the potential of eliminating or reducing the volume of produced water reinjected into the formation following oil recovery activities. The benefits from eliminating the reinjection of produced water may be an increase the oil yield from the formation, reduction in energy costs associated with reheating the reinjected produced water, and providing an alternative source of potable water to nearby users.

The San Ardo Oilfield is located in Monterey County in central California, approximately 45 miles north of the city of San Luis Obispo. There are two oilfield operators in the San Ardo Oilfiled, Aea Energy and Chevron Texaco. Aera's portion of the San Ardo Field covers an area of over 2,600 acres. The field consists of two main oil reservoirs, the Aurignac and the Lombardi. Both reservoirs are currently being produced using continuous steam injection. Field volumes for March 2002 were 8,294 barrels of oil per day, 44,015 barrels of steam per day, and 89,800 barrels of water disposal per day. Monterey County is the fifth largest crude oil producing county in California (Department of Conservation, 2001).

In order to stop Class II injection of the excess produced water, it is necessary to identify an appropriate alternative method for managing produced water. Alternatives include treatment for NPDES discharge into streams for groundwater recharge and/or treatment for beneficial use. This project is intended to show potential water users and regulatory agencies that produced water can be reliably treated to a quality acceptable for NPDES discharge, agricultural, or non-flange to flange municipal beneficial reuse.

After construction of the demonstration plant and system startup, it is estimated that the pilot study will be completed in two phases and be conducted over an eight month operating period to demonstrate that produced water can be treated to meet the following: 1) those criteria required by Aera; 2) those criteria required by the regulatory agencies; and 3) those criteria required by the end users of the treated water.

The first phase of operation will provide operational data on the technologies and operating procedures outlined by the Work Plan. Based on the information gathered from the first phase of operation the tests and operational scheme may be adjusted for additional testing in the second phase, which is also scheduled for approximately 4 months of operation.

Section 4: Planned Site Activities

The goal of this project is to design, construct, and operate a demonstration plant at Aera's San Ardo Oilfield to demonstrate that produced water can be treated to meet the project goals. The demonstration plant design will build on the DOE funded project that was completed at the Placerita Canyon oilfield. The demonstration plant will include warm softening to remove silica and hardness. Several chemicals will be used for this portion of the test. They include; virgin caustic, waste caustic, magnesium chloride, sodium hydroxide, dolomitic lime, and polymer chemicals. A claricon separation unit will be used to remove the precipitated solids from the produced water stream. The treated effluent will then be cooled from approximately 180 F inlet temperature to less than 115 F via a cooling tower. After which, sodium hydroxide and antiscalants are mixed into the stream before filtration through 5 micron cartridge filters. The stream is then treated by reverse osmosis before discharge of the permeate and reject back to the produce water reinjection stream.

The facility is anticipated to be constructed on a ½ acre of the San Ardo Oilfield. Construction will include installation of concrete pads and electrical service to be provided by Aera. Aera will be responsible for construction of the demonstration plant per Kennedy/Jenks designs and engineering support.

Following construction of the demonstration plant. Kennedy/Jenks and Aera will work together to test the system and complete the startup and shakedown phase of the project. Once the demonstration plant is deemed operational the system will be operated 24 hours a day, Monday through Friday. The plant will not operate on the weekends. Kennedy/Jenks will provide an onsite operator for approximately 8 hours each Monday through Friday. This work plan is intended to address safety issues related to the operation of the demonstration plant. Field staff will be familiar with this document and undergo all training required by Aera to be eligible to work on the demonstration plant site.

Section 5: Health and Safety Hazard Assessment

5.1 Potential Physical Hazards

Field personnel should be cognizant of potential physical hazards associated with use of heavy equipment and electrical equipment during field operations. Appropriate precautions include the following:

- ANSI-approved hardhats, safety glasses or goggles, and steel-toe boots will be worn.
- Loose clothing that may catch in moving parts will not be worn.

Prior to installation of equipment, a utility survey shall be conducted to identify overhead electrical hazards and potential ground hazards, such as underground storage tanks or underground utilities.

5.1.1 Excavation

Field personnel should not enter any excavations exceeding 5 feet in depth unless the excavations are properly shored, braced or sloped and a safety ladder is provided for ready access or egress. Twenty-four hours prior to any excavation activity underground service alert should be notified.

5.1.2 Confined Space Entry

Kennedy/Jenks personnel will not enter any confined space without advanced specific preparation, planning, training, and supervision by the Regional Safety Supervisor. A confined space is defined by OSHA as the concurrent existence of the following conditions.

- Is large enough and so configured that an employee can bodily enter and perform assigned work; and
- Has limited or restricted means for entry or exit (for example, tanks, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry); and
- Is not designed for continuous employee occupancy.

5.1.3 Tripping and Falling Hazards

Piping, hoses and other equipment may pose a tripping hazard at the site. Since most of the equipment will be installed above ground care should be taken when moving around the site. Obstacles that are obvious tripping hazards will be marked with caution tape to alert site employees and visitors.

5.1.4 Heat Stress

At times site conditions may pose a threat from a heat stress standpoint. The reported normal seasonal temperatures at the site range to approximately 90 degrees F. However, maximum temperatures historically have reached temperatures exceeding 110 degrees F at the site. In addition the heat from the operating equipment and heat radiating from the inlet piping with produced water at temperatures of approximately 180 degrees F may also contribute to heat stress. Preventative measures should include the following:

- Water and/or commercial electrolyte solutions will be available and drinking of these fluids will be encouraged. The water will be kept reasonably cool

Personnel exhibiting symptoms of heat stress (nausea, cramps, dizziness, clammy skin) will be removed from the work area, cooled, fluids will be administered, and the personnel will be observed. Personnel exhibiting symptoms of heat stroke (hot dry skin, mental confusion, unconsciousness) will be immediately cooled and taken to the hospital.

5.2 Hazardous Substances and Other Onsite Chemicals

It is anticipated that several hazardous chemicals will be used as part of the treatment process at the demonstration plant. These chemicals are 20% to 40% virgin and waste caustic and sodium hydroxide. In addition to these hazardous chemicals additional chemicals will be onsite. These include; magnesium chloride, dolomitic lime, Claricone polymer, and antiscalant/antifoulant. Field personnel will minimize potential chemical hazards by (1) avoiding direct contact with any chemical and feed water.

5.2.1 Virgin/Waste Caustic

Virgin and waste caustic at between 20% to 40% concentrations will be used to remove hardness from the influent water. It will be stored in polyethylene tank with secondary containment. It will be delivered using a metering pump by direct feed into the Claricone mixing unit. Worker exposure during normal operations is expected to be minimal. Appropriate precautions include the following:

- The storage tank will be labeled appropriately,
- All work and operating adjustments related to the caustic storage tank, metering pump, and associated feed lines will be conducted using a face shield over safety glasses and rubber gloves.
- Eye wash station will be located in close proximity to the caustic storage tank.
- The caustic storage tank will be located in a well-ventilated area.
- Adsorbent material will be stored nearby in case of a spill. Site personnel will familiarize themselves with the appropriate spill containment procedures for caustic that are described in the MSDS.

5.2.2 Sodium hydroxide

Sodium hydroxide will added to at the Claricone mixing unit and the cooling tower effluent. It will be stored in a polyethylene tank with secondary containment and delivered to the process stream using two metering pumps. Worker exposure is expected to be minimal. Appropriate precautions include the following:

- The storage tank will be labeled appropriately,
- All work and operating adjustments related to the sodium hydroxide storage tank, metering pump, and associated feed lines will be conducted using a face shield over safety glasses and rubber gloves.
- Eye wash station will be located in close proximity to the sodium hydroxide storage tank.
- The sodium hydroxide storage tank will be located in a well-ventilated area.
- Adsorbent material will be stored nearby in case of a spill. Site personnel will familiarize themselves with the appropriate spill containment procedures for sodium hydroxide that are described in the MSDS.

5.2.3 Dolomitic Lime

Dolomitic lime will be stored in polyethylene tank with secondary containment. It will be delivered using a metering pump by direct feed into the Claricone mixing unit. Worker exposure during normal operations is expected to be minimal. Appropriate precautions include the following:

- The storage tank will be labeled appropriately,
- All work and operating adjustments related to the caustic storage tank, metering pump, and associated feed lines will be conducted using a face shield over safety glasses and rubber gloves.
- Eye wash station will be located in close proximity to the storage tank.
- The caustic storage tank will be located in a well-ventilated area.
- Adsorbent material will be stored nearby in case of a spill. Site personnel will familiarize themselves with the appropriate spill containment procedures for dolomitic lime that are described in the MSDS.

5.2.4 Other Chemicals

A proprietary polymer as well as antiscalant/antifoulant will be stored in polyethylene tanks with secondary containment. These chemicals will be delivered using a metering pumps by direct feed into the process system. Worker exposure during normal operations is expected to be minimal. Appropriate precautions include the following:

- The storage tank will be labeled appropriately,
- All work and operating adjustments related to these tanks, metering pumps, and associated feed lines will be conducted using safety glasses and protective gloves.
- Eye wash station will be located in close proximity to these storage areas.
- Adsorbent material will be stored nearby in case of a spill. Site personnel will familiarize themselves with the appropriate spill containment procedures for these chemicals that are described in the MSDSs.

5.3 Hot Equipment

It is anticipated that piping and process units for the inlet produced water may reach temperatures up to 180 degrees F. Site staff and visitors will be alerted about the hot equipment upon their first arrival on site. In additional the accessible hot piping or process equipment will be marked with labels or signs to mark them as hot and potential burn hazards.

Section 6: Protective Actions

6.1 Personnel Protective Equipment

Field personnel will wear equipment to protect against the potential physical and chemical hazards, which have been identified herein, and those that become apparent in the field. Level D protection will be required at a minimum for field activities at the site. Level D personal protective equipment to be used will include:

- ANSI-approved hard hat
- Chemical resistant gloves - disposable PVC or nitrile when exposed to chemicals or process water
- Boots, steel toe and shank
- Work clothes or Tyvek
- ANSI-approved safety glasses
- Safety goggles or a face shield should be used when a foreseeable splash hazard exists
- Disposable hearing protection during high-noise activities

The level of protection employed may be upgraded, as deemed necessary by the SSO or FSSO.

If non-routine field activities are initiated, the level of protection will be specified in the activity-specific health and safety addenda.

6.2 Site Control

Site control measures will be established with Aera site personnel. Site security measures will include restrictive fencing around the facility. The site will be secured be a lockable gate when project personnel are not onsite. A visitors and employees log will be kept to document onsite personnel. Everyone that comes on site will be required to sign in and out upon arrival and departure. No unauthorized visitors will be allowed on site.

6.3 Training

Kennedy/Jenks personnel participating in field activities will have completed the a site specific health and safety training that covers the information presented in this Health and Safety Plan. In addition, all personnel will be required to complete the necessary training required by Area for workers in the San Ardo Oilfield. Routine safety meetings will be held to reiterate the site safety concerns and to identify additional safety issues.

6.4 Sanitation and Illumination

The site will have drinking water, washing water, and restroom facilities available. Operational activities will take place during daylight hours. Because natural illumination (approximately

50 to 200 foot candles) will be sufficient to meet the 5-foot candle requirement for general site areas, no additional illumination will be required.

Section 7: Emergency Response Plan

Hazard recognition is an essential part of the Emergency Response Plan. Initiation of the contingency plan relies on the employee's ability to recognize an emergency or potential for an emergency. The following is a list of events, which will immediately initiate emergency procedures:

- Explosion
- Fire
- Release of organic vapors or particulate above the action levels
- Personal injury
- Failure or expected failure of runon/runoff control measures
- Natural occurrences (i.e., lightning, tornado, high winds, etc.)
- Spills

7.1 Emergency Communications

Emergency communications will consist of two methods.

7.1.1 Verbal Communication

Verbal communication will be the primary method of emergency communication between onsite personnel, distance permitting.

7.1.2 Telephones

Telephones are used for routine communication and to notify offsite agencies of incidents and request assistance. Emergency telephone numbers are given in Table 1.

7.2 Emergency Protocol

When an event recognized as an emergency occurs, the alarm system will be used to notify personnel. As soon as the alarm system is activated, the SSO or FSSO will be notified.

The SSO or FSSO will take into account the following information:

- Nature of emergency
- Wind direction
- Location of personnel
- Emergency equipment available

Based on this information, the SSO or FSSO will direct appropriate emergency action and agency notification. After the emergency has been controlled and the site is considered safe to re-enter, the SSO or FSSO will direct remedial action to restore the site to full operating condition.

The SSO or FSSO will investigate the nature and cause of the incident so that work procedures can be modified to minimize the likelihood of the incident's recurrence. All incidents must be reported in a timely, appropriate manner. An incident is any unplanned event resulting in injury, damage, loss of assets, adverse publicity, or which requires notification of a regulatory agency, regardless of severity. All Kennedy/Jenks personnel should report an incident to the SSO or FSSO. The SSO and FSSO will report to the project manager. Each incident will be investigated and a written report should be received by the project manager and the regional safety supervisor within five days of the incident.

7.3 Emergency Supplies

Onsite emergency equipment will include equipment used during operations. The following is a list of emergency equipment available to take to the site.

- Portable emergency eye wash
- Tarps/space blankets to reduce contamination potential while transporting injured personnel to medical facilities.
- Twenty-pound ABC fire extinguishers
- First-aid supplies
- Absorbent-spill control
- Extra batteries for radios, cell phones, etc.

All personnel will have a thorough understanding of the Emergency Response Plan before starting work. It will be reviewed periodically to keep it current with new or changing site conditions or information.

7.4 Injury Response

In the event of personal injury, first-aid personnel must decide if the victim's injuries are potentially the type that would be aggravated by movement. If there is any doubt, or the victim is unconscious and cannot respond, no attempt should be made to move the victim to the decontamination area. Only offsite paramedics may move such victims. Routine and emergency communication will be provided by the site telephone.

Section 8: Signatures

Site Safety Officer: ______________________________ Date: ______________

Regional Safety Supervisor: ______________________________ Date: ______________

Project Manager: ______________________________ Date: ______________

Tables

Table 1: Emergency Information

Emergency Telephone Numbers	
In Emergency	911
Site Telephone	*****
Hospital: *****	
Directions to hospital: *****	
Ambulance	911
Police	911
Fire Department	911
Kennedy/Jenks Consultants:	
Project Manager	*****
Regional Safety Supervisor	*****
Site Safety Officer	*****
Corporate Safety Officer	*****

Appendix A

Kennedy/Jenks Consultants

2151 Michelson Drive, Suite 100
Irvine, California 92612-1311
949-261-1577
949-261-2134 (Fax)

Sampling and Analysis Plan
San Ardo Oilfield
San Ardo, California

For

Cooperative Agreement No: DE-FC26-02NT15463

Recovery of More Oil-in-Place at Lower Production
Costs while Creating a Beneficial Water Resource

17 October 2003

Prepared for

Aera Energy LLC
10000 Ming Avenue
Bakersfield, CA 93389

K/J Project No. 024033.00

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Section 1: Introduction

This document provides the Sampling and Analysis Plan (SAP) for the Aera Energy LLC Demonstration Plant located at the San Ardo Oilfield, Monterey County, California (66983 Seargent Canyon Rd, San Ardo, CA 93450). The SAP provides a guide for collecting, handling, and analyzing water quality samples during the demonstration study.

1.1 Background

Kennedy/Jenks Consultants will construct and operate a demonstration plant at the San Ardo Oilfield to assess treatment technologies for treating produced water generated during oil production. The goal of this project is to evaluate the potential of eliminating or reducing the volume of produced water reinjected into the formation following oil recovery activities. The benefits from eliminating the reinjection of produced water may be an increase the oil yield from the formation, reduction in energy costs associated with reheating the reinjected produced water, and providing an alternative source of potable water to nearby users.

The San Ardo Oilfield is located in Monterey County in central California, approximately 45 miles north of the city of San Luis Obispo. There are two oilfield operators in the San Ardo Oilfield, Aera Energy LLC and Chevron Texaco. Aera Energy LLC 's portion of the San Ardo Field covers an area of over 2,600 acres. The field consists of two main oil reservoirs, the Aurignac and the Lombardi. Both reservoirs are currently being produced using continuous steam injection. Field volumes for March 2002 were 8,294 barrels of oil per day, 44,015 barrels of steam per day, and 89,800 barrels of water disposal per day. Monterey County is the fifth largest crude oil producing county in California (Department of Conservation, 2001).

In order to stop Class II injection of the excess produced water, it is necessary to identify an appropriate alternative method for managing produced water. Alternatives include treatment for NPDES discharge into streams for groundwater recharge and/or treatment for beneficial use. This project is intended to show potential water users and regulatory agencies that produced water can be reliably treated to a quality acceptable for NPDES discharge, agricultural, or non-flange to flange municipal beneficial reuse.

After construction of the demonstration plant and system startup, it is estimated that the pilot study will be completed in two phases and be conducted over an eight month operating period to demonstrate that produced water can be treated to meet the following: 1) those criteria required by Aera Energy LLC; 2) those criteria required by the regulatory agencies; and 3) those criteria required by the end users of the treated water.

The first phase of operation will provide operational data on the technologies and operating procedures outlined by the Work Plan. Based on the information gathered from the first phase of operation the tests and operational scheme may be adjusted for additional testing in the second phase, which is also scheduled for approximately 4 months of operation

1.2 Objectives

The primary objective of the SAP is to identify the sample locations, describe sample collection procedures, and provide guidelines for the water quality analyses. The SAP will also discuss the laboratories involved in the water quality analyses and describe the established QA/QC procedures.

Section 2: Pilot System Sampling Requirements

Figure 2-1 shows the sampling locations for the overall test set-up. Table 2-1 provides a summary of the identification codes and descriptions of the sample locations.

The source water for the demonstration study will be from the produced water reinjection pipeline. A slipstream will be installed off of the pipeline to supply the water for treatment.

2.1 Sample Locations

The goal of this project is to design, construct, and operate a demonstration plant at Area's San Ardo Oilfield to demonstrate that produced water can be treated to meet the project goals. The demonstration plant design will build on the DOE funded project that was completed at the Placerita Canyon oilfield. The demonstration plant will include warm softening to remove silica and hardness. A ClariCone separation unit will be used to remove the precipitated solids from the produced water stream. The treated effluent will then be cooled from approximately 190°F inlet temperature to less than 115°F via a cooling tower. Then, sodium hydroxide and antiscalants are mixed into the stream before filtration through 5-micron cartridge filters. The stream is then treated by reverse osmosis before discharge of the permeate and reject back to the produce water reinjection stream.

The following describes sample locations for the demonstration plant.

2.1.1 Source Water

Source water for the demonstration plant will be from a slipstream that is tapped into the existing Aera Energy LLC oil field reinjection pipeline. Sample location SF010 will provide data to identify the characteristics of the untreated produced water.

2.1.2 Warm Precipitative Softener

The raw produced water will first be treated to remove silica and hardness. Sample location SF020 will be after the ClariCone unit that is designed to remove the solids (silica and hardness) precipitated out from the chemical addition. Silica needs to be reduced in the inlet stream as it reduces the performance of the reverse osmosis system. Sample location SF030 and SF040 will be of the ClariCone sludge. SF030 will be a sample of the dewatered solids and SF040 will be a sample of the decanted water from the solids sludge.

2.1.3 Cooling Tower

The softened water will be cooled using a cooling tower to bring the water temperature from 190 F to below 115 F (acceptable temperature for the reverse osmosis unit). Sample location CT010 will be at the effluent of the cooling tower to identify changes in the water characteristics due to reduction of temperature.

2.1.4 Cartridge Filter

Sodium hydroxide and antiscalants will be added to the cooling tower effluent before it is filtered using 5-micron cartridge filters. Sample location CF010 will be located at the effluent side of the cartridge filters.

2.1.5 Reverse Osmosis Inlet

Sample location RO010 will be of the combined reverse osmosis inlet, which includes the cartridge filter effluent and the recirculation stream from the reverse osmosis unit. Sample location RO020 will be of the system permeate. Sample location RO030 will be of the reverse osmosis system concentrate. RO040 will be of the wastewater from periodic cleaning of the reverse osmosis membrane. In addition to the metals analysis, some additional analyses may be conducted on the membrane cleaning wastewater in accordance with membrane vendors' recommendations.

Section 3: Sample Handling, Analytical Methods, and Laboratory

Samples will be collected from the demonstration plant processes to characterize the raw produced water and treated water at the various locations through the treatment process. Field measurements will be made to benchmark the daily performance of the treatment processes and to assist in determining if adjustments are needed to process units. The following contract laboratories will perform more detailed laboratory analyses: Trusdail Laboratory at Tustin, CA and TOXSCAN Laboratory at Watsonville, CA to document the effectiveness of the treatment processes and the anticipated quality of the treated water and residual streams. Table 3-1 provides a summary of the sample analyses and sample frequency for each sample location.

3.1 Field Measurements

Table 3-1 provides a summary of the water quality parameters to be measured in the field at various sampling locations on a daily basis. Demonstration plant staff will take samples during plant operations and perform the field analyses using onsite equipment located at the Aera Energy LLC facility.

3.1.1 Sample Containers

Field samples will be collected in labeled plastic 1-L bottles. There is no preservative required, but the samples will be chilled if analyses are not conducted immediately following the sampling event.

3.1.2 Sampling and Sample Handling

Sample collection will occur in the morning and afternoon every day by plant personnel. These bottles will be rinsed with fresh sample water prior to collection. Once the analyses are complete, these samples will be disposed of into the onsite storage tank for produced water to be reinjected into the Area oil field. The bottles will be rinsed with distilled water for use at the next sampling event.

3.1.3 Field QA/QC

Where appropriate (e.g., once per treatment condition), field measurements will be taken from split samples collected for both field analysis and analysis by a fixed analytical laboratory. A comparison between the operators' and a certified laboratory analyst will also be conducted at the start of sampling to verify proper analytical technique. All instruments will be properly calibrated and maintained according to manufacturer instructions. Equipment calibration results will be recorded and maintained onsite with the appropriate instrument.

3.2 Contract Laboratory Analyses

Table 3-1 also provides a summary of the laboratory water quality analyses to be performed on a weekly or less frequent basis. The contract laboratory, Trusdail Laboratories, will perform the analyses. Some specialized analyses to evaluate compliance with California Toxics Rule will be conducted by TOXSCAN Laboratories, due to the low detection limit requirements for these analyses.

Table 3-2 provides a summary of the method detection limits and reporting limits for each of the analyses performed by the associated laboratory (most of the California Toxic Rule required analyses information is presented in Appendix A).

3.2.1 Sample Containers/Preservation

Samples to be sent to the contract laboratory will be collected in bottles provided by the contract laboratory. The number and type of bottles provided may vary depending on analyses to be conducted that week. These bottles should be sorted and labeled prior to collection. When required, the samples bottles will already contain the necessary preservative for the analyses. Table 3-3 provides a summary of the required container, volumes, and preservative required for each of the analyses.

3.2.2 Sampling and Sample Handling

The plant operator will collect samples in accordance with the frequency presented in Table 3-1. Samples that do not contain preservative will be rinsed with sample prior to collection. During sample collection the sample ports will be opened for a short period of time to purge potential stagnant water and debris from the sample port. Samples for CTR analyses will be collected based on the EPA Method 1669 (Sampling Ambient Water For Trace Metals at EPA Water Quality Criteria Levels).

Samples collected for offsite analysis will be labeled with a unique sample, sample date and time, appropriate analysis and sample preservative. An example of the sample identification system used is as follow: sample collected from location RO010 on 20 October 2003 at 4:00 pm would be RO010-102003-1600 (time in 24-hours).

Following sample collection, the sample information will be recorded on a chain of custody form. The samples will then be placed in a refrigerator or cooler filled with ice. Prior to shipment, samples will be packaged in an ice filled cooler. Packaging will include protecting all glass bottles with bubble wrap or foam packing material. The cooler will be taped closed with the chain of custody inside the cooler and the outside of the cooler labeled with the appropriate project information using the overnight carriers shipping label.

3.2.3 Laboratory QA/QC

The California Department of Health Services has certified the contract laboratories, TOXSCAN and Trusdail. QA/QC data will be provided with the analytical reports.

TABLE 2-1
SAMPLE LOCATIONS AND DESCRIPTIONS

Sample Identification	Sample Description
Source Water	
SF010	Produced water from reinjection pipeline
Water Softener	
SF020	Softened produced water
SF030	Sludge solids
SF040	Decanted sludge water
Cooling Tower	
CT010	Cooling tower water effluent
Cartridge Filter	
CF010	Cartridge filtered water
Reverse Osmosis Unit	
RO010	Combined Inlet water to the RO unit
RO020	Combined system permeate
RO030	Concentrate stream
RO040	Membrane cleaning wastewater

TABLE 3-1
SAMPLE ANALYSES, LOCATION, AND FREQUENCY

Water Parameters	SF010 Influent	SF020 Softener Effluent	SF030 Warm Lime Feed	SF040 Warm Lime Feed	CT010 Cooling Tower Effluent	CF010 Cartridge Filter Effluent	RO010 Combined RO Inlet	RO020 System Permeate	RO030 System Concentrate	RO040 Membrane Waste Water
Field Readings										
Flow Rate	D	D				D		D		
Total Flow Rate		D								
Flow Calibration		D						D	D	
Pressure	D					D	D	D	D	
Temperature		D			D		D	D		
Field Analyses										
pH	D	D			D	D	D	D	D	
Conductivity	D						D	D	D	
Turbidity	D	D				D				
Silt Density Index							D			
Alkalinity	D	D					3C		3C	
Total Hardness	D	D							3C	
Calcium		D							3C	
UV	D	D						D		
SiO_2	D	D						D	3C	
Oil & Grease	D		3C	3C		D				

TABLE 3-1 (CONT)
SAMPLE ANALYSES, LOCATION, AND FREQUENCY

Water Parameters	SF010 Influent	SF020 Softener Effluent	SF030 Warm Lime Sludge Solids	SF040 Warm Lime Sludge Water	CT010 Cooling Tower Effluent	CF010 Cartridge Filter Effluent	RO010 Combined RO Inlet	RO020 System Permeate	RO030 System Concentrate	RO040 Membrane Waste Water
Laboratory Analyses										
pH	3C	3C	3C	3C	3C				3C	
Alkalinity			3C	3C					3C	
Carbon Dioxide	C		3C	3C		C				
Boron	D	D						D	3C	
Iron	3C	3C	3C	3C					3C	
SiO_2	D	D	3C	3C					3C	
TOC	D	D			C			D		
NH3	D	D			3C			D		
Total Suspended Solids		D								
Total Dissolved Solids								3C	3C	
Heavy Metals	C	C	3C	3C				C	C	C

TABLE 3-1 (CONT)
SAMPLE ANALYSES, LOCATION, AND FREQUENCY

Water Parameters	**SF010 Influent**	**SF020 Softener Effluent**	**SF030 Warm Lime Sludge Solids**	**SF040 Warm Lime Sludge Water**	**CT010 Cooling Tower Effluent**	**CF010 Cartridge Filter Effluent**	**RO010 Combined RO Inlet**	**RO020 System Permeate**	**RO030 System Concentrate**	**RO040 Membrane Waste Water**
Laboratory Analyses										
California Toxic Rule Analytes[a]		C						C	C	
Cations	3C	3C	3C	3C						
Anions	3C	3C	3C	3C						
Percent Solids			3C							

Notes
D – 2 samples collected daily (morning and afternoon)
C – 1 sample collected each treatment condition
3C – 3 samples collected per treatment condition
a – List of California Toxic Rule Analyses.
Semivolatiles (method updated from USEPA 8270 to 8270C), Metals, Cyanide, Pesticides/PCBs, Volatiles (method USEPA 524.2), Asbestos, 1,4 Dioxane, Dioxin (singly), Dioxin (all congeners plus furans), Total Petroleum Hydrocarbons, and Perchlorate. See Appendix A

TABLE 3-2
METHOD DETECTION LIMITS AND REPORTING LIMITS FOR LABORATORY ANALYSES^{C}

WQ Parameters	Method	Method Detection Limit$^{(a)}$	Minimum Reporting Limit$^{(a)}$	Laboratory$^{(b)}$
1. General Physical				
Alkalinity, Total (as $CaCO_3$)	SM 2320B	10	10	Field + TL
Dissolved Solids, Total (TDS)	SM 2540 C	40	40	TL
Hardness, Calcium	Hach 8222	2.0	2.0	Field
Hardness, Total	Hach 8226	2.0	2.0	Field
Organic Carbon, Total (TOC)	SM 5310C	0.5	0.5	TL
pH	SM 4500 H	0.1 Unit	0.1 Unit	Field + TL
Silt Density Index	ASTM D-4189-95			Field
Solids, Percent	SM 2540 G	0.1 percent	0.1 percent	TL
Specific (Electric) Conductance	SM 2510 B	1 µmhos/cm	1 µmhos/cm	Field
Suspended Solids, Total	EPA 160.2	4	4	TL
Temperature	SM 2550B	0.5° C	0.5° C	Field
Turbidity	EPA 180.1	0.05 NTU	0.05 NTU	Field
UV Absorbance (at 254nm)	SM 5910B	0.009 l/cm	0.009 l/cm	Field
2. General Minerals				
Calcium	EPA 200.7	1.0	1.0	Field + TL
Chloride	EPA 300.0	1.0	1.0	TL
Magnesium	EPA 200.7/ EPA 6010	1.0	1.0	TL
Nitrate (as NO3)	EPA 300.0	0.4	0.4	TL
Potassium	EPA 200.7	1.0	1.0	TL
Sodium	EPA 200.7	1.0	1.0	TL
Silica	ASTM D-859A			Field + TL
Sulfate	EPA 300.0	1.0	1.0	TL
3. Additional Inorganics				
Aluminum	EPA 200.8/ EPA 6010	0.05	0.05	TL
Antimony	EPA 200.8/ EPA 6010	0.006	0.006	TS
Arsenic	EPA 200.8/ EPA 6010	0.002	0.002	TS
Barium	EPA 200.8/ EPA 6010	0.01	0.01	TL+TS
Beryllium	EPA 200.8/ EPA 6010	0.001	0.001	TS
Cadmium	EPA 200.8/ EPA 6010	0.001	0.001	TS
Chromium, total	EPA 200.8/	0.01	0.01	TL+TS

WQ Parameters	Method	Method Detection Limit(a)	Minimum Reporting Limit(a)	Laboratory(b)
	EPA 6010			
Chromium III	EPA 200.8	10	10	TS
Chromium VI	EPA 218.6	0.3	0.3	TL
Cobalt	EPA 200.8/ EPA 6010	0.020	0.020	TS
Copper	EPA 200.8/ EPA 6010	0.05	0.05	TS
Iron	EPA 200.7/ EPA 6010	0.05	0.05	TL
Lead	EPA 200.8/ EPA 6010	0.005	0.005	TS
Manganese	EPA 200.7/ EPA 6010	0.01	0.01	Field + TL
Mercury	EPA 245.1/ EPA 6010	0.001	0.001	TS
Molybdenum	EPA 6010	0.005	0.005	TL+TS
Nickel	EPA 200.8/ EPA 6010	0.01	0.01	TS
Selenium	EPA 200.8/ EPA 6010	0.005	0.005	TS
Silver	EPA 200.8/ EPA 6010	0.01	0.01	TS
Thallium	EPA 200.8/ EPA 6010	0.001	0.001	TS
Vanadium	EPA 6010	3.0	3.0	TLL+TS
Zinc	EPA 200.8/ EPA 6010	0.05	0.05	TS

<u>Notes:</u>

(a) Units =mg/l unless otherwise noted.

(b) KJ = Kennedy/Jenks, TS = TOXSCAN Laboratories, TL = Trusdail Analytical Laboratories

(c) Appendix A contains a list of analytes for the analyses conducted in accordance with California Toxic Rule

TABLE 3-3
SAMPLE HANDLING GUIDE FOR LABORATORY ANALYSES

WQ Parameters	Method	Container[a]	Suggested Volume	Preservative Agent[b]	Holding Time
1. General Physical					
Alkalinity, Total (as $CaCO_3$)	SM 2320B	PE	500 ml	4°C	14 Days
Chlorine Residual, Total	SM 4500Cl G	PE	10 ml	4°C	Immediate
Color	SM 2120 C	PE	500 ml	4°C	2 Days
Dissolved Solids, Total (TDS)	SM 2540 C	PE	500 ml	4°C	7 Days
Hardness, Calcium	Hach 8222	PE	500 ml	H_2SO_4	6 Months
Hardness, Total	Hach 8226	PE	500 ml	H_2SO_4	6 Months
Organic Carbon, Total (TOC)	SM 5310C	VOA	2 x 40 ml	H_2SO_4	28 Days
pH	SM 4500 H	PE	250 ml	None	Immediate
Saturation Index	calculation	NA	NA	NA	NA
Silt Density Index	ASTM D-4189-95	NA	NA	None	Immediate
Solids, Percent	SM2540 G	G	8 oz	4°C	7 Days
Solids, Total	SM 2540 B	G	8 oz	4°C	7 Days
Specific (Electric) Conductance	SM 2510 B	PE	1 L	4°C	28 Days
Suspended Solids, Total	EPA 160.2	PE	500 ml	4°C	7 Days
Temperature	SM 2550B	PE	1 L	None	Immediate
THM Formation Potential	SM 5710D	AG / VOA	2 x 250 ml / 2 x 40 ml	4°C / Ascorbic Acid	7 Days
Turbidity	EPA 180.1	PE	500 ml	None	2 Days
UV Absorbance (at 254nm)	SM 5910B	PE	250 ml	4°C	24 hours
2. General Minerals					
Calcium	EPA 200.7	PE	500 ml	HNO_3	6 Months
Chloride	EPA 300.0	PE	100 ml	None	4 Weeks
Magnesium	EPA 200.7/ EPA 6010	PE	500 ml	HNO_3	6 Months
Nitrate (as NO_3)	EPA 300.0	PE	100 ml	H_2SO_4	2 Days
Potassium	EPA 200.7	PE	500 ml	HNO_3	6 Months
Sodium	EPA 200.7	PE	500 ml	HNO_3	6 Months
Silica	ASTM D-859A	PE	250 ml	None	28 Days
Sulfate	EPA 300.0	PE	1 L	None	4 Weeks
3. Additional Inorganics					
Aluminum	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Antimony	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Arsenic	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Barium	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Beryllium	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Cadmium	EPA 200.8/6010	PE	500 ml	HNO_3	6 Months
Chromium, total	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months

WQ Parameters	Method	Container(a)	Suggested Volume	Preservative Agent(b)	Holding Time
Chromium III	EPA 200.8	PE	500 ml	HNO_3	6 Months
Chromium VI	EPA 218.6	PE	500 ml	None	24 Hours
Cobalt	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Copper	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Iron	EPA 200.7/ EPA 6010	PE	500 ml	HNO_3	6 Months
Lead	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Manganese	EPA 200.7/ EPA 6010	PE	500 ml	HNO_3	6 Months
Mercury	EPA 245.1/ EPA 6010	VOA	80 ml	HNO_3	28 Days
Molybdenum	EPA 6010	PE	500 ml	HNO_3	6 Months
Nickel	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Selenium	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Silver	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Thallium	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months
Vanadium	EPA 6010	PE	500 ml	HNO_3	6 Months
Zinc	EPA 200.8/ EPA 6010	PE	500 ml	HNO_3	6 Months

Notes:

(a) AG = Amber-Glass; VOA = glass VOA-vial, PE = polyethylene

(b) HNO_3 = nitric acid;H_2SO_4 = sulphuric acid.

Appendix B: Pilot Study Data

Raw Water Laboratory Data

Constituent	Unit	4/13/2000	10/12/2004	1/30/2005	2/2/2005
Total Alkalinity	mg/l as CaCO3	367	360	420	370
Hydroxide Alkalinity	mg/l as CaCO3		ND		
Carbonate Alkalinity	mg/l as CaCO3		ND		
Bicarbonate Alkalinity	mg/l as CaCO3	448	360		370
Hardness	mg/l as CaCO3	303	250	240	220
pH	Unit	7.54	7.5	7.92	7.1
Calcium	mg/l	111	88		88
Magnesium	mg/l	6	6.4		ND
Silica	mg/l	227	230	180	190
Specific Conductance	umhos/cm	10700			13000
Total Dissolved Solids	mg/l	7540		7700	7300
Bromide	mg/l				12
Chloride	mg/l	4050			3800
Ammonia-Nitrogen	mg/l	31			9
Nitrate as Nitrogen	mg/l	<4			ND
Sulfate	mg/l	63	63		63
Potassium	mg/l	61.6			62
Manganese	mg/l	0.1			ND
Sodium	mg/l	2540			2500
Boron	mg/l	26.8			29
TOC	mg/l			80.7	62
Oil & Grease	mg/l	46.2			

Clarifier Effluent Data

Date	Caustic (mg/L)	Mg (mg/L)	pH	Silica (mg/L)	Hardness (mg/l as CaCO$_3$)
6/2/2004	400	0			9.2
6/10/2004	375		9.08		40.4
6/11/2004	500	0	9.65	188	28
6/11/2004	700	0	10.78	185	7.5
6/23/2004	800	70	10.9	134	30.4
7/21/2004			10.36	10	
7/21/2004		130 mg/l	10.81	74	
7/22/2004	1500	160	10.75	40	
7/22/2004			10.68	76	
7/22/2004			10.76	49	
7/22/2004	1500	160	10.75	40	
7/23/2004	1550	175	10.5	27	
7/23/2004	1300	155	10.56	32	
7/23/2004	1550	175	10.5	27	
7/23/2004	1300	155	10.56	32	
8/11/2004	600	150	9.88	24	
8/11/2004	600	100		54	
8/11/2004	500	100		56	
8/11/2004	500	100	9.47	65	

8/11/2004	500	100	9.32	65	
8/11/2004	500	77	9.5	68	
8/11/2004	500	77	9.81	78	
8/11/2004	500	60	10.03	106	
8/11/2004	600	100	9.8	34	
8/11/2004	600	150	9.9	24	
8/11/2004	600	100	11	54	
8/11/2004	500	100	9.93	56	
8/11/2004	500	100	9.47	65	
8/11/2004	500	100	9.32	65	
8/11/2004	500	77	9.5	68	
8/11/2004	500	77	9.81	78	
8/11/2004	500	60	10.03	106	
8/11/2004			9.8	67	
8/11/2004			8.6	149	
8/11/2004		100	8.6	117	
8/11/2004	600	100	9.8	34	
8/17/2004	600	75	10		
8/17/2004			8.96	104	
8/17/2004			9.56	50	
8/17/2004			9.44	63	
8/18/2004	700	100	11.1	46	
8/18/2004			9.69	132	
8/18/2004	700	100	11.1	46	
8/19/2004	650	100	11	82	
8/19/2004	650	100	11	82	
8/20/2004	580	100	10.75	71	
8/20/2004	580	100	10.75	71	
8/20/2004	580	100	10.83		
8/20/2004	580	100	9.7		
8/20/2004	500	60	10.7	-	
8/23/2004	390	60	9.1	-	
8/24/2004	600	50	10.11		
8/24/2004	600	50	10.11		
8/24/2004	600	50	8.54		
8/25/2004	475	45	9.7	126	
8/26/2004	550	75	9.65	73.5	
8/26/2004	600	75	10.08	79.4	
8/27/2004	600	105	9.73	33	
8/31/2004	600	75	10.04	70	
8/31/2004	600	75	10.041	64	
9/2/2004	695	38	10.26	110	
9/2/2004	566	118	9.06	39	
10/15/2004	590	120		81	
11/3/2004	500	100	10.2	66	1.3
11/4/2004	700	114	10.2	129	
11/9/2004	700	135	10.6	109	
11/9/2004	700	135	10.4	106	
11/24/2004	680	120	10	135	
11/29/2004	500	100	9.87	139	5.7

11/29/2004	480	100	9.31	120	6.5
11/30/2004	650	140	9.6	99	
11/30/2004	650	140	9.6	118	
12/3/2004	610	140	9	112	
12/3/2004	640	140	9.3	113	
12/21/2004	680	125	9.3	102	
12/21/2004	705	125		114	
1/3/2005	700	125	9.4	65	
1/3/2005	700	125	9.4	78	
1/4/2005	700	125	9.2	41	55
1/19/2005	700	115	9.7	93	<10
1/21/2005	675	100	9.97	48.5	<10
1/24/2005	650	100	10.1	97	
1/24/2005	590	100	9.9	87	
2/24/2005	500	100	8.7	80	
2/24/2005	600	100	8.7	59	
2/28/2005	500	100	8.8	53	
11/9/2005	650	115	10.05	114	
12/17/2005	780	127	9.56	113	
12/20/2005	680	100	9.5	105	

RO Flow/Recovery Data

Date	Time	Flow (gpm)			% Recovery
		Feed Flow	Permeate Flow (gpm	Concentrate Flow (gpm)	
11/10/04	9:50	7	5	2	71.43%
11/10/04	11:30	7	5	2	71.43%
11/11/04	11:15	7.5	5	2.5	66.67%
11/11/04	13:00	7.5	5	2.5	66.67%
11/11/04	14:30	7.5	5	2.5	66.67%
11/12/04	11:00	7.5	5	2.5	66.67%
11/12/04	12:15	7.5	5	2.5	66.67%
11/12/04	14:30	7.5	5	2.5	66.67%
11/15/04	10:00	7.5	5	2.5	66.67%
11/15/04	13:40	7.5	5	2.5	66.67%
11/17/04	12:15	7.5	5	2.5	66.67%
11/17/04	15:04	7.5	5	2.5	66.67%
11/18/04	10:45	7.5	5	2.5	66.67%
11/18/04	12:00	7.5	5	2.5	66.67%
11/18/04	14:00	7.5	5	2.5	66.67%
11/19/04	10:45	7	4.5	2.5	64.29%
11/19/04	11:45	7	4.5	2.5	64.29%
11/19/04	13:10	6.5	4	2.5	61.54%
12/08/04	11:15	7.6	5	2.6	65.79%
12/08/04	13:11	7.5	5	2.5	66.67%
12/08/04	15:05	7.5	5	2.5	66.67%
12/09/04	13:45	6.4	4	2.4	62.50%
12/10/04	10:10	7.5	5	2.5	66.67%

12/10/04	13:37	7	4.5	2.5	64.29%
12/14/04	11:07	7.5	5	2.5	66.67%
12/14/04	13:30	7.4	4.9	2.5	66.22%
12/15/04	11:52	6.5	4	2.5	61.54%
12/15/04	15:00	6.5	4	2.5	61.54%
12/16/04	11:00	6.6	4	2.6	60.61%
12/16/04	14:40	6.5	4	2.5	61.54%
12/22/04	11:20	7.5	5	2.5	66.67%
12/22/04	13:00	7.4	4.9	2.5	66.22%
12/22/04	15:00	7.3	4.8	2.5	65.75%
12/23/04	10:35	7.3	4.8	2.5	65.75%
12/23/04	13:00	7.3	4.8	2.5	65.75%
12/27/04	13:30	7	4.5	2.5	64.29%
12/27/04	15:15	7	4.5	2.5	64.29%
12/30/04	12:05	6.5	4	2.5	61.54%
12/30/04	14:50	6.5	4	2.5	61.54%
01/05/05	14:00	6.4	4	2.4	62.50%
01/05/05	15:30	6.4	4	2.4	62.50%
01/07/05	12:00	7.5	5	2.5	66.67%
01/07/05	14:25	6.5	4	2.5	61.54%
01/07/05	17:00	6.5	4	2.5	61.54%
01/10/05	11:20	6.2	3.8	2.4	61.29%
01/10/05	13:15	6.1	3.7	2.4	60.66%
01/11/05	11:25	6.5	4	2.5	61.54%
01/11/05	13:30	6.4	3.9	2.5	60.94%
01/12/05	12:10	4.2	3	1.2	71.43%
01/13/05	11:45	7	3.5	3.5	50.00%
01/14/05	10:35	7.6	3.1	4.5	40.79%
01/14/05	12:23	8	3	5	37.50%
01/14/05	16:00	7.5	3	4.5	40.00%
01/20/05	12:00	7.5	3	4.5	40.00%
01/20/05	13:00	7.5	3	4.5	40.00%
01/24/05	13:00	7.5	3	4.5	40.00%
01/24/05	16:00	7.5	3	4.5	40.00%
01/24/05	17:15	5.8	3.8	2	65.52%
01/25/05	10:20	5.7	4	1.7	70.18%
01/25/05	13:35	4.5	3.2	1.3	71.11%
01/28/05	12:00	5.2	3.5	1.7	67.31%
01/28/05	14:40	5.3	3.5	1.8	66.04%

RO Flow/Recovery Data

Date	Time	Koch - Flow (gpm)				Hydranautics - Flow (gpm)			
		Feed Flow	Permeate Flow (gpm	Concentrate Flow (gpm)	% Recovery	Feed Flow	Permeate Flow (gpm	Concentrate Flow (gpm)	% Recovery
02/17/05	13:45	2.65	1.65	1	62.26%	2.4	1.4	1	58.33%
02/18/05	11:30	2.8	1.8	1	64.29%	2.5	1.5	1	60.00%
02/18/05	14:45	2.55	1.75	0.8	68.63%	2.2	1.4	0.8	63.64%
02/21/05	11:30	2.85	1.85	1	64.91%	2.5	1.5	1	60.00%
02/21/05	15:15	2.4	1.4	1	58.33%	2.1	1.1	1	52.38%
02/22/05	11:50	2.25	1.25	1	55.56%	2	1	1	50.00%
02/22/05	14:35	2.25	1.25	1	55.56%	2	1	1	50.00%
02/24/05	13:30	2.4	1.5	0.9	62.50%	2.45	1.55	0.9	63.27%
02/28/05	16:00	2.55	1.55	1	60.78%	2.6	1.6	1	61.54%
03/01/05	10:50	2.65	1.65	1	62.26%	2.8	1.8	1	64.29%
03/01/05	15:00	2.65	1.65	1	62.26%	2.7	1.7	1	62.96%
03/02/05	13:15	2.6	1.6	1	61.54%	2.7	1.7	1	62.96%
03/02/05	16:00	2.55	1.55	1	60.78%	2.6	1.6	1	61.54%
03/03/05	14:15	4.35	2.55	1.8	58.62%				
03/03/05	16:15	3.7	2	1.7	54.05%				
03/04/05	10:35	2.9	1.8	1.1	62.07%				
03/04/05	14:00	7.6	4.6	3	60.53%				
03/07/05	11:30	3.2	2.4	0.8	75.00%	5.05	4.2	0.85	83.17%
03/07/05	12:30	2.5	0.8	1.7	32.00%	3.3	1.6	1.7	48.48%
03/08/05	14:10	3.3	2.3	1	69.70%				
03/08/05	15:00	3.25	2.25	1	69.23%				

RO Operational Data

			Cartridge Pressure (psi)		System Pressure (psi)				
Date	Time	% Recovery	In	Out	RO Feed	1st Inter stage	Conc.	T1	Booster Discharge
11/10/04	9:50	71.43%	28	28	385	385	382	37.5	395
11/10/04	11:30	71.43%	27	27	387	387	385	37.5	398
11/11/04	11:15	66.67%	27	27	388	384	382	34	391
11/11/04	13:00	66.67%	26.8	26.8	389	387	385	34	392
11/11/04	14:30	66.67%	27	27	390	389	388	33	392
11/12/04	11:00	66.67%	27.2	27	380	375	375	31.5	390
11/12/04	12:15	66.67%	27.5	27.5	380	379	378	32	390
11/12/04	14:30	66.67%	26	26	380	379	377	33	392
11/15/04	10:00	66.67%	27.5	27	380	376	375	29	392
11/15/04	13:40	66.67%	27	26.5	380	379	375	30	390
11/17/04	12:15	66.67%	26.5	26.5	380	380	379	36	395
11/17/04	15:04	66.67%	24	24	380	375	375	38	392
11/18/04	10:45	66.67%	28	27	382	381	380	30	392
11/18/04	12:00	66.67%	27	26.5	382	381	380	31.5	398
11/18/04	14:00	66.67%	26	26	382	381	380	32.5	398
11/19/04	10:45	64.29%	28	28	390	389	389	28	395
11/19/04	11:45	64.29%	28	27.5	390	389	388	27.5	393
11/19/04	13:10	61.54%	27.5	26	389	385	382	29	392
12/08/04	11:15	65.79%	28	26	382	380	380	26.5	390
12/08/04	13:11	66.67%	28	25.5	385	381	380	27	390
12/08/04	15:05	66.67%	28	21	385	380	380	27	390
12/09/04	13:45	62.50%	27.5	27	361	360	359	28	395
12/10/04	10:10	66.67%	28	27	390	385	380	27	395
12/10/04	13:37	64.29%	27	26	389	388.5	388	28	390
12/14/04	11:07	66.67%	28	25.5	385	381	380	33	390
12/14/04	13:30	66.22%	27	22	387	380	379	38	388
12/15/04	11:52	61.54%	28.5	26.5	389	385	385	25	390
12/15/04	15:00	61.54%	26	24	389	383	381	26	390
12/16/04	11:00	60.61%	29.5	29	391	390	389	23	395

12/16/04	14:40	61.54%	27.5	23	389	382	382	25	390
12/22/04	11:20	66.67%	28	26	384	381	380	33	390
12/22/04	13:00	66.22%	28	24	385	381	380	33.5	390
12/22/04	15:00	65.75%	26	21	385	379	378	34	390
12/23/04	10:35	65.75%	29	28	390	385	380	28	392
12/23/04	13:00	65.75%	28	27	390	383	382	29.5	392
12/27/04	13:30	64.29%	28	27	390	380	380	25	395
12/27/04	15:15	64.29%	28	21	380	380	375	25	390
12/30/04	12:05	61.54%	28.2	28.1	390	385	283	25.5	395
12/30/04	14:50	61.54%	28.6	28	392	388	385	25.5	395
01/05/05	14:00	62.50%	28	27	385	381	380	38	390
01/05/05	15:30	62.50%	28	27.5	388	382	381	37	392
01/07/05	12:00	66.67%	28.5	28	388	380	380	28.5	390
01/07/05	14:25	61.54%	28.2	27.5	389	382	381	29	395
01/07/05	17:00	61.54%	28.5	27.9	391	386	385	28.5	395
01/10/05	11:20	61.29%	28	27	390	382	381	27	392
01/10/05	13:15	60.66%	28	27	390	384	382	28	390
01/11/05	11:25	61.54%	28.5	28	390	383	382	26	392
01/11/05	13:30	60.94%	28.1	27.1	391	385	383	28	391
01/12/05	12:10	71.43%	29	28	398	395	395	26	400
01/13/05	11:45	50.00%	29	28	375	370	365	22	391
01/14/05	10:35	40.79%	29.5	28	291	281	279	21	390
01/14/05	12:23	37.50%	29	27.5	210	200	199	22.5	390
01/14/05	16:00	40.00%	26.5	21	230	221	219	23	389
01/20/05	12:00	40.00%	27.5	27	389	385	384	42	390
01/20/05	13:00	40.00%	27	27	210	209	206	42.5	389
01/24/05	13:00	40.00%	27	27	235	230	225	31	
01/24/05	16:00	40.00%	27	26	235	230	225	32	390
01/24/05	17:15	65.52%	27	27	390	388	388	31	392
01/25/05	10:20	70.18%	27.9	27.8	390	389	389	47	395
01/25/05	13:35	71.11%	27	27	391	389	389	46	396
01/28/05	12:00	67.31%	28	27	390	388	388	37	395
01/28/05	14:40	66.04%	28.2	27.2	390	388	388	35	398

RO Operational Data

Date	Time	Cartridge Pressure (psi)		System Pressure (psi)							
		In	Out	Pump Pressure (psi)	RO Feed	T1	Booster Discharge	Koch - Inlet	Koch - Conc	SWC4 - Inlet	SWC4 - Conc
02/17/05	11:40										
02/17/05	13:45	85	85	87	448	28	460	445	460	440	440
02/18/05	11:30	97	97	98	450	29	470	445	456	440	431
02/18/05	14:45	102	100	100	452	30	479	450	470	445	489
02/21/05	11:30	82	81	83	435	28	460	438	452	430	422
02/21/05	15:15	92	92	94	365	28	465	352	370	348	340
02/22/05	11:50	80	80	81	318	28	455	320	335	310	305
02/22/05	14:35	80	79.5	82	320	28	455	320	338	312	302
02/24/05	13:30	100	100	100	490	27	570	485	500	480	470
02/28/05	16:00	81	80	81	435	34	450	435	450	430	420
03/01/05	10:50	81	79	80	430	48	450	430	450	420	415
03/01/05	15:00	80	73	75	425	48	445	425	440	420	410
03/02/05	13:15	100	100	100	460	47	590	455	470	450	440
03/02/05	16:00	100	100	100	460	47	600	467	475	450	440
03/03/05	14:15	100	100	100	575	47	600	570	560		
03/03/05	16:15	100	100	100	585	45	610	580	581		
03/04/05	10:35	100	100	100	550	40	580	545	540		
03/04/05	14:00	100	100	100	410	48	540	410	395		
03/07/05	11:30	100	100	100	460	35	560	460	480	453	430
03/07/05	12:30	105	110	105	70	35	490	63	73	63	10
03/08/05	14:10	100	100	100	495	35	520	490	510		
03/08/05	15:00	100	100	100	495	35	530	495	510		

RO Feed Water Field Water Quality Data

Date	pH	Conductivity	Silica	Hardness	Alk	Turbidity	UV
10/19/2004	10.4	14880					
10/21/2004		13710					
10/22/2004		13260					
10/27/2004	10.1	14100					
10/28/2004	10.36	14020					
11/1/2004	10.15	13610					
11/10/2004		14520	111				
11/11/2004			110	<10			
11/12/2004			106	<10			
11/15/2004	11.14	14450	107				1.308
11/15/2004	11.15	14300	105				1.229
11/17/2004	11.52	14680	142				1.462
11/17/2004	11.52	14700	105				1.229
11/18/2004			143				
11/19/2004			142				
11/19/2004			111				
12/9/2004			111	<10	950		1.333
12/9/2004			116				1.33
12/14/2004			86	<10	690		1.467
12/15/2004			105	16.8			
12/16/2004			102	<10	745	1.81	1.38
12/16/2004			99				
12/22/2004	10		81	24	705		
12/23/2004	10		80	27		12.2	
12/30/2004			69				
12/30/2004			76				
1/5/2005	9.8	12940	46	41	526		
1/7/2005	9.84	12710	38	42			
1/7/2005	9.84	12740	41				
1/7/2005	9.82	12720	31				
1/10/2005	9.9	12820	43	45	720		
1/11/2005	9.9	12570	38		552		
1/11/2005	9.84	12210	33				
1/11/2005	9.97	12540					
1/12/2005	10	12590	40	52	586		
1/20/2005	10.3		92	<10			
1/24/2005			63				
1/25/2005	10.14	13940	73	12	750		
1/25/2005	10.12	13830	69				
1/28/2005	9.9	13790	61	<10	678		
1/28/2005	9.92	13750	59	<10	699		
1/31/2005	10.2	13820	42	<10	737		
2/2/005	11.28	15310	27.5	<10	940		
2/16/2005		14000					
2/18/2005	9.84	13830	16	76	520		
2/18/2005	9.92	13850	22	74.4	543		
2/21/2005	9.91	12480	16		472		
2/21/2005	9.68	13260	18	86	484		

2/22/2005	9.78	13780	18	68	569		
2/22/2005	9.47	12480	36	46	472		
2/24/2005	9.5	12690					
2/28/2005	9.6	13750	29.1				
3/1/2005	9.38	13530	51.3				
3/2/2005	9.3	13680	46.5				
3/2/2005	9.3	13660	49.5				
3/3/2005	9.4	13740					
3/3/2005	9.46	13780	52.2		592		
3/3/2005	9.47	13790	29.3		646		

RO Permeate Field Water Quality Data

Date	pH	Conduc	Silica	Hardness	Alk	Turbidity	UV
11/10/2004		968					
11/15/2004	11.07	474					1.07
11/15/2004	11.27	480	0.6				0.007
11/17/2004	11.5	1059					0.109
11/17/2004	11.6	1237	0.6				0.007
11/18/2004			1.9				
11/19/2004			2.1				
12/8/2004			1				
12/9/2004			0	<10	220		0.019
12/9/2004			5				0.021
12/14/2004			3.9	<10	108		0.027
12/15/2004				<10			
12/16/2004			1	<10	77	0.15	0.042
12/16/2004			0.5				
12/22/2004	11		2	<10	99		
12/23/2004	11.1			<10		0.57	
1/5/2005	10.8	571	4	0	12.4		
1/7/2005	10.9	404	2	<10			
1/7/2005	11.03	422	0				
1/7/2005	11.07	410	2				
1/10/2005	11	398	0	<10	135		
1/11/2005	10.92	341	1		76		
1/11/2005	11.03	384	4				
1/11/2005	11.04	374					
1/12/2005	11	496	2	<10	90		
1/25/2005	10.8	1176	10	<10	155.2		
1/25/2005	10.79	1183	6				
1/28/2005	10.71	728	5		117		
1/28/2005	10.77	671	5		120		
1/31/2005	10.96	425	4		90		
2/2/005	11.3	635	1.3		98		
2/4/2005	10.52						

RO Concentrate Field Water Quality

Date	pH	Conduc	Silica	Hardness	Alk	Turbidity	UV
11/10/2004		50000					
11/15/2004	10.94	42900					2.872
	10.79	43400					2.451
11/17/2004	11.44	46700					2.914
11/17/2004	10.56	45700					2.451
12/9/2004			>200	<10	2200		3.215
12/9/2004			195				2.6
12/14/2004			200	24.8	1830		3.01
12/15/2004			200	16.8			
12/16/2004			200	17.5	2030	0.9	3.135
12/16/2004			177				
12/22/2004	9.7		188	66	1830		
12/23/2004	9.7			65.6		12.5	
12/30/2004			137				
12/30/2004			102				
1/5/2005	9.4	36400	127	126	1385		
1/7/2005	9.42	26600	91	248			
1/7/2005	9.6	32300	92				
1/7/2005	9.56	32000	65	150			
1/10/2005	9.6	32500	120	145	1870		
1/11/2005	9.44	25000	80		995		
1/11/2005	9.63	31600	90				
1/11/2005	9.63	26700					
1/12/2005	9.6	42300	118	192	1885		
1/25/2005	9.78	44300	107	28	2280		
1/25/2005	9.68	48600	177				
1/28/2005	9.53	42600	161	20.7	2165		
1/28/2005	9.56	42700	129		2130		
1/31/2005	9.95	37300	99		1995		
2/2/005	10.98	37800	98		2550		

RO (Koch Membrane) Field Conductivity and pH Data

		Conductivity									pH		
Date	Time	Permeate	Feed	Concentrate	1A	2A	3A	1B	2B	3B	Feed	Permeate	Concentrate
11/10/04	9:50	968	14520	50000	609	598	1005	1399	1822	993	11.3	11.15	11
11/10/04	11:30	964	14400	49700	626	602	1035	1380	1951	1032	11.05	11.23	11.36
11/11/04	11:15	688	14650	47500	465	446	727	1036	1265	744	11.2	11.2	11.1
11/11/04	13:00	679	14560	46500	476	456	701	1004	1197	685	11.2	11.2	11.1
11/11/04	14:30	668	14540	46200	459	444	688	687	1212	677	11.2	11.2	11.1
11/12/04	11:00	619	14440	44700	420	413	627	915	1117	627	11.3	11.2	11
11/12/04	12:15	614	14380	44600	425	409	618	907	1073	619	11.3	11.2	11
11/12/04	14:30	295	8030	27800	230	200	268	448	475	288	11.2	11.1	11
11/15/04	10:00	474	14450	42900	335	330	465	763	732	461	11.1	11.1	11
11/15/04	13:40	480	14300	43400	345	329.4	452	722	734	460	11.3	11.15	10.79
11/17/04	12:48	1059	14680	46700	701	679	1014	1769	1802	1003	11.5	11.52	11.44
11/17/04	15:04	1237	14700	45700	857	826	1212	2180	2110	1070	11.6	11.52	11.56
11/18/04	10:45	856	14580	42700	598	578	848	1367	1400	841	11.6	11.6	11.6
11/18/04	12:00	899	14710	42800	608	588	866	1364	1463	863	11.6	11.6	11.6
11/18/04	14:00	925	14680	42300	620	597	850	1356	1368	849	11.6	11.5	11.5
11/19/04	10:45	716	14500	41200	517	514	735	1056	1118	778	11.55	11.6	11.65
11/19/04	11:45	694	14520	41300	509	489	689	1030	1117	704	11.6	11.6	11.6
11/19/04	13:10	693	14530	40700	524	510	682	1016	1004	694	11.5	11.5	11.6
12/08/04	11:15	453	13960	37100	353	351	456	626	643	446	11.08	10.29	10.11
12/08/04	13:11	451	13900	39100	356	343	448	616	691	451	11.1	10.33	10.16
12/08/04	15:05	447	13860	38600	355	346	450	586	633	448	10.6	10.2	10
12/09/04	13:45	466	13780	37500	379	374	468	624	739	476	11.36	10.49	10.09
12/10/04	10:10	430	13910	38100	337	332	423	603	595	424	11.5	10.83	10.57
12/10/04	13:37	435	13880	38500	349	338	427	575	630	432	10.77	10.08	9.78
12/14/04	11:07	467	14000	38400	392	379	480	785	677	481	10.85	10.04	10.02
12/14/04	13:30	568	14000	40000	435	418	554	795	850	559	10.8	9.9	9.58
12/15/04	11:52	422	13760	36100	309	408	423	519	575	420	11.1	10.38	10.1
12/15/04	15:00	413	13770	36900	305	298	413	507	593	409	11.15	10.32	10.07
12/16/04	11:00	364	13780	34800	275	297	363	459	475	363	11.2	10.42	10.14

12/16/04	14:40	398	13810	36700	293	287	391	485	566	377	11.22	10.36	10.15
12/22/04	11:20	468	12810	37900	366	351	460	680	676	458	11	10	9.8
12/22/04	13:00	510	12840	35800	392	374	498	709	724	467	11	10	9.7
12/22/04	15:00	545	12820	33100	432	397	540	760	777	519	11	10	9.7
12/23/04	10:35	394	12710	33800	324	317	388	504	519	388	11.1	10	9.8
12/23/04	13:00	464	12730	32600	366	356	450	563	630	435	11.1	10	9.8
12/27/04	13:30	379	12640	31600	305	332	386	459	495	398	11.04	10.1	9.86
12/27/04	15:15	506	12720	30400	305	317	397	447	507	401	11	10	9.9
12/30/04	12:05	382	12540	29500	312	328	398	465	498	403	11.2	10.1	9.9
12/30/04	14:50	378	12200	30400	305	307	394	453	523	392	11.1	10.16	9.9
01/05/05	14:00	583	12920	36700	457	453	609	812	846	585	10.8	9.8	9.4
01/05/05	15:30	571	12940	36400	457	429	580	748	866	584	10.8	9.8	9.4
01/07/05	12:00	404	12710	26600	310	308	365	476	460	367	10.9	9.84	9.42
01/07/05	14:25	422	12740	32300	329	320	413	510	579	421	11.03	9.84	9.6
01/07/05	17:00	410	12720	32000	325	317	434	497	438	586	11.1	9.8	9.6
01/10/05	11:20	380	12520	31700	293	291	360	474	470	357	11	10	9.6
01/10/05	13:15	398	12620	32500	315	306	390	490	543	398	11	9.9	9.6
01/11/05	11:30	341	12,570	25,000	278	292	336	402	405	334	9.9	10.92	9.44
01/11/05	13:30	384	12,210	31,600	301	311	438	438	592	425	9.97	11.04	9.63
01/12/05	12:10	496	12,590	42,300	341	339	493	684	605	485	10	11	9.6
01/20/05	12:00	787	13,590	43,500	561	543	781	1285	1256	753	10.4	11	9.9
01/20/05	13:00	752	13,620.0	23,400.0	638	633	756	904	978	759	10.3	11.1	10
01/24/05	13:00	522	13,940	22,700	434	475	548	557	609	524	10.4	11	10.2
01/24/05	16:00	557	13,990	22,100	464	497	554	600	667	545	10.4	11.2	10.2
01/24/05	17:15	602	14,010	41,400	440	448	595	849	892	568	10.5	11.1	10.1
01/25/05	10:20	1176	13,940	44,300	808	770	1098	2350	1798	1143	10.14	10.8	9.78
01/25/05	13:35	1183	13,830	48,600	790	774	1196	1812	1908	1158	10.12	10.79	9.68
01/28/05	14:40	671	13,750	42,700	491	477	683	1053	913	662	9.92	10.77	9.56

Cooling Tower Water Quality

Constituent	Unit	Date	Influent	Effluent
Total Alkalinity	mg/l as CaCO3	2/2/2005	990	1000
Hydroxide Alkalinity	mg/l as CaCO3	2/2/2005	210	120
Carbonate Alkalinity	mg/l as CaCO3	2/2/2005	780	880
Bicarbonate Alkalinity	mg/l as CaCO3	2/2/2005	ND	ND
Hardness	mg/l as CaCO3	2/2/2005	ND	ND
Specific Conductance	umhos/cm	2/2/2005	17000	18000
pH	pH Units	2/2/2005	11.5	11.3
Total Dissolved Solids	mg/l	2/2/2005	8800	9200
Bromide	mg/l	2/2/2005	24	25
Chloride	mg/l	2/2/2005	4700	4500
Ammonia-Nitrogen	mg/l	2/2/2005	19	6.5
Nitrate as Nitrogen	mg/l	2/2/2005	ND	ND
Nitrite as Nitrogen	mg/l	2/2/2005		
Sulfate	mg/l	2/2/2005	93	98
Calcium	mg/l	2/2/2005	ND	ND
Magnesium	mg/l	2/2/2005	ND	ND
Manganese	mg/l	2/2/2005	ND	ND
Potassium	mg/l	2/2/2005	60	66
Sodium	mg/l	2/2/2005	3200	3300
Boron	mg/l	2/2/2005	25	26
TOC	mg/l	2/2/2005	79	62
Silica	mg/l	2/2/2005	15	16

Cooling and Ammonia Stripping Field Water Quality Data

Date	Time	Influent pH	Effluent pH	Influent NH3-N	Effluent NH3-N	Influent Temp	Effluent Temp
1/31/2005	10:00	10.32	10.29	9	6	57.5	52.7
1/31/2005	11:00	10.32	10.29			57.2	52.1
1/31/2005	12:00	10.32	10.27	9	3	57.9	53.2
1/31/2005	13:00	10.3	10.24			59.1	53.7
1/31/2005	14:00	10.31	10.25	10	5	58.2	55.4
2/2/2005	10:45	10.77	11.34	20	5	105.2	61.5
2/2/2005	11:45	10.76	11.29	21	7	106.6	66.7
2/2/2005	12:45	10.78	11.27	18	4	105.1	65.3
2/2/2005	13:45	10.81	11.28	17	5	103.8	65.1
2/2/2005	14:45	10.82	11.24	16	6	102.3	69.6

RO Feed Water Laboratory Data

Date	Total Alkalinity	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity	Hardness	Specific Conductance	pH	Total Dissolved Solids	Bromide	Chloride	Ammonia-Nitrogen	Nitrate as Nitrogen	Nitrite as Nitrogen	Sulfate	Calcium	Magnesium	Manganese	Potassium	Sodium	Boron	TOC	Silica
10/27/2004	780	ND	760	20	ND	17000	10 1	8500		4000	8 7	ND	ND	120	ND	ND	ND	56	3000	21	64	66
11/1/2004	730	ND	560	160	ND	13000	10	8200	22	4100	6	ND	ND	120	ND	ND	ND	59	3200	22	66	
11/10/2004					ND	15000	11 1	12000	20	4300	10	ND	ND	110	ND	ND	ND	63	3400	25		100
11/15/2004	1000	120	920	N	N	18000	11	8900	20	4300	7 5	ND	ND	100	ND	ND	ND	68	3500	27	70	110
11/17/2004	1400	470	880	ND	ND	19000	11 5	9000	19	4200	12	ND	ND	77	ND	ND	ND	56	3300	25	82	160
12/6/2004	830	18	820	ND	ND	17000	10 2	8500	21	4200	12	ND	ND	99	ND	ND	ND	57	4000	22	72	
12/14/2004	710	ND	590	130	ND		9 9	8200			12									22		88
12/22/2004	750	ND	ND	750	66	15000	10	7600	22	3800	12	ND	ND	110	ND	16	ND	59	3100	22	78	99
1/5/2005	570	ND	360	210	ND	14000	9 7	7600	26	3000	13	ND		130	ND	ND	ND	59	3100	20	64	49
1/25/2005	720	ND	640	80	ND	15000	10 3	8600	23	4300	57	ND		90	ND	ND	ND	64	4100	27	96	
1/31/2005	790	ND	680	100	ND	15000	10 1	8600	19	4100	7 6	ND		82	ND	ND	ND	58	2900	25	77	66
2/2/2005	1000	180	820	ND	ND	18000	11	9100	25	5300	5 6	ND		97	ND	ND	ND	62	3200	26	50	16
2/17/2005	570	ND	290	280	ND	16000	9 3	8500	15	4100	12		ND	110	ND	ND	ND	55	2900	23	45	34
2/24/2005							9 5													21	38	
3/1/2005	550	ND	320	230	ND	16000	9 4	7700	20	4200	17		ND	96	ND	ND	ND	55	3000	25	50	52
3/2/2005							9 5	7900			18									24	51	53
3/3/2005							9 8	4500			17									23	56	51

RO Permeate Laboratory Data

Date	Total Alkalinity	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity	Hardness	Specific Conductance	pH	Total Dissolved Solids	Bromide	Chloride	Ammonia-Nitrogen	Nitrate as Nitrogen	Nitrite as Nitrogen	Sulfate	Calcium	Magnesium	Manganese	Potassium	Sodium	Boron	TOC	Silica
10/27/2004	76	58	18	ND	4.1	370	10.8	200		56	7.5	ND	ND	ND	1.6	ND	ND	ND	56	1.7	ND	0.4
11/1/2004	62	43	19	ND	ND	370	10.7	160	ND	65	4.8	ND	ND	ND	ND	ND	ND	ND	58	2.4	ND	
11/10/2004					ND	1000	11.3	1200	ND	130	11	ND	ND	1	ND	ND	ND	2.3	140	0.6		1.4
11/15/2004	86	ND	56	30	ND	400	11.3	170	ND	62	7.3	ND	ND	ND	ND	ND	ND	1.1	65	ND	ND	0.4
11/17/2004	240	220	16	ND	ND	1300	11.5	340	0.6	93	13	ND	ND	ND	ND	ND	ND	2.2	140	0.3	ND	1.1
12/8/2004	100	76	24	ND	ND	440	11.3	160	ND	63	9.8	ND	ND	ND	ND	ND	ND	1.2	66	1.6	ND	
12/14/2004	120	86	29	ND	ND		10.9	270			10									5.8		0.8
12/22/2004	100	ND	ND	100	ND	490	11	230	ND	83	10	ND	ND	0.6	ND	ND	ND	1.5	120	4.6	ND	0.8
1/5/2005	120	74	43	ND	ND	620	10.9	280	ND	110	10	ND		0.8	ND	ND	ND	1.6	100	7.5	ND	0.6
1/25/2005	160	120	40	ND	ND	1100	11.4	510	1	220	51	ND		1	ND	ND	ND	3.6	190	10	ND	
1/31/2005	64	38	26	ND	ND	430	10.9	180	ND	77	6.6	ND		0.5	ND	ND	ND	1.1	65	2.3	ND	0.6
2/2/2005	90	72	18	ND	ND	630	11.4	230	0.5	97	5.6	ND		0.6	ND	ND	ND	1.6	100	0.6	0.9	0.4
2/17/2005	68	37	31	ND	ND	190	10.6	100	ND	26	6.1		ND	ND	ND	ND	ND	ND	35	4.3	ND	ND
2/24/2005							10.7													4.3	ND	
3/1/2005	140	103	40	ND	ND	440	10.8	240	ND	69	13		ND	ND	ND	ND	ND	1.4	92	12	1.1	0.4
3/2/2005							10.8	230			14	ND	ND							12	1.4	0.6
3/3/2005							11.2	190			15									5.5	0.6	0.2
<u>Hydranautics</u>																						
2/17/2005	42	18	24	ND	ND	69	10.4	32	ND	4	6.3		ND	ND	ND	ND	ND	ND	8.3	1	ND	ND
2/24/2005							10.5													1	ND	
3/1/2005	83	55	28	ND	ND	160	10.7	60	ND	7.6	14.0		ND	ND	ND	ND	ND	ND	23	3.2	ND	ND
3/2/2005							10.8	56			13.0	2.8	ND							2.8	ND	ND

RO Concentrate Laboratory Data

Date	Total Alkalinity	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity	Hardness	Specific Conductance	pH	Total Dissolved Solids	Bromide	Chloride	Ammonia-Nitrogen	Nitrate as Nitrogen	Nitrite as Nitrogen	Sulfate	Calcium	Magnesium	Manganese	Potassium	Sodium	Boron	TOC	Silica
10/27/2004	2500	ND	2200	270	ND	55000	9 9	29000		14000	10	ND	ND	390	ND	ND	ND	220	11000	74	250	200
11/1/2004	2300	ND	1800	660	ND	55000	9 7	28000	72	16000	8 2	ND	ND	380	11	ND	ND	220	11000	70	250	
11/10/2004					ND	66000	11	33000	93	9900	12	ND	ND	420	ND	ND	ND	250	13000	89		350
11/15/2004	3400	140	3300	ND	ND	57000	10 8	29000	70	14000	8 3	ND	ND	330	ND	ND	ND	230	21000	82	270	320
11/17/2004	4000	790	3200	ND	ND	58000	11 6	30000	59	15000	13	ND	ND	ND	ND	ND	ND	210	1200	90	290	520
12/8/2004	2400	ND	2300	110	5 4	54000	10 1	27000	65	13000	14	ND	ND	290	ND	ND	ND	190	9000	87	200	
12/14/2004	1900	ND	1300	550	ND		9 6	25000			16									55		210
12/22/2004	2000	ND	ND	2000	61	46000	9 7	24000	65	13000	18	ND	ND	300	ND	15	ND	180	9000	53	210	190
1/5/2005	1600	ND	830	760	ND	47000	9 4	24000	77	13000	19	ND		340	ND	23	ND	190	9700	43	240	140
1/26/2005	2600	ND	2200	460	ND	51000	9 8	39000	84	15000	55	ND		290	ND	ND	ND	260	11000	73	340	
1/31/2005	2200	ND	1900	280	ND	45000	9 9	25000	39	7400	9 3	ND		230	ND	ND	ND	180	9300	69	220	160
2/2/2005	2600	190	2400	ND	ND	46000	11	20000	73	19000	5 5	ND		260	ND	ND	ND	190	8700	71	140	76
2/17/2005	1500	ND	630	900	86	47000	9 1	23000	41	13000	22		ND	300	ND	21	ND	170	8100	57	88	97
2/24/2005							9 2													55	140	
3/1/2005	1200	ND	420	770	ND	38000	9 1	20000	34	9700	26		ND	210	ND	ND	ND	140	7300	42	92	139
<u>Hydranautics</u>																						
2/17/2005	1300	ND	610	700	71	38000	9 2	20000	34	11000	20		ND	250	ND	17	ND	140	7000	52	82	81
2/24/2005							9 3													60	98	
3/1/2005	1400	ND	700	680	ND	38000	9 2	18000	53	11000	25		ND	220	ND	ND	ND	150	7600	58	96	130
3/2/2005							10 8	66			13 0	2 8	ND							2 8	ND	ND

Laboratory Data for California Toxic Rule Compliance for 10 Metals

Constituent	Unit	Raw Produced Water (Filtered)	Koch Permeate		
Date		3/5/2005	3/2/2005	3/2/2005	3/5/2005
Mercury	ug/l	0.44	0.012	0.013	0.026
Silver	ug/l	ND	ND	ND	ND
Beryllium	ug/l	ND	ND	ND	ND
Cadmium	ug/l	ND	ND	ND	ND
Copper	ug/l	0.82	0.63	ND	ND
Molybdenum	ug/l	7.8	ND	ND	ND
Lead	ug/l	ND	ND	ND	ND
Antimony	ug/l	ND	ND	ND	ND
Selenium	ug/l	ND	ND	ND	ND
Thallium	ug/l	ND	ND	ND	ND

Laboratory Data for THM Formation Potential

Constituent	Unit	Date	Permeate
Bromodichloromethane	μg/l	3/16/2005	7.5
Bromoform	μg/l	3/16/2005	14
Chloroform	μg/l	3/16/2005	2
Dibromochloromethane	μg/l	3/16/2005	16
Total THMs(THM's/TTHM)	μg/l	3/16/2005	40
% Surrogate Recovery	%	3/16/2005	120

Analyses of Acidic CIP Solutions Before and After Cleaning

Constituent	Unit	Date	Before Cleaning	After Cleaning	Before Cleaning	After Cleaning	Before Cleaning	After Cleaning
			1/14/05		3/8/05		3/9/05	
Hardness	mg/l as CaCO3		340	1300	340	410	350	610
Calcium	mg/l	1/14/05	81	110	81	85	84	92
Magnesium	mg/l	1/14/05	33	240	33	49	33	92
Silica	mg/l	1/14/05	53	200	48	71	58	110

TOC (mg/l) Levels in High pH CIP Solutions Before and After Cleaning

Date	Before Cleaning	After Cleaning
1/24/05	160	94
3/9/05	77	73
SCW4 Membrane		
3/9/05	79	77

Solids and CAM Metals Analyses of Softening Sludge

Constituent	Unit	Date	PQL	Wet Sample	Dry Sample	Wet Sample	Dry Sample
				1/20/2005		2/2/2005	
Total Solids	%	1/20/2005		2.9		2.3	
Antimony	mg/kg	1/20/2005	5	ND	ND	ND	ND
Arsenic	mg/kg	1/20/2005	1	ND	ND	ND	ND
Barium	mg/kg	1/20/2005	0.5	8.2	280	7.2	310
Beryllium	mg/kg	1/20/2005	0.5	ND	ND	ND	ND
Boron	mg/kg	1/20/2005	1	ND	ND	ND	
Cadmium	mg/kg	1/20/2005	1	ND	ND	ND	ND
Chromium	mg/kg	1/20/2005	1	ND	ND	ND	ND
Cobalt	mg/kg	1/20/2005	1	ND	ND	ND	ND
Copper	mg/kg	1/20/2005	0.5	ND	ND	ND	ND
Lead	mg/kg	1/20/2005	1	ND	ND	ND	ND
Mercury	mg/kg	1/20/2005	0.1	ND	ND	ND	ND
Molybdenum	mg/kg	1/20/2005	1	ND	ND	ND	ND
Nickel	mg/kg	1/20/2005	1	ND	ND	ND	ND
Selenium	mg/kg	1/20/2005	5	ND	ND	ND	ND
Silver	mg/kg	1/20/2005	1	ND	ND	ND	ND
Thallium	mg/kg	1/20/2005	5	ND	ND	ND	ND
Tin	mg/kg	1/20/2005	1	ND	ND	ND	
Vanadium	mg/kg	1/20/2005	1	ND	ND		ND
Zinc	mg/kg	1/20/2005	1	ND	ND		ND

X-Ray Fluorescent Spectrometry

Constituent	Weight %	
	1/20/2005	2/2/2005
Carbon	60	60
Boron	9.9	12
Sodium	7.8	8.3
Chlorine	7.8	7.7
Magnesium	6.4	4.95
Calcium	4.1	3.5
Silicon	3	2.6
Potassium	0.11	0.11
Sulfur	0.12	0.09
Strontium	0.1	0.08
Iron	0.1	0.06
Bromide	0.04	0.035

X-Ray Fluorescent Spectrometry (Ignition at 1000 oC, followed by fusion with lithium metaborate)

Constituent	Reporting Limit	Weight %	
		1/20/2005	2/2/2005
CaO		16.05	16.04
Na2O	0.02	3.27	6.63
MgO	0.02	15.24	12.9

Al_2O_3	0.02	0.17	0.18
SiO_2	0.2	19	20.42
P_2O_5	0	0.006	0.009
K_2O	0.04	ND	0.06
TiO_2	0	0.006	0.009
MnO_2	0	0.015	0.012
Fe_2O_3	0.1	0.46	0.35
SrO	0.02	0.31	0.31
SO_3	0.02	0.49	0.46
Loss on ignition	0.5	50.81	47.65

Appendix C: Regulatory Agency Correspondence

DEPARTMENT OF CONSERVATION
STATE OF CALIFORNIA

CALIFORNIA CONSERVATION

DIVISION OF OIL,
GAS, & GEOTHERMAL
RESOURCES

■ ● ■

5075 S. BRADLEY ROAD
SUITE 221
SANTA MARIA
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93455-3077

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INTERNET
consrv.ca.gov

■ ■ ■

GRAY DAVIS
GOVERNOR

KENNEDY/JENKS CONSULTANTS
BAKERSFIELD, CA
RECEIVED
FEB 18 2003
JOB #__________

February 11, 2003

Roger S. Funston
Kennedy/Jenks Consultants
200 New Stine Rd., Ste. 205
Bakersfield, CA 93309

Re: Reverse Osmosis Pilot, San Ardo Field

Dear Mr. Funston:

We have reviewed the proposal for the pilot project for treating San Ardo oilfield produced water for beneficial reuse. The Division of Oil, Gas, and Geothermal Resources does consider the waste products of the reverse osmosis process as a Class II fluid, as long as the constituents are shown to be non hazardous. Any non hazardous waste produced will be allowed to be disposed in existing or new Class disposal wells in San Ardo field or in the adjacent Monterey County Class II disposal wells.

If you have any questions, please call William E. Brannon or Al Koller at (805) 937-7246.

Sincerely,

Koller for
William E. Brannon
Deputy Supervisor

AK:hc

Proj File

California Regional Water Quality Control Board
Central Coast Region

Winston H. Hickox
Secretary for Environmental Protection

Internet Address: http://www.swrcb.ca.gov/rwqcb3
895 Aerovista Place, Suite 101, San Luis Obispo, California 93401
Phone (805) 549-3147 • FAX (805) 543-0397

Gray Davis
Governor

April 8, 2003

RECEIVED
APR 10 2003
KENNEDY / JENKS CONSULTANTS
IRVINE, CA

Raymond E. Ouellette, R.E.A., QEP
Kennedy/Jenks Consultants
2151 Michelson Drive, Suite 100
Irvine, CA 92612

Dear Mr. Ouellette:

REGULATIONS FOR OILFIELD PRODUCED WATER DISCHARGES

On March 18, 2003 my staff met with you and Aera Energy LLC representatives to discuss the applicability of water regulations for the proposed discharge of treated produced water from the San Ardo Oilfield. After the meeting we received your March 31, 2003 letter, which summarized your understanding of the March 18, 2003 meeting's conclusions. Your letter demonstrates that you properly interpreted our position on water regulations applicability for the proposed treated produced-water discharge.

If you have questions, please call **Tom Kukol at (805) 549-3689** or Eric Gobler at (805) 549-3689.

Sincerely,

for Roger W. Briggs
Executive Officer

TJK: S:\WB\Central Watershed\Staff Temp Files\ Tom\Aera Energy - San Ardo\Applicability of Water Regulations.doc
Task: 101-01
File: Texaco San Ardo

Kennedy/Jenks Consultants

Engineers & Scientists

2151 Michelson Drive, Suite 100
Irvine, California 92612
949-261-1577
FAX 949-261-2134

31 March 2003

Mr. Thomas Kukol
Water Resources Control Engineer
Central Coast Regional Water Quality Control Board
895 Aerovista Suite 101
San Luis Obispo, CA 93401

Subject: Applicability of Water Regulations for the San Ardo Project
Aera Energy LLC and Department of Energy Project
K/J 024033.01

Dear Mr. Kukol:

Thank you for meeting with representatives of Aera Energy LLC (Aera) and Kennedy/Jenks Consultants (Kennedy/Jenks) on Tuesday, 18 March 2003 to discuss the applicability of various water regulations that might be associated with a project being jointly sponsored by the Department of Energy, Aera and Kennedy/Jenks. As discussed, the project is seeking ways to improve the recovery of oil from the San Ardo Field. It is believed that an additional 150 million barrels of oil might be recovered if an alternative produced water management method is found to the current produced water disposal method, which is injection into a Class II disposal well. The Department of Energy and Aera are working to identify potential alternative water management scenarios to accomplish this objective.

Several alternatives methods have been developed. As part of the project deliverables, the Department of Energy requires that each alternative be reviewed and that all permitting requirements be identified. The purpose of our meeting was to discuss these various alternatives and to identify the specific regulations that might be applicable in each of the scenarios discussed. This letter presents our understanding of how the various regulations might be applicable. We request that you review this letter and our understanding to determine whether we have properly interpreted the application of the various regulations. We request that a written response be developed concurring or commenting on our understanding.

Alternative 1 - Direct Discharge to Salinas River

In this alterative, produced water would be treated and then, discharged directly to the Salinas River. The treated water would need to meet the requirements found in the following regulations and/or policy documents: 40 CFR 435.30 *et seq*, 40 CFR 435.50 *et seq*, the National Toxics Rule (NTR), the California Toxics Rule (CTR), the State Water Resources Control Board Policy for Implementation of Toxics (Resolution 2000-015 as amended by Resolution 2000-30), the Anti-degradation Policy (Resolution 68-16), and the narrative and specific numeric water quality objectives contained in the Central Coast Basin Plan for the Salinas River and any groundwater that might be impacted by the discharge. It is our understanding that the Water Board would apply these regulations and/or policy documents in the following manner:

Applicability of 40 CFR 435.30 *et seq.*

This is the federal regulation promulgated by the Environmental Protection Agency (EPA) in which effluent guidelines for the oil and gas extraction industry were developed. Specifically, 435.30 *et seq.* addresses discharges from the "onshore" subcategory of the oil and gas extraction industry that are located landward of the inner boundary of the territorial seas. In paragraph 435.32, the effluent guideline states, "there shall be no discharge of waste water pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion, or well treatment". It is our understanding that unless the waste water discharge to the Salinas River is subject to other provisions combined in 40 CFR 435, the Water Board will not allow any discharge of waste water to the Salinas River.

Applicability of 40 CFR 435.50 *et seq.*

This section of the federal regulations promulgated by the EPA addresses onshore facilities "located in the continental United States and west of the 98th meridian for which the produced water has a use in agriculture or wildlife propagation when discharged into navigable waters". The onshore facilities in the San Ardo Field are located in the continental United States and they are located west of the 98th meridian. The waste water will be treated before discharge to meet quality standards for use in agricultural applications. In 435.51, the term "use in agricultural or wildlife propagation" is defined to include produced water of good enough quality to be used for agricultural uses. It is our understanding that by treating the waste water to meet the necessary water quality standards for use in agricultural applications, then the Water Board will allow the discharge of treated waste water. The discharge will be subject to certain limitations specified in 40 CFR 435.52, namely, that the produced water (after treatment) will not exceed a daily maximum limitation for oil and grease of 35 mg/l and other limitations as discussed below.

Applicability of NTR and CTR, Water Board Implementation Policy

These two regulations and the State Board policy are intended to limit the discharge of "toxics" into navigable waters. It is our understanding that the Water Board will require that any discharge of treated water into the Salinas River meet the requirements contained in each of these documents. Furthermore, if there is any conflict between the documents, it is understood that the most restrictive requirement will be imposed on the discharge. The Regional Board will require that any pilot plant work that is undertaken characterize the treated water by testing for those parameters that have a "reasonable probability of being present" in the water. Sufficient samples will need to be analyzed to allow a statistical analysis of the data.

Applicability of Antidegradation Policy

The Water Resources Control Board passed this policy in the late 1960s to maintain the quality of existing water resources that are better than new water quality standards to be established at a later date. Under this policy, the discharge must not cause a degradation of the existing quality of the receiving water unless it has been demonstrated that the change will be consistent with maximum benefit to the people of the state, that it will not unreasonably affect the present and anticipated beneficial use of such water, and that it will not result in water quality less than that prescribed in the policies. It is our understanding that the Water Board will allow discharge of the treated waste water provided the discharge of the treated waste water will meet the requirements under the antidegradation policy.

Applicability of Central Coast Basin Plan

As indicated previously, the produced water will be treated to meet the agricultural water quality parameters prior to discharging. However, it is our understanding that the Central Coast Basin Plan contains beneficial use designations for the Salinas River that include Municipal and Domestic Water Supply (MUN) as well as Agricultural Water Supply (AG) and Industrial Water Supply (IND) uses among other uses. Therefore, it is our understanding that the Water Board will require that the treated water be treated to meet the most stringent of the narrative and specific numerical water quality objectives as identified in the Basin plan prior to discharge.

Alternative 2 - Application of Treated Water for Agricultural Irrigation

As discussed, another alternative is to hard-pipe the treated water directly to end-users. In this scenario, the end user would apply the treated water for agricultural irrigation. It is our understanding that the Water Board would require a Waste Discharge Requirement (WDR) for this use. However, because of the potential benefits of this project for the reuse of a valuable water resource, the specific monitoring requirements would be limited. The water would need to be tested to ensure that the water quality objectives of the Basin Plan are not violated.

Alternative 3 - Indirect Discharge via Seasonal Storage of Excess Treated Water

As discussed, the treated water may not be constantly needed whereas the treatment process will be a year-round operation. Therefore, some type of seasonal storage alternative may be needed. It is our understanding that the Water Board may waive the requirements of Chapter 15 provided it can be demonstrated that the treated water meets all of the water quality objectives of the Basin Plan and the Toxics Implementation Policy for the potentially impacted waters. However, any containment structure will need to meet the structural standards of the rule.

Alternative 4 - Application of Treated Water for Alternative Beneficial Uses

Lastly, there are a number of other potential alternatives that involve the use of existing ground and/or surface waters, e.g. the saltwater barrier project. A scenario in which the treated produced water could be used as replacement water for this or other "source water" is a possibility. In such a case, the existing groundwater or other "source water" could be pumped for agricultural use or some other beneficial use, either directly or indirectly, via discharge into the Salinas River. Aera and Kennedy/Jenks are working with various water agencies and other entities to identify new potential end-users. It is our understanding that the Water Board would be very interested in participating in these discussions and working with the parties in trying to enhance the beneficial recycling of water resources in the region.

We hope that you find that our understanding of the various water regulations is similar to yours. We await your response to this letter.

Very truly yours,

KENNEDY/JENKS CONSULTANTS

Raymond E. Ouellette

Raymond E. Ouellette, R.E.A., QEP
Associate Environmental Scientist

cc: Mr. Robert A. Liske, Aera Energy LLC
Mr. Ron Chambers, Aera Energy, LLC
Mr. Roger Funston, K/J
Mr. Ganesh Rajagopalan, K/J ✓

Appendix D: Copies of Tech Transfer Activity

APPENDIX D: TECH TRANSFER ACTIVITIES

Appendix D

Appendix D-1: Abstract Submitted for Various SPE Sections, West Coast Petroleum Technology Conference and Channel County Water Utilities Association

Appendix D-2: Manuscript Submitted for the 20th WateReuse Symposium Conference

Appendix D-3: Manuscript Submitted for 12th IPEC Conference

Appendix D-4: Abstract Submitted for CA/NV Section AWWA Spring 2006 Conference

Appendix D-5: Paper Submitted for Water Environment Federation 2006 Annual Conference (WEFTEC 06)

Appendix A

Abstract Submitted for Various SPE Sections, West Coast Petroleum Technology Conference and Channel County Water Utilities Association

Treatment of oilfield-produced water for beneficial reuse is being evaluated as an alternative to disposal by re-injection within the San Ardo oilfield. This project investigates the opportunity to create a "win-win" situation of both increased oil production and increased reclaimed water supply. The project was jointly funded in 2002 by the U.S. Department of Energy, Aera Energy LLC, and Kennedy/Jenks Consultants. The scope of the project includes: i) identifying opportunities for the use of treated produced water in the project area, ii) identifying water quality goals and regulations related to use of the water, iii) evaluating various water treatment options, iv) performing pilot studies and, v) developing treatment cost estimates for full scale operation. A nine-month pilot test was completed in March. This presentation will discuss the project's results, as well as some of the challenges and obstacles that remain.

Appendix B

Manuscript Submitted for the 20th WateReuse Symposium Conference

EVALUATING THE POTENTIAL FOR BENEFICIAL USE OF OILFIELD PRODUCED WATER FOR AGRICULTURAL IRRIGATION IN SAN ARDO, CA

Dr. Rajagopalan Ganesh, Kennedy/Jenks Consultants, Irvine, CA
Dr. Lawrence Y.C. Leong, Kennedy/Jenks Consultants, Irvine, CA

BACKGROUND

Oil production generates a large amount of by-product water, commonly known as "produced water". As oil is produced from an oil field, the amount of produced water can account for over 90 percent of the fluids pumped from a well. In fact, California heavy oil production typically generates 10 to 15 barrels (420 to 630 gallons) of water for every barrel of oil. In 2002, approximately 14 billion barrels (1.8 million acre-feet) of produced water was generated in the United States from onshore oil production alone (1).

The most prevalent method of using or disposing of oil field produced water is to inject it underground. A significant portion (50 to 65 percent) of produced water from onshore sources is currently reinjected into oil producing zones where it enhances oil recovery (using water flooding and steam flooding) or for subsidence control. The other 35 to 50 percent is disposed of via deep well injection. Unfortunately, deep well injection disposal may increase reservoir pressure and lead to lower oil recovery and increased production costs. In such cases, eliminating deep well injection by finding a beneficial use for the treated water may increase oil production, increase recoverable oil reserves, and reduce production costs. Furthermore, treatment of oilfield produced water may provide a new reclaimed water supply for specific uses in water-short areas such as California.

However, the feasibility of produced water reclamation depends on a number of factors. For example, the chemical composition of the produced water, which is typically very saline, can significantly impact the treatability of these waters. The total dissolved solids (TDS) of produced waters in the United States can range from about 3,000 to more than 350,000 mg/l, with sodium and chloride generally comprising 70 - 90 percent of the TDS. The produced water may also contain high concentrations of calcium, iron, manganese, ammonia, boron, and dissolved organics (2). Often, the complexities involved in treating these waters (e.g. TDS > 10,000 mg/l) may render produced water reclamation cost-prohibitive. In addition, regulations adopted pursuant to the Clean Water Act prohibit the discharge of treated produced water from onshore oil and gas wells into surface waters, except in areas west of the 98th Meridian (a north-south line approximately running from just west of Minnesota down through Dallas, Texas). Discharge of treated produced water directly into surface waters west of the 98th Meridian is allowed only if the treated water is of acceptable quality for agricultural use or wildlife propagation. If the treated water is intended for any other beneficial use, it must be delivered through direct piping or alternate means.

Produced Water Resources in California

The California Division of Oil, Gas, and Geothermal Resources (DOGGR) reports that about 280,000 acre-feet of produced water were generated from oil and gas production in 2000 (3). About 50 percent of this produced water is probably unavailable as a water resource because of reinjection for enhanced oil production or subsidence control, or because of the high costs of treating the water. DOGGR records indicated that the majority of oil fields in California have produced water with

15,000 to 35,000 mg/l TDS. However, there are a number of large fields which produce waters below 10,000 mg/l TDS. Treating the produced water from these lower salinity fields could generate a water resource that might be cost competitive with other, new sources of fresh water

As Figure 1 illustrates, oil field water is primarily produced in 10 counties along the southern and central coast and lower central valley areas of California. This is the same area where there is significant interest and experience in water reuse.

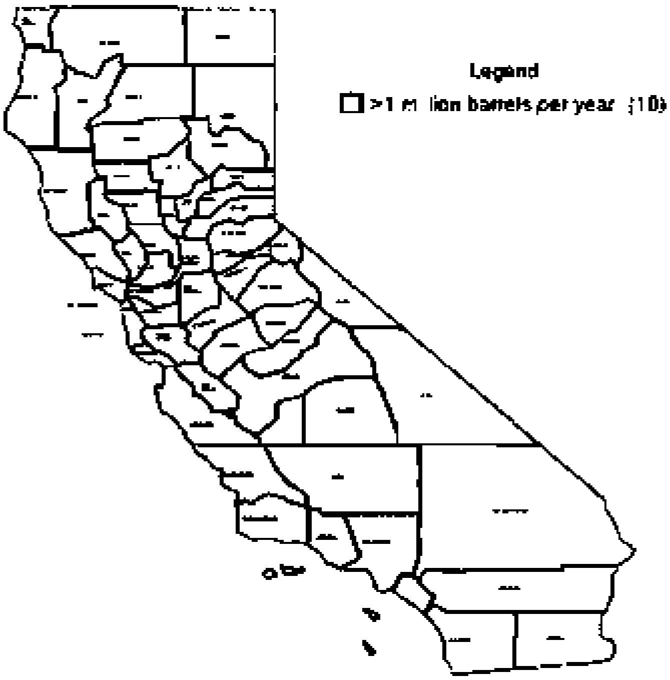

Figure 1: California Counties With More Than 1 Million Barrels Per Year Of Produced Water

Demonstration Project for Produced Water Reclamation at San Ardo, CA

The potential for treatment and beneficial reuse of produced water from the San Ardo oilfield in Monterey County, CA was evaluated through a project jointly funded by Department of Energy (DOE), Aera Energy LLC, and Kennedy/Jenks Consultants. The moderate salinity level of the produced water from this oilfield (less than 10,000 mg/l TDS, Table 1) should provide a reasonable opportunity for successful treatment. In the San Ardo area, the Salinas Valley groundwater basin provides most of the water supply needs. Due to high water demands from population growth and agriculture, groundwater extraction currently exceeds the sustainable yield of this basin. The high dependence on groundwater has resulted in a long-term average overdraft of about 19,000 acre-feet per year (AFY). The overdraft conditions have caused seawater to intrude for approximately 6 miles in the northern Salinas Valley, where the Salinas River empties into the Pacific Ocean. Based on the current daily rate of produced water generation from the Aera Energy LLC operation at the San Ardo oilfield, a successful produced water treatment project could generate an estimated 3,500 AFY (~ 18 percent of the annual overdraft) of treated water.

The overall project was divided into two phases. Phase I of the project identified the potential end users of the treated water, regulatory requirements for treatment and delivery of the water, and potential treatment alternatives for various end use options. Under Phase II, a demonstration pilot treatment train was constructed and operated.

OBJECTIVE

Potential purchasers of treated oilfield produced water in the San Ardo area are limited because there are currently no low-cost regional conveyance facilities in this portion of the Salinas Valley, except for the Salinas River. One of the potential uses of the treated water in the project area is agricultural irrigation for current or additional agricultural production. This paper presents water quality challenges, regulatory requirements, treatment alternatives, estimated costs and other challenges to convert this moderately saline "wastewater" for potential agricultural irrigation use in the project area.

AGRICULTURAL WATER USE IN THE PROJECT AREA

Agricultural Land and Water Demand in the San Ardo Oilfield Area

In 1995, agricultural land in the Salinas Valley extended across an area of approximately 200,000 acres (5). In the Upper Salinas Valley (the southern portion near San Ardo), agricultural land use is estimated to be 48,000 acres (5). Field and row crops occupy the most land (26,000 acres), with vineyards being the second largest land-users (16,000 acres). The 1995 Salinas Valley agricultural land use by crop is shown in Table 1.

Table 1: Upper valley sub-area crop acreage (1995)[5]

Type of Crops	Upper Salinas Valley (Acres)	Total Salinas Valley (Acres)
Pasture	1,900	4,200
Field	450	7,000
Row	25,800	143,000
Orchards	450	1,100
Vineyards	16,300	35,000
Grain	3,000	5,000
Total Acreage	48,000	196,000

Preliminary evaluations indicated that economical delivery of treated water for agricultural irrigation required the farmlands to be within a 5-mile radius of the oilfield. A Geographical Information System (GIS) analysis was performed to categorize the 3,500 acres of farmland within this boundary. Since these farms are located downstream of the oilfield, water could potentially be delivered either through the Salinas River or directly through a pipeline. These farms were identified as the most likely agricultural users for treated produced water.

About 2,700 acres of the 3,500 farmland acres can be served using a 2.5-mile pipeline from the San Ardo oilfield. One owner accounts for nearly 50% of the 3,500 acres and three others have about 900 acres. The MCWRA 1995 data indicated that for this area, the average irrigation water usage was 2.75 AF/acre (5) with peak irrigation water needs being from June through August. All of the available treated produced water from the oilfield could potentially be used by less than 2,000 acres of farmland; however, since some of the crops are seasonal, agricultural demand would not match the continuous production of water.

Agricultural Crops in the San Ardo Oilfield Area and Water Quality Requirements

Table 2 shows the perennial and annual row crops typically grown in the project area. Water quality guidelines for general irrigation, and those for the crops grown in the project area, are shown in Table 3. Untreated San Ardo produced water characteristics are also shown for comparison.

Table 2: Crops grown in San Ardo area

Type	Crops
Perennial Crops	*alfalfa*, asparagus, grapes (predominantly *wine* grapes, such as cabernet, merlot, and chardonnay), and walnuts
Annual "Row" Crops	beans (lima, seed), broccoli, cabbage, cauliflower, garlic, lettuce (leaf, head, Romaine), onions, parsley, peppers, spinach, tomatoes.

Tables 3 compares untreated oilfield produced water quality and Central Coast Regional Water Quality Control Board (CCRWQCB) water quality requirements for irrigation use. In addition, if the treated water is delivered through the Salinas River, treated produced water must also meet requirements of the National Toxicity Regulation (NTR). As shown in Table 3 concentrations of ammonia, nitrogen, boron, chloride, fluoride, salinity, sodium and TOC in the untreated produced water exceed CCRWQCB requirements.

Table 3: San Ardo produced water and CCRWQCB water quality requirements

Compound	*San Ardo Produced Water (mg/l)*	*CCRWQCB Basin Plan (Agricultural use) Criteria*
Alkalinity	367	
Aluminum	0.2	5[a]
Arsenic		0.1[a]
Ammonia - Nitrogen	31.1	5 – 30[b]
Barium	0.41	
Beryllium	<0.0005	0.1[a]
Bicarbonate	448	90 – 520[b]
Boron	26.8	0.75 [a]
Cadmium	<0.0005	0.01[a]
Calcium (Ca^{+2})	111	
Carbonate	1	
Chloride	4,050	150[c]
Chromium		0.1[a]
Cobalt		0.05[a]
Copper	0.0008	0.2[a]
Fluoride	1.8	1[a]
Hardness, Total	303	
Iron	0.17	5[a]
Lead		5[a]
Lithium		2.5[a]
Magnesium (Mg^{+2})	6.07	
Manganese	0.105	0.2[a]
Molybdenum	0.008	0.01[a]
Nitrate-Nitrogen	4	5 – 30[b]
pH	7.54	6.5 – 8.4[b]
Potassium	61.6	
Salinity (mmho/cm)	10.7	0.75 – 3[b]
Selenium	<0.0005	0.02[a]

Silica (SiO_2)	227	
Sodium	2,540	70[c]
Sodium Adsorption Ratio		3 - 9
Strontium	2.68	
Sulfate	63	150[c]
Sulfide	12	
TDS	7,540	600[c]
TPH (oil and grease)	1.9	35 (for NPDES discharge)
TOC	80	<2[d]
Vanadium		0.1[a]
Zinc		2[a]

a – CCRWQCB Water Quality Objective for Agricultural Water Use
b – Guidelines for interpretation of quality of water for irrigation. The range shown is for "increasing problems" for crops.
c – Median groundwater quality objective for upper Salinas Basin
d – Adapted based on anti-degradation policy

REGULATORY REQUIREMENTS AND AGENCIES

Key regulatory issues affecting the treatment, delivery and use of treated produced water for agricultural use include

- Water quality
- Disposal of treatment process waste streams
- Air emissions
- Water rights issues if treated produced water is delivered via the Salinas River
- Storage of treated water

The agencies involved in various permit processes for a potential San Ardo project are listed in Table 4. It is believed that these permit requirements can be met although these requirements for a potential project appear extensive. One exception is permitting a direct discharge of treated water into the Salinas River, which appears to be highly unlikely due to the limitations of agricultural and wildlife propagation in the NPDES program and the sensitivities to process upsets that could result in releases to a flowing waterway.

Table 4: Agencies involved with permit processes for delivery and Use of San Ardo oilfield produced water

Agency	Activities Regulated
Central Coast Regional Water Quality Control Board	Water/waste quality issues related to treatment, delivery, storage and end use, NPDES permit for Salinas River discharge
California Water Resources Department – Water Rights Division	Water rights/water allocation issues if treated water is discharged into Salinas River
California Water Resources Department –Division of Dam Safety	Storage of treated water in surface impoundments

US Army Corps of Engineers	Storage facilities near navigable waters for federal funded projects
US Fish and Wildlife Service	Ecological Impacts of federal funded projects
Monterey County Planning & Building Inspection Department	Zoning and Land Use compliance and grading permits for decentralized storage of treated produced water
Monterey Air Pollution Control District	Potential air emissions from treatment facilities and expanded oil production

WATER QUALITY GOALS AND TREATMENT TECHNOLOGIES

Depending on the intended use, San Ardo produced water requires treatment for a number of constituents. Because the produced water in this field is delivered at temperatures above 170° F, pathogenic microorganisms are not of concern. However, the water temperature must be controlled for some of the processes to be effective. For example, warm precipitation softening, air stripping, and vapor compression desalination can be accomplished at these produced water temperatures, while some other processes perform better at cooler temperatures.

Table 5 summarizes key water quality parameters of the San Ardo produced water that exceed the goals for agricultural use in the Upper Salinas groundwater basin. The levels of dissolved salts (7,000 mg/l TDS), ammonia (30 mg/l), boron ((25 mg/l B), and organics (oil and grease up to 50 mg/l, TOC up to 100 mg/l) must be dramatically reduced to become an agricultural water resource. In addition, the concentration of silica (~200 mg/l SiO_2) and hardness (~250 mg/l as $CaCO_3$) in the produced water are well-known problems for most TDS removal technologies. Potential treatment alternatives for these constituents are discussed below.

Table 5: Key Parameters of Concern in Untreated San Ardo Produced Water for Agricultural Irrigation in the Upper Salinas River Groundwater Basin

Parameter	Untreated San Ardo Produced Water	Basin Plan/Crop Requirements
TDS, mg/L	6500	< 600
Boron, mg/L	26	0.75
Ammonia, mg/L	31	5 - 30
TOC, mg/L	100	< 2
Temperature, °F	175	75

Dissolved Salt Removal

The dissolved salt in produced water must be reduced to below 600 mg/l for agricultural use in the Upper Salinas Basin. The most promising treatment technologies are distillation using mechanical vapor compression (MVC), membrane separation using reverse osmosis (RO) and Electrodialysis Reversal (EDR) membranes. RO and EDR are generally the technologies of choice for brackish (TDS < 10,000 mg/l) water applications.

A pretreatment process, such as warm softening, to remove silica and hardness is required for both thermal and membrane desalination processes. Some MVC systems incorporate silica removal as part of the core process, using seeded-silica slurry. The EDR process may require pretreatment of the water to remove hardness but may not for silica removal.

Organics Removal

A total organic carbon (TOC) goal of 2 mg/l is selected based on the CCRWQCB anti-degradation policy. MVC and RO processes can remove a large fraction (but not all) of the organics. Doran, et al., (1999) reported that permeate TOC levels below 2 mg/l can be obtained during treatment of oilfield produced water by RO process (6). The removal of organics, particularly the high amounts of low molecular weight aromatic compounds and naphthenic acids found in heavy oil, will be a major challenge for EDR based treatment. Pretreatment using fixed-film biological oxidation, granular activated carbon (GAC) or membrane bioreactor (MBR) are candidate processes for organics removal if an EDR-based treatment process is selected for produced water treatment. Because many of the organics present in heavy oil fields are refractory (hard to degrade), pilot tests are necessary to determine the efficacy of organic removal by these processes.

Ammonia Removal

Ammonia levels of the treated water for most agricultural use must be below 5 mg/l. 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 (by use of a cooling tower) or in separate strippers at high pH. Ammonia can also be removed by breakpoint chlorination.

Boron Removal

Boron removal is particularly important for irrigation water (Table 4), and a treated water goal of less than 1 mg/l was selected for this project. If sufficient magnesium is added, some of the boron can be removed along with the silica during the warm softening process. Boron can also be removed by RO at high pH or by ion exchange using special anion exchange resins.

Silica Removal

Although there is no silica standard for irrigation water, low silica concentrations are desirable for steam production and other industrial uses, and a project goal of 30 mg/l was selected. Silica removal can be accomplished by precipitation softening through magnesium addition. Silica can also be removed by anion exchange.

Hardness Removal

Hardness in the range of < 20 mg/l is generally desirable to control scaling in a desalination process. The EDR process, due to larger membrane pore size, may tolerate slightly higher levels of hardness than the RO process. Total hardness, including calcium and magnesium, can also be removed along with silica in the warm softening process. In addition, residual hardness remaining in the softened water can be removed by using cation exchange. This is important if salinity removal is carried out at high pH.

Brine and Sludge Management

The production of sludge during precipitation softening, and of brine during desalination, may be significant issues in the selection/operation of the treatment process. The amount of sludge produced and the strength of brine will partially determine the amount of pretreatment needed to prevent fouling by inorganic constituents. The composition of the sludge will also determine whether the residuals can be managed as a non hazardous waste. Therefore, the volumes and compositions of the sludge and brine wastes must be confirmed by pilot studies.

TECHNOLOGY SELECTION AND PLANNING LEVEL TREATMENT COSTS

Treatment Alternatives

The technical and economic feasibility of various thermal and membrane processes are summarized in Table 6. Since the RO process is more cost effective than thermal processes, and it can remove organic compounds (TOC) more effectively than the EDR process, an RO based treatment is selected for desalination of San Ardo oilfield produced water. Figure 2 presents a simplified schematic of the pilot process selected.

Table 6: Summary of technical evaluation of treatment alternatives for San Ardo Produced Water

Water Quality Goals	MVC	EDR + MBR	Warm Softening + RO
TDS	Very energy Intensive. Not cost Effective for brackish water. Generally better suited for water with TDS > 30,000 mg/l	Can Remove TDS to below 600 mg/l. Very energy intensive.	TDS < 200 mg/l can be achieved. Required less energy than MVC or EDR.
TOC	Can destroy most organics	Not effective for TOC removal. Most (~ 70%) of the oilfield organics are recalcitrant.	RO can remove TOC to below 2 mg/l.
Boron	Need additional treatment.	Need supplemental treatment	RO can remove boron to < 1 mg/l at pH > 10.5.
Ammonia	May need additional treatment	May be effective for ammonia removal	Most ammonia can be removed in the cooling process (cooling tower). Supplemental treatment may be required.
Hardness Removal	May need additional treatment	May tolerate higher hardness level than MVC and RO.	Pretreatment (warm softening) is required.
Silica	May need additional treatment.	Can tolerate higher silica levels.	Need pretreatment (warm softening with Mg addition).
Temperature	Cooling is required	Cooling is required	Cooling is required

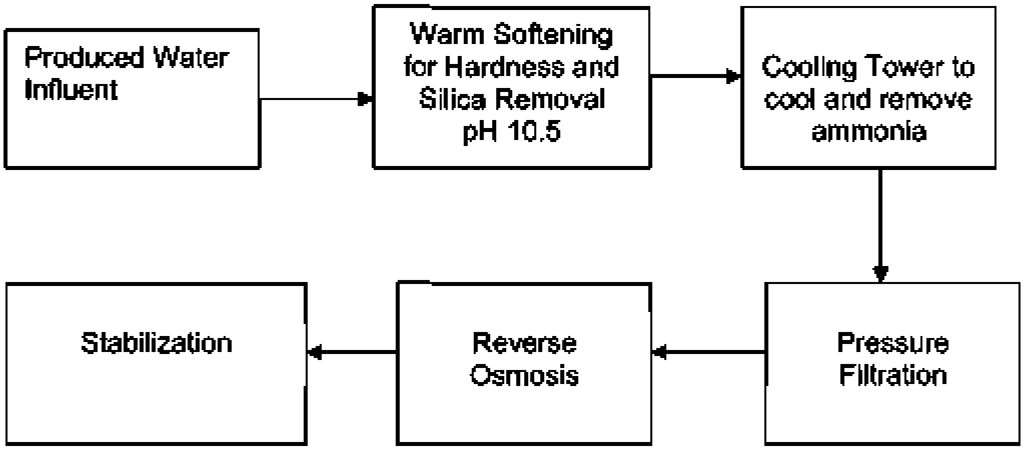

Figure 2: Simplified schematic of RO based process for treatment of produced water

Capital and operating cost estimates for a facility capable of treating 4.2 MGD (100,000 bbl/day) were developed using information from equipment vendors, cost estimate models, and preliminary data from the recently completed pilot study at the San Ardo site. The RO process train includes warm softening at pH 9.5 to remove scale forming compounds, a cooling tower, pH adjustment to 10.5, reverse osmosis to remove dissolved solids and boron, and pH neutralization (Figure 2). Total capital costs include equipment and direct construction costs, such as installation costs, as well as indirect costs such as legal fees and administration. Operating costs include chemicals, sludge disposal, energy, and labor. Capital costs were amortized over 20 years at an interest rate of 7 percent per year. These amortization rates are typical for municipal water utilities that often finance capital expenses through bonds.

Table 7 shows the estimated cost breakdown for various components of the process train. The planning level capital cost estimate is about $ 19 million and O&M cost is about $7.1 million per year. The estimated cost of treated water is about $2,740 per acre-foot.

Table 7: Cost Breakdown for Reverse Osmosis System

Process	Total Capital Cost (M 2005 $)	Annual Operations Cost (M 2005 $)	Total Annual Cost (M 2005 $)	Total Unit Cost (2005 $/AF of water produced)	Total Unit Cost (2005 ¢/ barrel of water treated)
Warm Softening	2.2	4.6	4.8	1,450	13.2
Cooling Tower	0.65	0.23	0.29	87	0.80
Reverse Osmosis	3.8	2.2	2.6	790	7.1
Polishing	2	0.075	0.26	79	0.7
Treatment	10		0.9	333	3.0

Building & Indirect Expenses					
Total	**19**	**7.1**	**9.0**	**2,740**	**25**

CONSTRAINTS ON THE USE OF TREATED PRODUCED WATER FOR AGRICULTURE USE IN SAN ARDO, CA

Although the demonstration project identified the need for additional water resource in the project area and showed the technical feasibility of treating the San Ardo oilfield produced water for agricultural use, there are several concerns that must be addressed prior to implementation of this concept. For example, there is a significant seasonal variation in water demand for agriculture, with the peak demand period extending from June through August. The treated produced water from oilfield operation is, however, generated continuously. Hence, a large above ground or underground storage facility may be required for storing water generated during the non-peak irrigation period. Secondly, significant effort may be required to convince farmers to accept a recycled water source for irrigation. Finally, the cost of treating and delivering the water must be compared with the benefit of increased oil production.

SUMMARY

Water extraction from the Salinas Valley groundwater basin has resulted in a long-term average overdraft of ~ 19,000 AFY. The treated San Ardo oilfield produced water would help address this overdraft. It is estimated that the treated produced water would meet the agricultural irrigation requirements for 2,000 acres, all of which are within 2.5 miles of the oilfield. The planning level (-30 percent, + 50 percent) cost estimate for treating produced water is about $2,740/AF. Overcoming the challenges posed by costs, deliverability, variable demand and regulatory permitting could result in the development of a new usable water resource for the Southern Salinas Valley. At the same time, removal of excess produced water would reduce the hydraulic pressure in the oil reservoir by reducing the volume of Class II well injection. This reduction may reduce the cost of oil production and increase recoverable reserves at this oil field. However, several concerns including storage of treated water during non-peak agricultural demand period, acceptance of recycled water for agricultural use by the farmers, and the economic benefits of increased oil production compared with the overall project costs, must be addressed prior to field implementation of this project.

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Appendix C

Manuscript Submitted for 12th IPEC Conference

OVERVIEW OF REGULATIONS FOR POTENTIAL BENEFICIAL USE OF OILFIELD PRODUCED WATER IN CALIFORNIA

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ABSTRACT

Produced water generated during oil production by thermal (steam) recovery processes is often disposed by Class II deep well injection within the oil production zones. Such in-field injection may increase the water to oil ratio and reservoir pressure, resulting in decreased oil production. Reducing Class II injection through alternative disposition of the produced water may enhance oil field development and crude oil production.

The use of produced water involves treatment to meet specified water quality goals, delivery and storage of treated water and safe disposal of the residuals. Each of these activities is or may be subject to regulation by Federal, State and local agencies. A focus of this project, jointly funded by USDOE, Aera Energy LLC and Kennedy/Jenks Consultants, is to identify alternate end uses for produced water in the immediate vicinity of the San Ardo oilfield, located in the Salinas Valley near the Central Coast of California. This paper presents an overview of regulatory requirements and issues related to treatment, delivery, storage and waste stream management to potentially use produced water in the San Ardo area and concludes that the regulatory obstacles are, in some respects, significant. The regulatory agencies include United States Army Corps of Engineers; the California Regional Water Quality Control Board; California Department of Water Resources; California Department of Fish and Game, and Monterey County Water Resources Agency. The types of permits required vary with mode of treated water delivery and location of treated water storage facilities.

Background

Production of crude oil through enhanced steam recovery is typically associated with a large amount of produced water. Although the quality of the water produced varies, these waters typically have salinity concentrations from 1000 mg/l to more than 350,000 mg/l. The waters are generally high temperature (150 to 200 °F), and usually contain elevated levels of silica, boron, ammonia and dissolved organics. These waters are often injected into Class II wells. Such in-field injection may increase the produced water-to-oil ratio and reservoir pressure, resulting in lower oil production and higher oil production costs. Reducing Class II injection through alternative disposition or use of treated produced water may enhance oil production and increase recoverable reserves in an oilfield.

Limited water resources and increases in population have put a strain on California's water supply. Several reports indicate that the overall water demand for California will exceed supply after the year 2020. The effective and efficient treatment and use of the produced water could create a win-win situation for both oil producers and water users by increasing oil recovery while increasing much needed water resources.

This DOE funded (No.DE-FC26-02NT15463) study evaluates the potential for treatment and use of produced water from an oilfield near San Ardo in Monterey County, CA. Around San Ardo, the

Salinas Valley groundwater basin provides most of the water supply needs. Due to high water demands from population growth and agriculture, groundwater extraction exceeds the sustainable yield of this basin. The dependence on groundwater has resulted in a long-term average overdraft of 19,000 acre-feetfeet per year (AFY) in the Salinas Valley basin. The overdraft conditions have resulted in seawater intrusion for about six miles into the northern Salinas Valley, before the Salinas River empties into the Pacific Ocean. A successful produced water treatment process could make available more than 4,000 AFY of water from the San Ardo oilfield. This is about one-fifth of the annual overdraft.

This paper describes the Federal, State and local regulations related to delivery, storage and use for possible end uses of the treated oilfield produced water in the project area. It must be emphasized that the uses identified in this paper are based on initial screening of potential alternatives.

Alternative Use and Water Delivery Options

In this section, the possible uses for the treated water, based on preliminary evaluations, are presented. These possible uses, however, must satisfy stringent regulatory, economic, user-perception, and long-term reliability criteria prior to actual implementation. Furthermore, depending on the type of use, implementation may also require complex water trade arrangements with one or more water agencies. Finally, large storage facilities (hundreds of million gallons capacity) would be needed if there is a large seasonal variation in water demand for the identified end use. Such limitations may increase the overall costs of the project significantly and render the use non-viable. These uses are presented in this section only to facilitate a discussion on regulatory requirements for various alternatives in the following sections.

The potential users of treated oilfield-produced water in the San Ardo area are limited because, among other things, there are no regional conveyance facilities in the Salinas Valley other than the Salinas River. Potential uses of the treated water in the project area could include the following:

- Agricultural applications in nearby farms, including those that currently utilize groundwater, and those landowners who desire to bring land into agricultural production
- Agencies at downstream locations
- Industrial applications
- Creation of wetlands in the Salinas Basin

Agriculture

A report by Monterey County Water Resources Agency (MCWRA, 2000) indicates that approximately 48,000 acres of farmland are available in the upper Salinas Valley Basin (San Ardo area). About 3,500 acres of farmland are located within five miles of the oilfield, downstream of the Salinas River. The key crops cultivated in these farms include broccoli, lettuce, spinach, carrots, potato, cabbage and chile peppers. Data from MCWRA indicate that the average amount of water applied for irrigation in 1995 in the Upper Salinas Valley was about 2.75 AF/acre (MCWRA, 1998). Hence, all of the treated produced water generated from this project could, theoretically, be used on less than 2,000 acres of farmland. Treated water from the oilfield might be delivered through the Salinas River or by direct pipeline.

The limitations in the use of oilfield water for agriculture include i) efforts required to convince farmers to use recycled water for irrigation; ii) need for a large storage system/alternate use arrangement during the low demand season (September – May) since the oilfield produced water is generated throughout the year; and iii) transportation / conveyance of the water to farmers.

Agencies at Downstream Locations

The MCWRA is a public agency that has been charged with the long-term management and preservation of water resources in Monterey County. In order to prevent seawater intrusion into the Salinas Valley Basin and protect agricultural water use, MCWRA has undertaken two major projects: 1) the Salinas Valley Water Project (SVWP), and 2) the Castroville Seawater Intrusion Project (CSIP). The key components of these projects are to identify alternate sources of water for agricultural use in the Salinas Valley Basin and prevent seawater intrusion by reducing groundwater drawdown at the lower Salinas Valley Basin. The main objective of the SVWP is to increase the capacity of the Nacimiento Dam reservoir by i) modifying the Nacimiento Dam spillway; and ii) constructing a diversion facility to divert part of Salinas River water for the CSIP. Under the CSIP, the excess water from the Salinas River diversion would be diverted to the Castroville service area for agricultural use. This would replace the groundwater that is currently pumped for agricultural irrigation in this area, and would help prevent seawater intrusion into drinking water aquifers. The operational objective of the project is to stop seawater intrusion into the Salinas Basin and provide up to 1000 AFY net groundwater outflow to Monterey Bay. In addition, the average annual Salinas River diversion capacity is about 12,000 AFY. By comparison, the amount of water that would be generated by treatment of produced water at the San Ardo oilfield is about 4,000 AFY. However, one of the key limitations in this use is the loss of added water during transport due to evaporation and percolation, particularly in dry weather conditions.

Industrial Use

A power plant located at King City, California was initially considered as a candidate for using treated produced water for its cooling water needs. This plant is located about 30 miles north of San Ardo, downstream of the Salinas River. For this application, delivery of water through the Salinas River is not possible due to the beneficial use requirements in 40 CFR 435.30 (discussed below). In addition, delivery of water by a new, unsubsidized 30-mile pipeline appears to be cost prohibitive. Hence, this option is no longer under consideration.

Wetlands Development and Other Applications

The treated produced water could conceivably be used to create wetlands in the Salinas Basin. Such an end use would require a biodiversity study to identify potential benefits to animal and plant species in the project area. However, potential use of treated produced water for wetlands development may require long-term reliability of water supply from the oilfield. This may be a concern if the oilfield operations are curtailed for any reason or terminated at the end of the economic life of the oilfield or for other reasons.

Water Trade/Water Delivery Issues

The following water trade/delivery scenarios were considered for alternative disposition of the treated water:

- Convey the treated water directly (through hard pipe) to agricultural growers in the vicinity of the project area and allow a partnering water agency to obtain the agricultural end-user's unused groundwater. This groundwater would be discharged into the Salinas River, which would provide the conveyance system for downstream diversion to areas impacted by seawater intrusion and declining water levels.

- Provide treated produced water to a water agency that would discharge it directly to the Salinas River for downstream diversion to areas impacted by seawater intrusion.

Regulations for Delivery, Use and Storage of Treated Produced Water

Water quality requirements vary with the use and the mode of delivery. In addition, delivery of treated water through the Salinas River must address water rights issues for downstream users. Finally, permits related to the structural integrity of the containment basin and water quality must be obtained if the water is stored during periods of low demand. This section describes the agencies and regulations related to the above activities.

Table 1. Activities regulated and responsible agencies for potential delivery, use and storage of treated produced water

Agency	Activities Regulated
Central Coast Regional Water Quality Control Board	Water/waste quality issues related to treatment, delivery, storage and end use
California Water Resources Control Board – Water Rights Division	Water rights/water allocation issues if treated water is discharged into the Salinas River
California Department of Water Resources –Division of Safety of Dams	Storage of treated water near surface waters
US Army Corps of Engineers	Storage facilities near surface waters, if federal funding is involved
Monterey County Planning and Building Inspection Department	Grading permits for storage of treated produced water
California Department of Fish and Game	Activities which alter stream flows (e.g. construction of discharge structures in the river bank)

Regulations Related to Water Quality

Central Coast Regional Water Quality Control Board

The Central Coast Regional Water Quality Control Board (CCRWQCB) is the principal regulatory agency responsible for overseeing the discharge of any water that could impact California water resources in this region. This authority comes from the Porter-Cologne Water Quality Control Act (Porter-Cologne) that established the California State Water Resources Control Board (CWRCB) and nine Regional Water Quality Control Boards. The CCRWQCB is one of these nine regional boards.

The CCRWQCB, in its role of implementing the State Policy for Water Quality Control, has adopted a Basin Plan that identifies the beneficial uses of the various existing water resources in the region, including surface and ground water. Any discharge from this project would most likely occur within the Salinas Hydrologic Unit. This hydrologic unit is subdivided into various sub-units and each sub-unit has its own set of beneficial uses.

All beneficial uses are protected by the development of water quality objectives that, in turn, are used to establish local waste discharge requirements (WDRs). The WDRs must also comply with the existing State Implementation Policy related to the National Toxics Rule (NTR) and the specific California Toxics Rule (CTR).

Authorization from the CCRWQCB is required for any discharge that may have an impact on the region's water resources. Two types of authorization are issued. The first is the National Pollutant Discharge Elimination System (NPDES) permit, a national program delegated to the State and Regional Boards for implementation. This permit affects any discharge to a water of the U.S. (primarily surface waters). The second is a set of WDRs which are a California authorization intended to protect state waters not covered by the NPDES permit program. In practice, it is common for the CCRWQCB to issue one permit that covers both program requirements.

The permit requirements under various water discharge (delivery) and water use scenarios are described below:

Water Quality Regulations Related to Delivery of Treated Produced Water through the Salinas River

In this scenario, produced water for irrigation would be treated and then discharged directly to the Salinas River. The treated water would need to meet the requirements found in the following regulations and/or policy documents:

- 40 CFR 435.30 *et seq*,
- 40 CFR 435.50 *et seq*,
- NTR)the CWRCB Policy for Implementation of Toxics (Resolution 2000-015 as amended by Resolution 2000-30),
- The Anti-degradation Policy (Resolution 68-16), and
- The narrative and specific numeric water quality objectives contained in the Central Coast Basin Plan for the Salinas River and any groundwater that might be impacted by the discharge.

40 CFR 435.30 *et seq.*

This is a federal regulation promulgated by the Environmental Protection Agency (EPA) in which effluent guidelines for the oil and gas extraction industry were developed. Specifically, 435.30 *et seq.* addresses discharges from the "onshore" subcategory of the oil and gas extraction industry that are located landward of the inner boundary of the territorial seas. In section 435.32, the effluent guideline states, "there shall be no discharge of waste water pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion, or well treatment" to the west of the 98th meridian. Unless wastewater discharge to the Salinas River is subject to other provisions contained in 40 CFR 435 (see below), the Water Board will not allow any discharge of wastewater to the Salinas River.

40 CFR 435.50 *et seq.*

This section of the federal regulations addresses onshore facilities "located in the continental United States and west of the 98th meridian for which the produced water has a use in agriculture or wildlife propagation when discharged into navigable waters". Onshore facilities in the San Ardo Field are located in the continental United States and they are located west of the 98th meridian. The wastewater would be treated before discharge to meet quality standards for use in agricultural applications. In 435.51, the term "use in agricultural or wildlife propagation" is defined to include produced water of sufficient quality to be used for agricultural uses. Discharge would be subject to certain limitations specified in 40 CFR 435.52, namely, that the produced water (after treatment) does not exceed a daily maximum limitation for oil and grease of 35 mg/l and other limitations as discussed below.

NTR and CTR, Water Board Implementation Policy

These two regulations and the State Board policy are intended to limit the discharge of "toxics" into navigable waters. CTR, promulgated in 2000, specifies water quality criteria for 128 priority pollutants based on their toxicity to aquatic species. These limits, presented in EPA Federal Register (USEPA, 2000), are generally lower than NPDES discharge limits based on Basin Plan criteria. Compliance with some of these limits would require significant, additional treatment processes and increased treatment cost.

Anti-degradation Policy

The CWRCB adopted this policy in the late 1960s to maintain the quality of existing water resources. Under this policy, the discharge must not cause a degradation of the existing quality of the receiving water unless it has been demonstrated that the change will be consistent with maximum benefit to the people of California, that it will not unreasonably affect the present and anticipated beneficial use of such water, and that it will not result in water quality less than that prescribed in the policies.

Central Coast Basin Plan

The CCRWQCB is responsible for adopting and implementing the Basin Plan that defines beneficial uses of surface and groundwater in the project area and sets narrative and numerical water quality objectives for the designated use. Accordingly, the beneficial use designations for the Salinas River include Municipal and Domestic Water Supply (MUN) as well as Agricultural Water Supply (AG) and Industrial Water Supply (IND) uses among other uses. In addition, the Basin Plan defines narrative and numeric criteria for groundwater recharge and agricultural use when the water is not delivered through the river. The Water Board may require that the produced water be treated to meet the appropriate criteria of the narrative and specific numerical water quality objectives as identified in the Basin Plan prior to discharge.

Water Quality Requirements Related to Delivery of Treated Water for Agricultural Irrigation by Hard Piping

In this scenario, the end user would get deliveries of treated water for agricultural irrigation by a hard pipe. The CCRWQCB would require a WDR for this use. The treated water must meet the following water quality criteria:

- Crop water quality requirements
- Water quality requirements of the Central Coast Basin Plan

Compared with delivery through the Salinas River, there would be fewer monitoring requirements. For example, a shorter list of parameters may be issued to routinely treat and report. These differences may or may not alter the treatment process train for the produced water.

Water Quality Requirements Related to Discharge of Groundwater into the Salinas River through Water Trade Agreement with Farm Owners

Under this scenario, treated water delivered for agricultural use would be traded for groundwater. The "freed–up" groundwater would then be pumped into the Salinas River for conveyance to downstream users. The groundwater pumped into the river must meet all the requirements specified in an earlier section for the discharge into the Salinas River.

Regulations Related to Water Rights

California Water Resources Control Board – Division of Water Rights

The CWRCB Division of Water Rights (DWR) is responsible for ensuring that water is shared equitably among all downstream users, based on historical or legally determined water rights. As such, the DWR establishes removal quotas or pumping limits based on the adjudicated volumes of water provided by the various sources. The addition of new sources of water, such as treated produced water, would likely need to be allocated to downstream users. The process requires identification of the volume of water and the potential downstream user. The permit to appropriate the released water by the identified user would be based on the amount of water delivered and potential losses during conveyance. The proposed use of the appropriated water must also be specified. The permit application must indicate the details of the diversion works (direct diversion by pump, storage dam, etc.). The permit application would have to be filed well in advance of the construction of diversion work.

The proposed project may be subject to the California Environmental Quality Act (CEQA) which requires agencies to consider environmental effects. This process may involve obtaining a certification of exemption, a negative declaration or a preparation of a full Environmental Impact Report (EIR). More details regarding the appropriation process is provided in the three pamphlets issued by the DWR (CWRCB 2000, 2000a, 2001).

Regulations Related to Storage

Due to potential differences in supply and demand for the treated produced water storage facilities may be required to store the water produced during non-peak demand period. For example, the peak water demand for agricultural use is between June and August. Depending on the location, size and funding source various agencies would be involved in the permit process for construction of storage facilities. Permit requirements from these agencies are briefly discussed below:

California Department of Water Resources – Division of Safety of Dams

The Division of Safety of Dams (DSD) would be involved with any project that creates a structure to impound water in a "navigable" water as defined by EPA if the structure is greater than 25 feet high or the impoundment contains more than 50 acre-feet of water. In this role, the DSD would ensure that the structural integrity of any jurisdictional dam (storage structure) is adequate for its intended purpose. Furthermore, the DSD would usually be the State representative for the US Army Corps of Engineers.

Water storage structures that are built solely for agricultural use and not located across a stream channel, watercourse, or natural drainage area are not considered to be a dam and not subject to the jurisdiction of the DSD. (California Water Code (CWC), Division 3, Part 1, Chapter 1, §6004(b)). The jurisdiction of the DSD normally applies to any structure that is 25 feet or more in height or has or will impound a capacity of 50 acre-feet or more. (CWC, §6002). However, the CCRWQCB would be involved because any water discharge into the storage area could have the potential to impact waters of the state, i.e. groundwater.

US Army Corps of Engineers

The Corps of Engineers is not normally involved in such projects unless there is direct U.S. Government funding for the construction of a dam. As such, the Corps of Engineers would rely upon the DSD to oversee any construction that does not involve federal funding (i.e., the COE will be directly involved only if the project receives federal funding).

Monterey County Planning and Building Inspection Department

The feasibility of local water storage in surface impoundments (ponds) on individual farmlands was explored. In order to install a pond, a farmer would be required to obtain grading permits from the Monterey County Planning and Building Inspection Department. As part of the permit process, the farmer must submit five sets of plans for each area where ponds are planned.

Central Coast Regional Water Quality Control Board

Chapter 3 of California Code of Regulations (Title 27, Division 2, Subdivision 1) classifies wastes to determine where the wastes can be discharged (stored). This chapter presents geologic and siting criteria for waste management units to store various waste streams. The CCRWQCB is responsible for defining the storage siting criteria if seasonal storage is required for treated produced water. However, an exemption from this requirement might be available if the waste (treated produced water) meets the criteria for inert waste as defined by section Ch15:§2524. An "inert waste" is a subset of waste that does not contain hazardous substances or soluble pollutants at concentrations in excess of applicable water quality objectives and does not contain significant quantities of decomposable waste.

Regulations Related to Wildlife Protection

California Department of Fish and Game

Any structure constructed for discharge of treated water into a waterway would require a stream alteration permit from the California Department of Fish and Game (CDFG). In addition, CDFG is responsible for ensuring sufficient water flow downstream of any water diversion point at all times in order to protect fish and wildlife resources. (Section 5937, Article 2, Chapter 3, Part 1, Division 6 of the California Fish and Game Code). Approval from the CDFG may be required to obtain water appropriation by an end user.

Summary

In summary, an evaluation of regulations indicates that, for delivery of treated water to agricultural land by hard pipe, the treated water quality must meet crop water quality and basin plan water quality requirements. WDRs must be obtained from the CCRWQCB. For delivering water via the river the following would be required:

- The released water must facilitate agricultural or wildlife restoration requirements.
- The water quality must be in compliance with NPDES, NTR, CTR and anti-degradation requirements.
- A permit from the CWRCB must be obtained for water appropriation.

- Approval from the CDFG may be required for the appropriation of water to verify that the loss of water will not have an adverse effect on fish and wildlife resources.

Finally, storage of water during periods of low demand may involve regulations from the DSD, Monterey County Environmental Health & Planning Department, and the CCRWQCB depending on storage location and water quality.

References

1) USEPA, 2000. Federal Register. 40 CFR Part 131. Part III. Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Rule.

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5) Monterey County Water Resources Agency. *1998 Ground water extraction summary report*. Salinas, CA: Monterey County, 2000

Appendix D

Abstract Submitted for CA/NV Section AWWA Spring 2006 Conference

PILOT STUDY FOR DESALINATION OF OILFIELD PRODUCED WATER CONTAINING HIGH LEVELS OF BORON AND AMMONIA

Abstract

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Kennedy/Jenks Consultants

Production of crude oil through enhanced steam recovery typically generates a large amount of produced water, a currently unusable by-product. Although the quality of the produced water varies by region, these waters typically have salinity concentrations from 1000 mg/l to more than 50,000 mg/l. The waters are often high temperature (150 to 200 °F), and usually contain high levels of silica, boron, ammonia and dissolved organics. These waters are often disposed by injection into Class II wells within the oilfield. If these disposal wells communicate with the oil-bearing formation, such on-field injection may increase the produced water to oil ratio and reservoir pressure, resulting in higher oil production costs. Reducing Class II injection through beneficial reuse of treated produced water can optimize oil production and increase recoverable reserves in such oilfields.

The project goal is to convert produced water into a water resource at a San Ardo, CA oilfield. A 10 - 30 gpm pilot plant, based on reverse osmosis technology, was constructed and operated for nine months. The key constituents of concern include TDS (7000 mg/l), boron (25 mg/l), and ammonia (20 mg/l NH3-N). Although treated water quality requirements vary with the type of end use, water quality goals of 400 mg/l TDS, 0.75 mg/l boron and 5 mg/l ammonia were set. Since boron and ammonia have conflicting ion chemistries, treatment of waters containing high levels of both of these contaminants is often challenging and cost prohibitive. The process configuration for this pilot study consisted of a warm softening unit to remove hardness and silica, a cooling tower to lower the temperature and remove ammonia, and a RO unit to remove TDS, boron and possibly ammonia. The highlights of the project include evaluation of a recently developed membrane for boron removal at lower pH (~9.5) than conventionally required for boron removal by RO (pH >10.5).

All of the water quality goals, except that for ammonia, were achieved during the pilot study using both the conventional membrane and the new boron rejection membrane systems. Although approximately 80% of ammonia was removed, an additional polishing unit will likely be required to meet the ammonia goal. Preliminary evaluations indicate that a recently developed high boron rejection membrane, operated in a 1X0 array mode at 2.5 gpm flow rate, will remove boron from 23 mg/l to 1 mg/l at pH=9.5. Modeling efforts are currently underway to design the optimum cooling tower/membrane configuration to meet treatment goals and to develop treated water cost estimates.

Appendix E

Abstract Submitted for Water Environment Federation 2006 Annual Conference (WEFTEC 06)

EVALUATION OF POTENTIAL BENEFICIAL REUSE OF SAN ARDO PRODUCED WATER

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Robert A. Liske
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ABSTRACT

The goal of this DOE, Aera Energy LLC, and Kennedy/Jenks Consultants funded project was to evaluate the potential for treatment and beneficial reuse of produced water from an oilfield in San Ardo, California. A 10 - 30 gpm reverse osmosis (RO) pilot plant was constructed and operated for nine months. The key constituents of concern include total dissolved solids (7000 mg/l TDS), temperature (190 ° F), boron (25 mg/l), ammonia (20 mg/l ammonia as N), and organics (75 mg/l TOC). Although water quality requirements vary with the type of end use, treated water quality goals for this pilot were set at 400 mg/l TDS, 1 mg/l boron, 5 mg/l ammonia as N, and 1 mg/l organics. Highlights of the project include an evaluation of a recently developed boron rejection membrane for boron removal at a lower pH than for a conventional brackish water membrane. The lower pH (9.5 versus >10.5) could result in significant savings on the caustic requirement.

All of the water quality goals, except for ammonia, were achieved during the pilot study using both the conventional and the new boron rejection membrane systems. Because ammonia and boron have conflicting pH requirements for removal by RO, a separate ammonia removal step was necessary to meet the ammonia treatment goal. Analysis of the low and high pH clean-in-place (CIP) solutions used following membrane cleanings, as well as evaluation of transmembrane pressure drop after cleaning, showed that most of the pressure drop was caused by inorganic scaling from magnesium and silica, rather than organic fouling. Although the new boron rejection membrane successfully removed more boron at a lower pH than the conventional brackish water membrane, this membrane was more prone to scaling.

KEY WORDS

Produced water, warm softening, Reverse Osmosis, TDS, boron rejection, ammonia, membrane fouling

BACKGROUND

Oil production generates a large amount of by-product water, commonly known as "produced water." As oil is produced from an oil field, the amount of produced water can account for over 90 percent of the fluids pumped from a well. The most prevalent method of using or disposing of oil field produced water is to inject it underground. A significant portion (50 to 65 percent) of produced water from onshore sources is currently reinjected into oil producing zones where it enhances oil recovery (using water flooding and steam flooding) or for subsidence control. The other 35 to 50 percent is disposed of via deep well injection or other methods. Unfortunately, deep well injection disposal may increase reservoir pressure and, in steam floods, lead to lower oil recovery and increased production costs. In such cases, eliminating deep well injection by finding a beneficial use for the treated water may increase oil production, increase recoverable oil reserves, and reduce production costs. Furthermore, treatment of oilfield produced water may provide a new reclaimed water supply for specific uses in water-short areas such as California.

The feasibility of produced water reclamation depends on a number of factors. For example, the chemical composition of the produced water, which is typically very saline, can significantly impact the treatability of these waters. The total dissolved solids (TDS) of produced waters in the United States can range from about 3,000 to more than 350,000 mg/l, with sodium and chloride generally comprising 70 - 90 percent of the TDS (U.S. Geological Survey, 2002). The produced water may also contain high concentrations of calcium, iron, manganese, ammonia, boron, and dissolved organics. Often, the complexities involved in treating these waters (e.g. TDS > 10,000 mg/l) may render produced water reclamation cost-prohibitive. In addition, regulations adopted pursuant to the Clean Water Act prohibit the discharge of treated produced water from onshore oil and gas wells into surface waters, except in areas west of the 98th Meridian (a north-south line approximately running from just west of Minnesota down through Dallas, Texas). Discharge of treated produced water directly into surface waters west of the 98th Meridian is allowed only if the treated water is of acceptable quality for agricultural use or wildlife propagation. If the treated water is intended for any other beneficial use, it must be delivered through direct piping or alternate means, which may not be cost effective. Finally, large storage facilities (hundreds of millions gallon capacity) would be needed if there is a large seasonal variation in water demand for the identified end use.

OBJECTIVE

This project, jointly funded by DOE, Aera Energy LLC, and Kennedy/Jenks consultants, evaluated reclamation of produced water from an oilfield at San Ardo, California. The major tasks included evaluation of treated water end use options, regulatory requirements, and a pilot study to evaluate the technical and economic feasibility of treating this produced water. This paper presents data from the pilot study performed to treat the San Ardo produced water for potential off-site use.

PILOT PROCESS AND TREATMENT GOALS

The San Ardo produced water is brackish, with high levels of ammonia, boron and organics (Table 1). Furthermore, the water contains high concentrations of scale-forming constituents (hardness, silica) that may impact a thermal or membrane desalination process for converting this water to a fresh water resource. Finally, due to the thermally enhanced recovery (i.e. steam drive) of heavy oil reserves, this water is generally high in temperature (150 to 200 °F). A treated water quality goal for the pilot study (Table 1) was set based on the California Central Coast Regional Water Quality Control Board Basin Plan groundwater recharge criteria.

Table 1. San Ardo Oilfield Produced Water Quality and Pilot Treatment Goal

Constituent	Untreated Produced Water	Pilot Treatment Goal
TDS (mg/l)	7000	400
Temperature (°F)	190 °F	< 90 °F
Ammonia (mg/l)	30	< 5
Boron (mg/l)	25	< 1
TOC (mg/l)	75	< 1
Hardness (mg/l as $CaCO_3$)	325	< 10

Silica (mg/l)	225	< 60

Figure 1. Simplified schematic of pilot process train

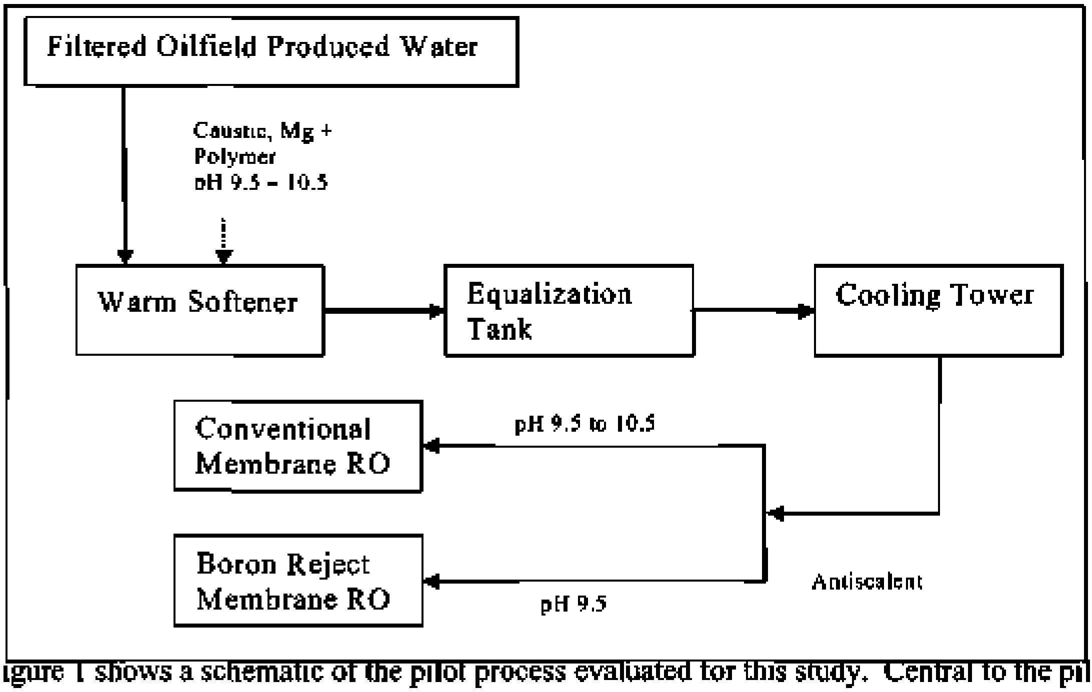


Figure 1 shows a schematic of the pilot process evaluated for this study. Central to the pilot process is a reverse osmosis (RO) unit for TDS removal. An upstream warm softening unit removed hardness and silica to minimize scaling of the membranes. Caustic was added to remove hardness, and magnesium was added to precipitate silica from the produced water. A cooling tower was used to cool the softened water and facilitate ammonia removal prior to RO. Most of the RO operations were performed using a brackish water membrane. In these studies the RO was operated at alkaline (9.5 – 11) pH levels to optimize boron removal. Several additional studies were performed to evaluate treatment cost reduction including i) investigation of RO membrane fouling characteristics to optimize the clean-in-place (CIP) process and membrane replacement frequency, and ii) evaluation of a special boron rejection seawater membrane at pH 9.5 to minimize chemical and operational cost associated with high pH (>10.5) operations using conventional membranes.

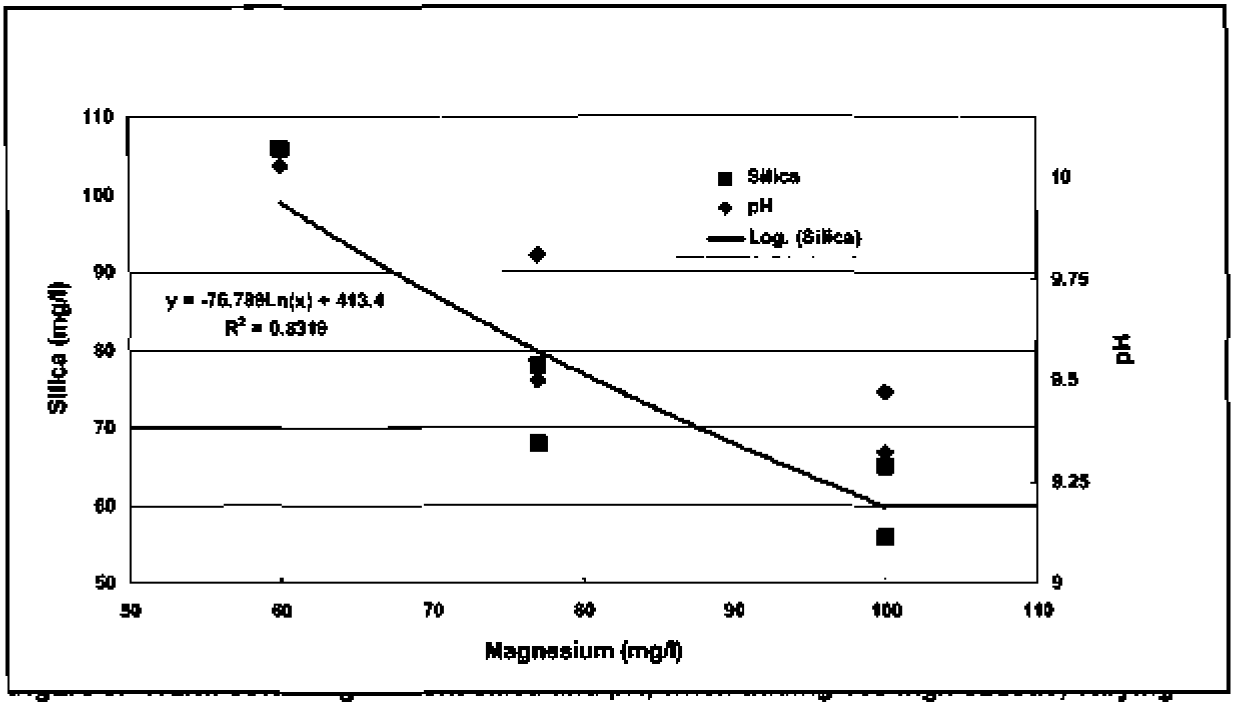
RESULTS

Warm Softening

The goals of the warm softening process were to remove scale forming calcium and silica from the produced water. Based on bench studies, caustic dosing rates of 400 to 700 mg/l, and magnesium dosing rates of 50 to 150 mg/l were used during most of the warm softening trials.

Figure 2 shows the silica levels in the treated water when adding 500 mg/l of caustic and varying amounts of magnesium. At a dosing rate of 60 mg/l magnesium, the effluent pH was 10, and silica level was about 100 mg/l (~ 50% removal). A silica level of ~60 mg/l was achieved at 100 mg/l magnesium dose. Figure 3 shows the silica levels in the treated water when the caustic dosing was increased to 600 mg/l caustic. Increasing the caustic dose to 600 mg/l improved silica removal. The effluent silica levels were 65, 40 and 20 mg/l at magnesium dosing rates of 75, 100 and 150 mg/l, respectively.

Figure 2. Warm softening effluent silica and pH, when adding 500 mg/l caustic, varying amounts of magnesium



amounts of magnesium

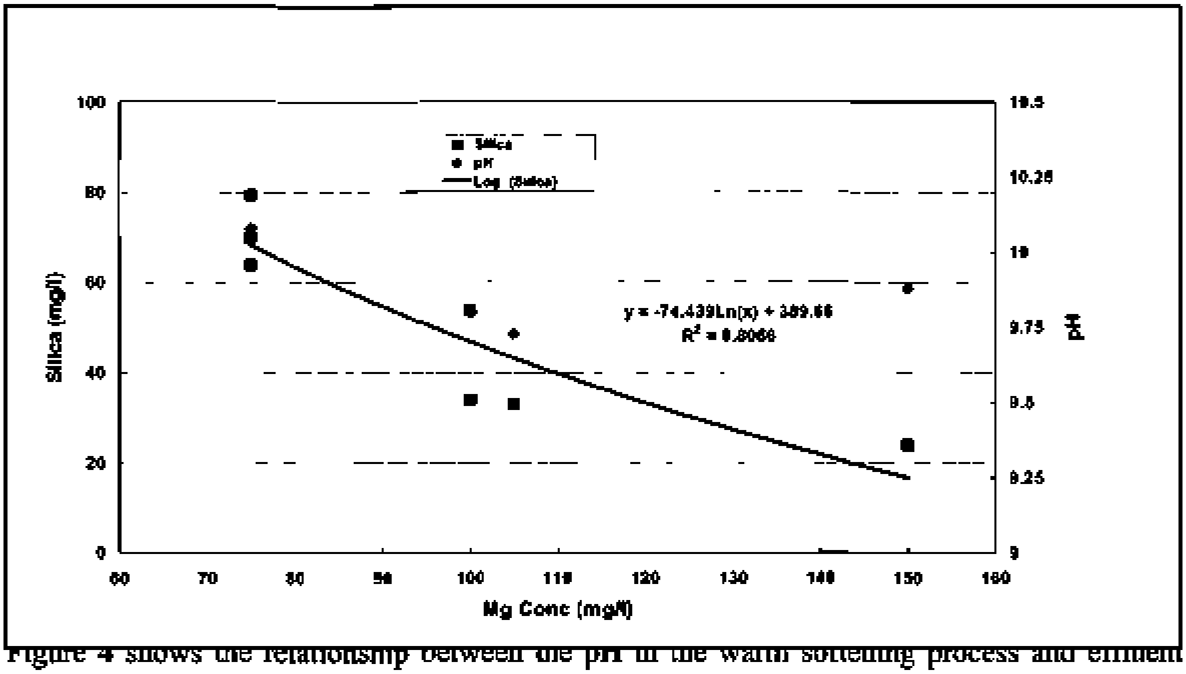


Figure 4 shows the relationship between the pH in the warm softening process and effluent silica levels. In general, the silica levels in the softened water increased with an increase in the pH. Drago, et al., (1997) (referring to Mujeriego, et al., 1976) reported that maximum silica precipitation by magnesium addition occurs at the pH corresponding to the average pKa values for the first and second dissociation constants (pK_1 and pK_2) of orthosilicic acid. The $pK_{1\&2}$ values vary with the water temperature during precipitation. In the current pilot study, the average temperature of the softened water in the settling tank was about 140 ° F. At this temperature, the pH optimum ($(pK_1+pK_2)/2$) for silica removal is calculated to be 9.8. Above this calculated pH, silica levels increased as predicted.

Figure 4. Effect of pH on warm softened effluent silica

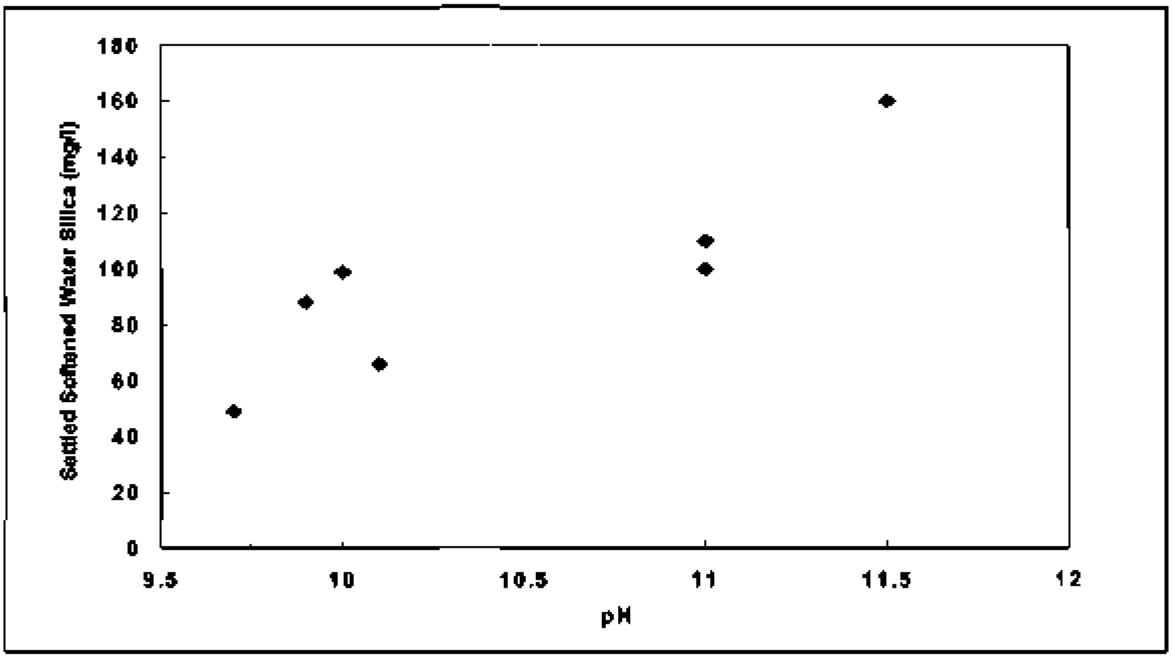


Figure 5. Warm softening effluent hardness as a function of pH

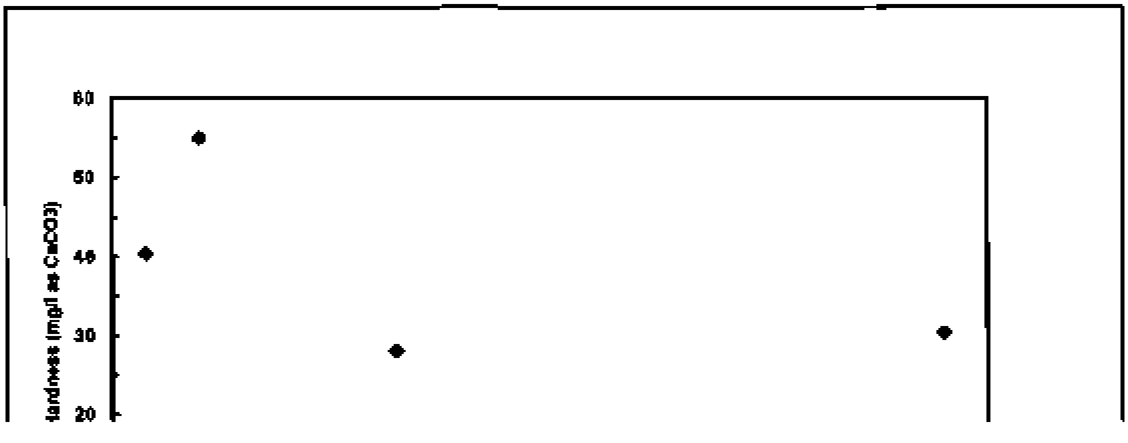


Figure 5 shows the hardness of the warm softening process effluent as a function of pH. The residual hardness of the clarifier effluent was below 10 mg/l when the effluent pH was between 9.3 and 10.5. Effluent pH was less than 9.3 (pKa of carbonate) at low caustic (<400 mg/l) or at high magnesium dosing rates (> 125 mg/l). The residual hardness was higher than the hardness goal (10 mg/l as $CaCO_3$) under these conditions. Also, effluent pH higher than 10.5 occurred at high caustic (e.g. 700 – 800 mg/l) and low magnesium (0 – 70 mg/l) dosing rates. The effluent hardness was higher than the treatment goal under these conditions, probably due to ineffective silica removal by the low magnesium dosing.

COOLING TOWER OPERATION

The cooling tower was used for i) cooling the warm softening effluent, and ii) evaluation for stripping ammonia. It consisted of 7,452 ft^2 of CPVC packing and a 15 HP fan rated at 23,100 cfm (Table 2). The cooling tower was operated at a flow rate of 15 gpm. The high pH and high air to water ratios used in the pilot trials generally favor ammonia stripping. During the pilot study, due to some concerns with solids carryover, the warm softening effluent was settled in an equalization tank prior to cooling tower operations. As a result, the influent water temperature to the cooling tower was lower (58–105 °F) than the designed inlet temperature (~150 °F). Table 2 summarizes the operating conditions and results from the cooling tower studies. Approximately 63 and 44% of ammonia were removed in the cooling tower at influent pH of 10.8 (104.6 °F) and 10.3 (58 °F), respectively.

Table 2. Cooling Tower Operation and Results

Parameter	Units	Condition 1	Condition 2
Water flow rate	gpm	15	15
Air flow rate	cfm	23,100	23,100
Air: Water ratio	vol: vol	11,600:1	11,600:1
Influent water temperature	°F	58.0	104.6
Effluent water temperature	°F	53.4	65.6
Average temperature reduction	°F	4.2	39.0
Average air temperature (wet bulb)	°F	42.9	45.2
Influent pH	Std units	10.3	10.8
Influent ammonia-N	mg/l	12	17
Effluent ammonia-N	mg/l	6.6	6.3
Average ammonia removal	%	44	63

Reverse Osmosis

Conventional Brackish Water Membrane: Most of the pilot evaluations were performed using a Koch Membrane System (KMS) RO unit fitted with the conventional brackish water membrane under various pH conditions (9.5–11) to remove TDS, boron, TOC, silica and ammonia from the softened, cooled San Ardo produced water. Table 3 shows the specifications of the membrane element and the operational conditions used during the pilot study. The feed and permeate flow rates for the RO studies were 7.5 and 5 gpm, respectively.

Table 3. Specifications of the Conventional Brackish Water Membrane

Parameter	Data
Membrane	TFC® - XR4,, Fluid Systems
Configuration	Spiral Wound
Membrane Polymer	Composite Polyamide
Diameter	4 inch
Nominal Membrane Area	78 ft^2
Maximum Applied Pressure	600 psi
Maximum Operating Temp	113 °F
Maximum Feedwater Silt Density Index (SDI 15 min)	5
Maximum Pressure Drop for Each Element	10 psi

The TDS of the RO feed water varied from 7,500 to 9,000 mg/l (Figure 6). The average TDS of the permeate was 215 mg/L. The pH of the RO feed did not significantly impact the permeate TDS. Post treatment operations such as stabilization of permeate for corrosion control, salt addition for Sodium Absorption Ratio (SAR) compliance and final disinfection will slightly increase the treated water TDS prior to its intended end use.

Figure 6. TDS levels in RO influent and permeate at various pH levels

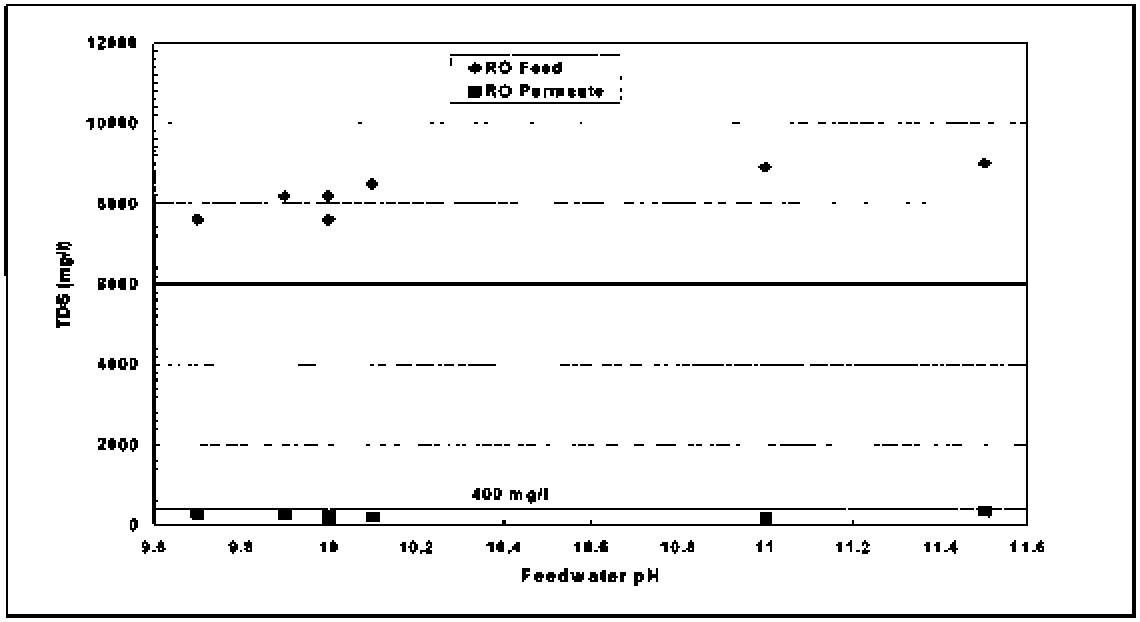
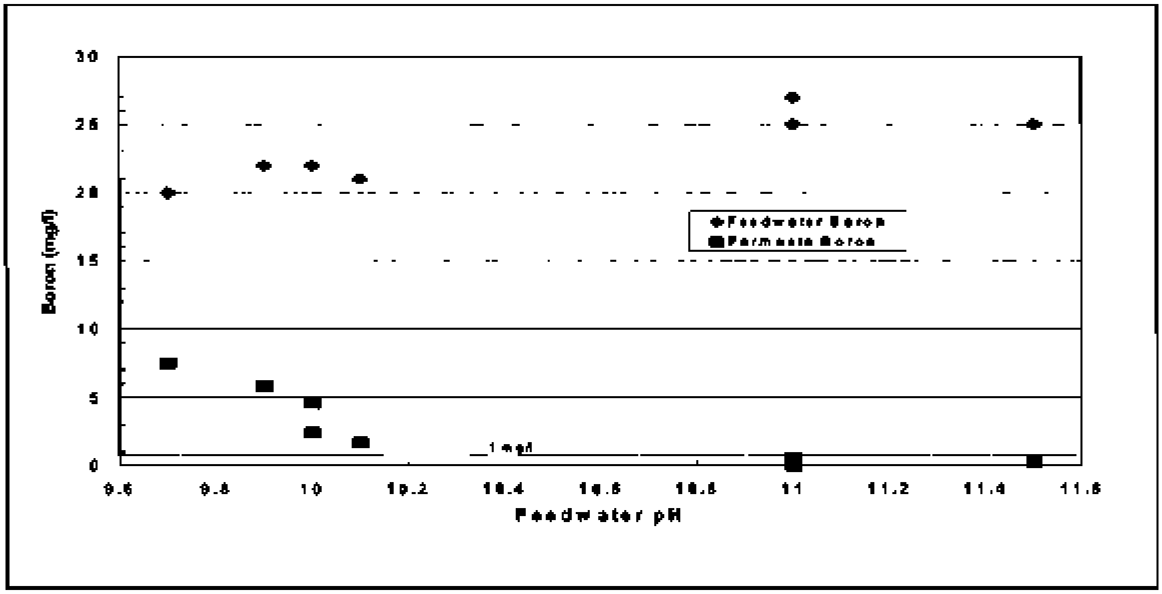


Figure 7 summarizes the removal of boron by the RO processes. The boron concentration in the permeate decreased with an increase in the feed water pH. The influent boron levels varied from 20 to 25 mg/l during the pilot study. The boron goal of <1 mg/l in the permeate was not achieved when the pH of the RO feed was 10.2 or lower. This trend, in general, is consistent with the speciation chemistry of boron. In the pH range at which the pilot was operated, an increase in pH increases the fraction of the ionic boron species ($B(OH)_4^-$) which is amenable for removal by the RO membrane.

Figure 7. Boron levels in RO influent and permeate at various pH levels



The influent ammonia concentration to the RO varied from 6 to 13 mg/l ammonia as N. Approximately 10 to 15% of the ammonia was removed by the membranes at pH 9.6 to 10.2. No ammonia was removed at pH 11 by the RO process. These trends are consistent with ammonia speciation chemistry. At pH above 9.2, at which the pilot was operated, a significant fraction of the ammonia remains in the un-ionized NH_3 form which is not conducive for removal by the RO process. At pH 9.5 to 10, only about 20% of ammonia remains in the ionized NH_4^+ form which is amenable for removal by RO. As the pH increases to near 11, less than 10 percent of the ammonia is ionized.

The TOC of the RO feed water varied from 60 to 80 mg/l throughout the pilot study. The permeate TOC was always below the detection limit (3 or 1 mg/l) in all the cases.

Membrane Fouling: The Operating and Maintenance (O&M) cost for RO treatment can be significant due to membrane replacement required because of scaling or fouling by produced water constituents. Hence, during this pilot study, the following were performed to characterize the impact of organic and inorganics on the RO membrane:

- Evaluation of transmembrane pressure recovery of the membrane during low and high pH CIP, and
- Analyses of low and high pH CIP cleaning solutions before and after membrane CIP

Evaluation of Transmembrane Pressure (TMP): A typical RO CIP is a two step process consisting of i) cleaning with an acidic solution designed to remove the inorganic scalents (e.g. Ca, Mg, SiO2), followed by ii) cleaning with an alkaline solution designed to remove the organic foulants. In this study the impact of organics and inorganics on the membrane was evaluated by operating the RO unit under normal conditions after each step of the cleaning process and measuring the pressure recovery obtained.

Table 4 shows the feed pressure required for produced water treatment before, during and after the CIP process. The pressure required to obtain the design yield using a virgin membrane was ~ 379.5 psi. After about 100 hours of operation, due to increase in pressure drop across the membrane, the permeate yield reduced to 40%. The corresponding feed pressure was 283 psi. Membrane cleaning using an acidic solution (KOCHKLEEN 100, KMS) was performed at this time to remove inorganic scalents. Subsequently, the membranes were rinsed with clean water and allowed to relax for about two hours. The RO was then operated to treat the produced water (warm softener effluent). The feed pressure required for operation decreased to 222.5 psi. This suggested that a significant fraction of the pressure drop across the membrane was caused by scaling of inorganic materials. The membranes were then cleaned using alkaline solution to remove organic foulants. The feed pressure required for 40% yield, however, did not change significantly after cleaning with the alkaline solution. Approximately 228 psi pressure was still required for operation. This suggested that only a small amount of organic compounds fouled the membrane during treatment of oilfield produced water.

Table 4. RO Transmembrane Pressure Before, During and After CIP

Operation Phase	Feed Flow (GPM)	Yield (%)	Transmembrane Pressure (psi)
Start of Test Run	7.5	67.5	379.5
Operation Prior to CIP	7.6	40.8	283
After Low pH CIP	7.5	40	222.5
After High pH CIP	7.5	40	228
At Design Yield After CIP	5.8	65.5	387

Following the low and high pH cleaning procedure, the pilot RO unit was restored to operating at ~65% yield, similar to that established at the start of the initial test run. Upon restoring these operating conditions, the TMP required to maintain the original yield was higher than the average TMP observed during the initial 20 hours of the test run (Table 4). This suggested that some permanent fouling of membrane may have occurred during the produced water treatment.

Analyses of CIP solutions: In addition to evaluation of operating feed pressure, acidic and alkaline CIP solutions were collected before and after the cleaning process, and analyzed for inorganic and organic constituents. Table 5 shows the concentrations of inorganic (Ca, Mg and SiO_2) and organic (TOC) constituents in the acidic and alkaline cleaning solutions. Calcium, magnesium, silica and hardness level in the acidic solution increased significantly after membrane cleaning. However, the TOC of the alkaline solution did not increase after cleaning, indicating that organic constituents did not significantly foul the membrane during treatment. These findings further supported the previous observation that the majority of the pressure drop across the membrane was due to inorganic scaling.

Table 5. Inorganic and organic constituents in low and high pH clean in place solutions

Parameter	Before Cleaning (mg/l)	After Cleaning (mg/l)	% Increase
Acidic Solution			
Calcium	81	110	36
Magnesium	33	240	627
Silica	53	200	277
Hardness *	340	1,300	282
Alkaline Solution			
TOC	160	94	-46

* mg/l as $CaCO_3$

Evaluation of Boron Rejection Seawater Membranes: As part of the pilot study, a special boron rejection seawater membrane, which is reported to remove boron more effectively at lower pH levels (~9.5) than a conventional brackish water membrane (Hydranautics, 2005), was evaluated for San Ardo produced water treatment. If boron can be successfully removed at this lower pH, it will significantly reduce the chemical cost associated with raising the RO feed water to pH 10.5 and the subsequent lowering of the permeate and concentrate stream pH.

Table 6 shows the specifications of the boron rejection membrane and Table 7 shows the operation conditions for the study. In summary, three 4-inch diameter membrane elements of each system were operated in parallel single stage mode for approximately 50 hours. The influent pH was maintained at about 9.5. Feed, permeate and concentrate samples were collected and analyzed periodically for process performance.

Table 6. Specifications of the Special Boron Rejection Membrane

Parameter	Data
Membrane	SWC4, Hydranautics
Configuration	Spiral Wound
Membrane Polymer	Composite Polyamide
Nominal Membrane Area	85 ft^2
Maximum Applied Pressure	1000 psi (4") & 1,200 psi (8")
Maximum Feedflow	16 gpm (4"), 75 gpm (8")
Maximum Operating Temp	113 °F
Maximum Feedwater Silt Density Index (15 min)	5
Maximum Pressure Drop for Each Element	10 psi

Table 7. RO Operation Conditions for the brackish water and boron rejection Membranes Evaluation

Parameter	Brackish Water Membrane (Fluid Systems)	Boron Rejection Membrane (SWC4)

Feed water Flow (gpm)	2.65	2.4
Permeate Flow (gpm)	1.65	1.7
Feed Pressure (psi)	460	460
pH	9.5	9.5

Table 8 shows the TDS, boron, ammonia, TOC and silica levels in the brackish water and boron rejection membrane permeate during the pilot study. Both the membrane systems were able to meet the TDS, silica and TOC goals under the operational conditions. The TDS and boron of the boron rejection membrane permeate were significantly lower than that of the brackish water membrane. The permeate boron concentration in the boron rejection membrane averaged about 1 mg/l as compared with 4.5 mg/l for the brackish water membrane system. At the end of the pilot study (~50 hours) the TDS and boron levels increased by two and three fold respectively in both the membrane systems. The reasons for this increase are not known, however, post-treatment evaluation of the boron rejection membranes indicated that at least one of the elements failed the vacuum test for structural integrity, indicating a physical break in this element.

Table 8. Treated Water Quality of Brackish Water and Boron Rejection Membranes

Parameter (mg/l)	Feed Water	Brackish Water Membrane	Boron Specific Membrane
TDS	8500	240	60
Boron	23	4.3	1
TOC	45	1.1	ND (< 1)
Ammonia as N	12	6	6.3

After about 50 hours of operation the study was suspended and a CIP was performed on both the brackish water and boron rejection membranes. The cleaning solutions were analyzed for inorganic and organic scalants and foulants (Table 9). As observed with the brackish water membranes in the earlier trials, most of the membrane fouling occurred due to inorganic scaling. However, the fouling on the boron rejection membrane was significantly higher than that on the brackish water membrane. The boron rejection membrane contained 125% more silica and 270% more magnesium fouling than the brackish water membrane. It is possible that the fouling across the boron rejection membrane was higher due to operation of this membrane at a higher recovery (73%) than the brackish water membrane (63%). Further investigation is required to understand the fouling characteristics of this membrane.

The data indicated that, while the boron rejection membrane can remove boron more effectively than the brackish water membrane, this membrane may be more prone to scaling.

Table 9. Inorganic and organic constituents in the CIP solutions before and after membrane cleaning

Parameter	Brackish Water Membrane			Boron Rejection Membrane		
	Before CIP (mg/l)	After CIP (mg/l)	% Increase	Before CIP (mg/l)	After CIP (mg/l)	% Increase

Acidic Solution						
Calcium	81	85	5	84	92	10
Magnesium	33	49	49	33	92	179
Silica	48	71	71	58	110	90
Hardness*	340	410	410	350	610	74
Alkaline Solution						
TOC	77	73	-5	79	77	-2.5

* mg/l as CaCO3

LIMITATIONS

Although the demonstration project showed the technical feasibility of treating San Ardo oilfield produced water, an ideally suited end use for the treated water has not been identified. Several end use issues challenge the viability of a full-scale project. For example, the possible treated water uses must satisfy stringent regulatory, economic, user-perception, and long-term reliability criteria prior to actual implementation. Furthermore, depending on the type of use, implementation may also require complex water trade arrangements with one or more water agencies. Finally, large storage facilities (hundreds of million gallons capacity) would be needed if there is a large seasonal variation in water demand for the identified end use. Such limitations may increase the overall costs of the project significantly. The cost of treating and delivering the water must be compared with the benefit of increased oil production.

CONCLUSIONS

The pilot study to treat San Ardo produced water indicated that approximately 600 mg/l of caustic and 100 mg/l of magnesium were required to meet the treated water hardness and silica goals. A cooling tower could meet the temperature treatment goal and remove some of the ammonia. However, air quality regulations in California may restrict ammonia emissions and make the use of a cooling tower problematic. The brackish water RO membrane was effective in meeting the TDS goals in all the trials. Treated water boron goal of 1 mg/l was achieved at a pH above 10.2 using this membrane. A special boron rejection membrane was more effective in meeting this boron goal at a lower pH (9.5). However, the fouling characteristics of this membrane are not well understood. Evaluation of the two membranes indicated that inorganic scaling was the major reason for performing the CIP.

REFERENCES

U.S. Geological Survey, (2002). *Produced Water Database*. Retrieved 26 May 2005 from http://energy.cr.usgs.gov/prov/prodwat/intro.htm

Hydranautics (2005). Boron Removal by Hydranautics SWC4. Technical Application Bulletin. Retrieved 15 May 2006 from http://www.membranes.com/docs/tab/TAB113.pdf.

Drago, J.A.; Fruth, D.A.; Doran, G.F.; Leong, L.Y.C. 1997. Simultaneous Removal of Silica and Boron from Produced Water by Chemical Precipitation. Proceedings of the *International Water Conference*, Engineers Society of Western Pennsylvania, Pittsburgh, PA.

Appendix E: Pilot Plant Electrical Drawing

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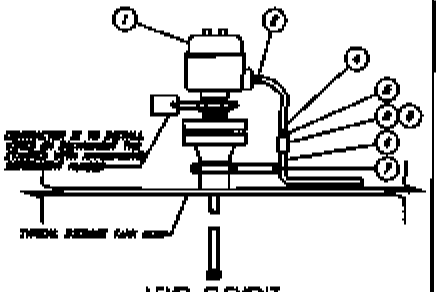

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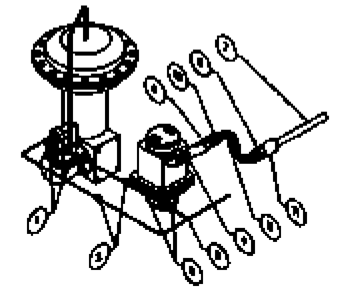

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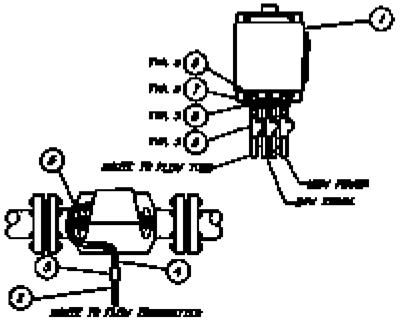

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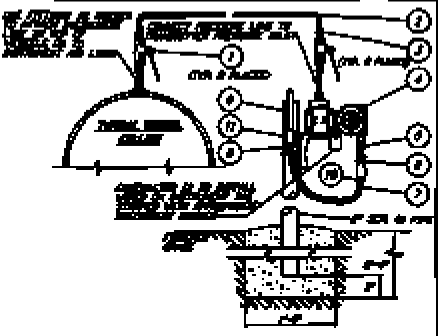

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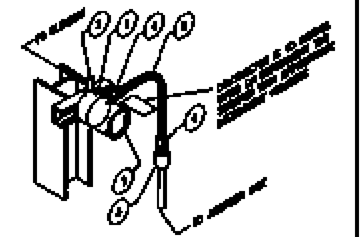

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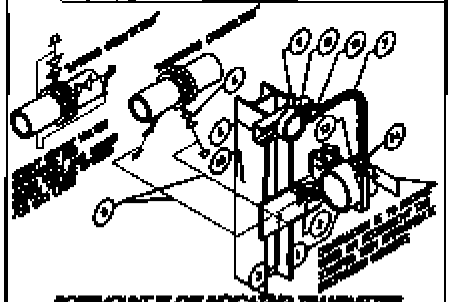

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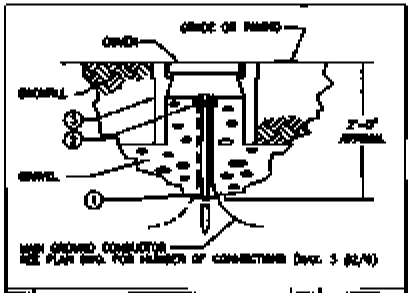
REV. D



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3	CONCRETE BOX WITH COVER MARKED GROUND	1	

ASSEMBLY AG-300
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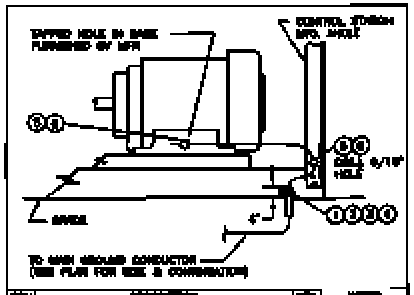

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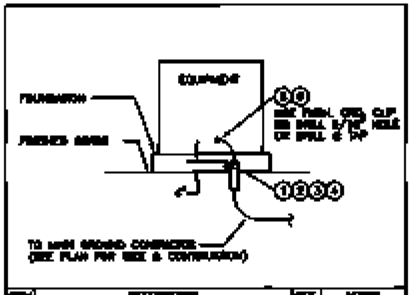
2	BOLT & LOCKWASHER	1	
3	ONE-HOLE CONDUIT CLAMP, GALV.	1	
4	1" SCHED. 80 PVC CONDUIT	1'	
5	SPLIT CONNECTOR, 1/2" LONG STUD	2	
6	1/2" HEX NUT & LOCKWASHER, SILICON BRONZE	1	

ASSEMBLY AG-301
MOTOR GROUNDING



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2	BOLT & LOCKWASHER	1	
3	ONE-HOLE CONDUIT CLAMP, GALV.	1	
4	1" SCHED. 80 PVC CONDUIT	1'	
5	SPLIT CONNECTOR, 1/2" LONG STUD	1	
6	1/2" HEX NUT & LOCKWASHER, SILICON BRONZE	1	

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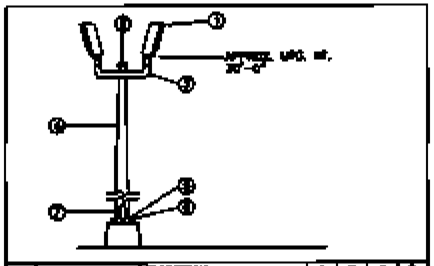
EQUIPMENT GROUNDING



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3	[illegible] MOUNTING BRACKET	1	1	1	1
4	GALVANIZED TAPER STEEL POLE	30'	30'	30'	30'
5	ANCHOR BOLTS	1	1	1	1
6	ANCHOR NUTS	1	1	1	1
7	ACCESS HATCH	1	1	1	1
8					
9					

ASSEMBLY AL-100
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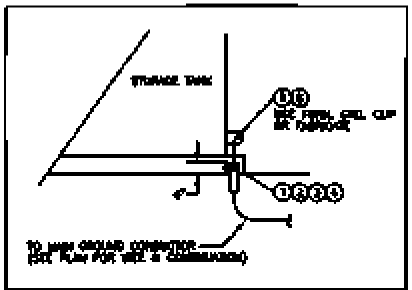

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4	1" SCHED. 80 PVC CONDUIT	1'	
5	SPLIT CONNECTOR, 1/2" LONG STUD	1	
6	1/2" HEX NUT & LOCKWASHER, SILICON BRONZE	1	

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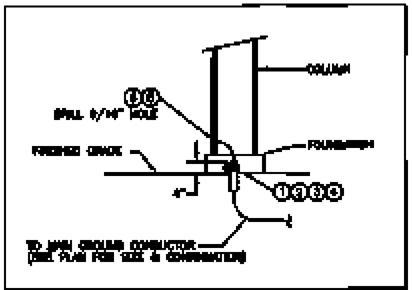

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4	1" SCHED. 80 PVC CONDUIT	1'	
5	SPLIT CONNECTOR, 1/2" LONG STUD	1	
6	1/2" HEX NUT & LOCKWASHER, SILICON BRONZE	1	

ASSEMBLY AG-307
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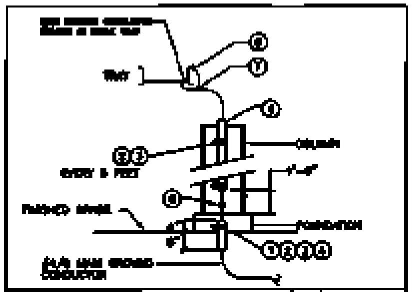

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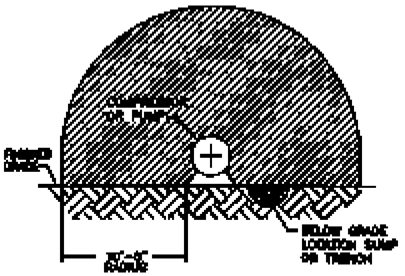

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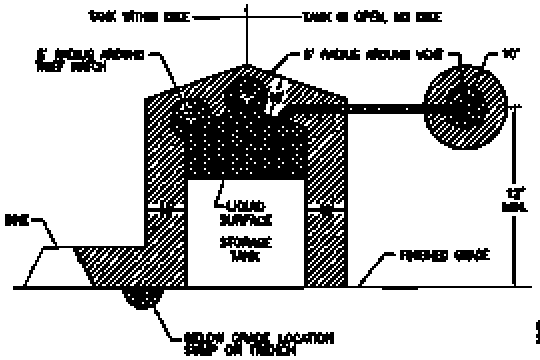

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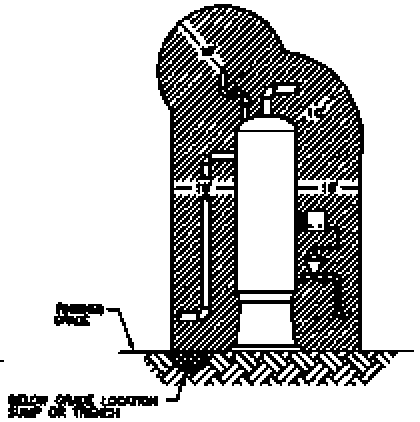

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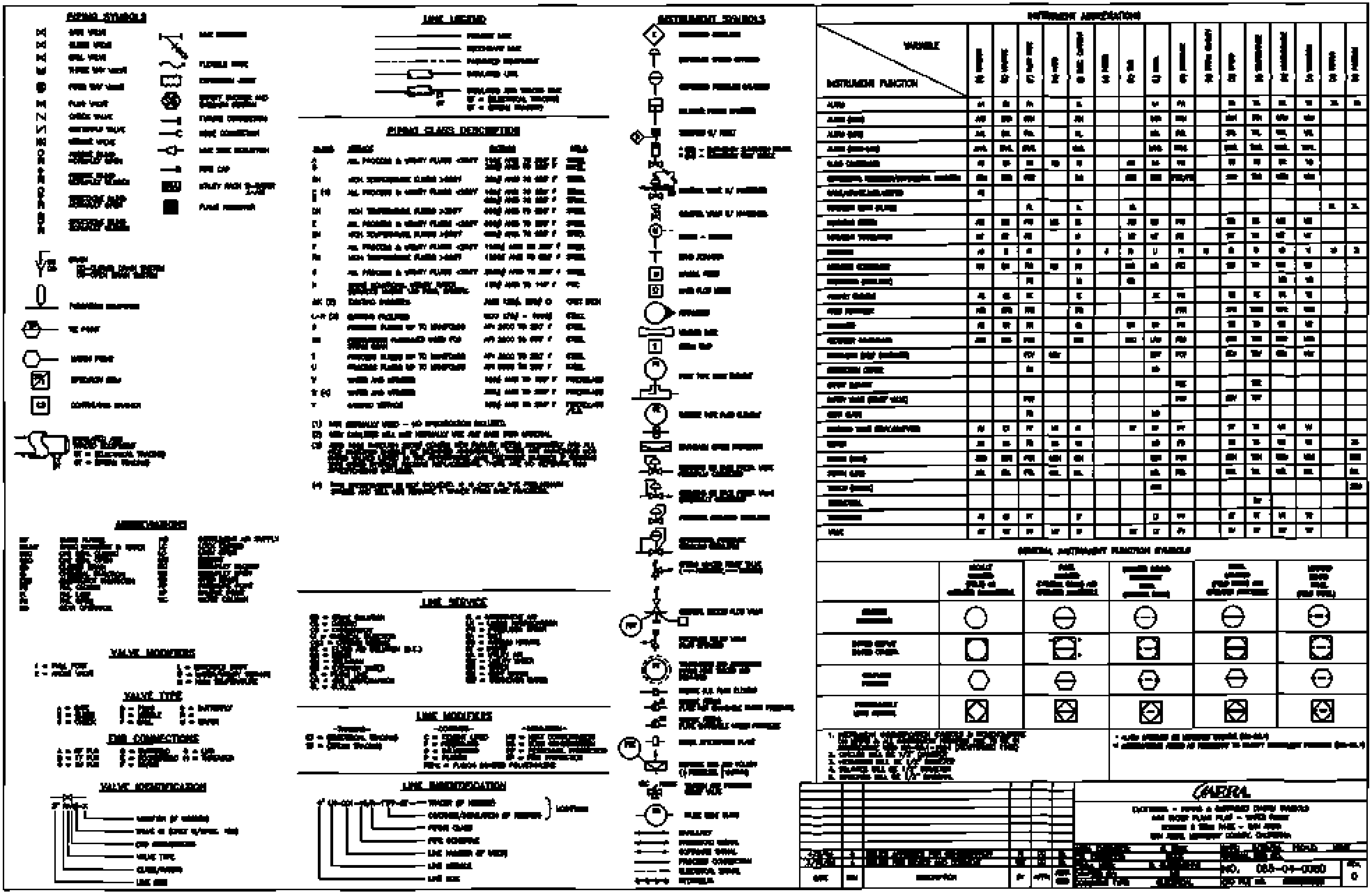
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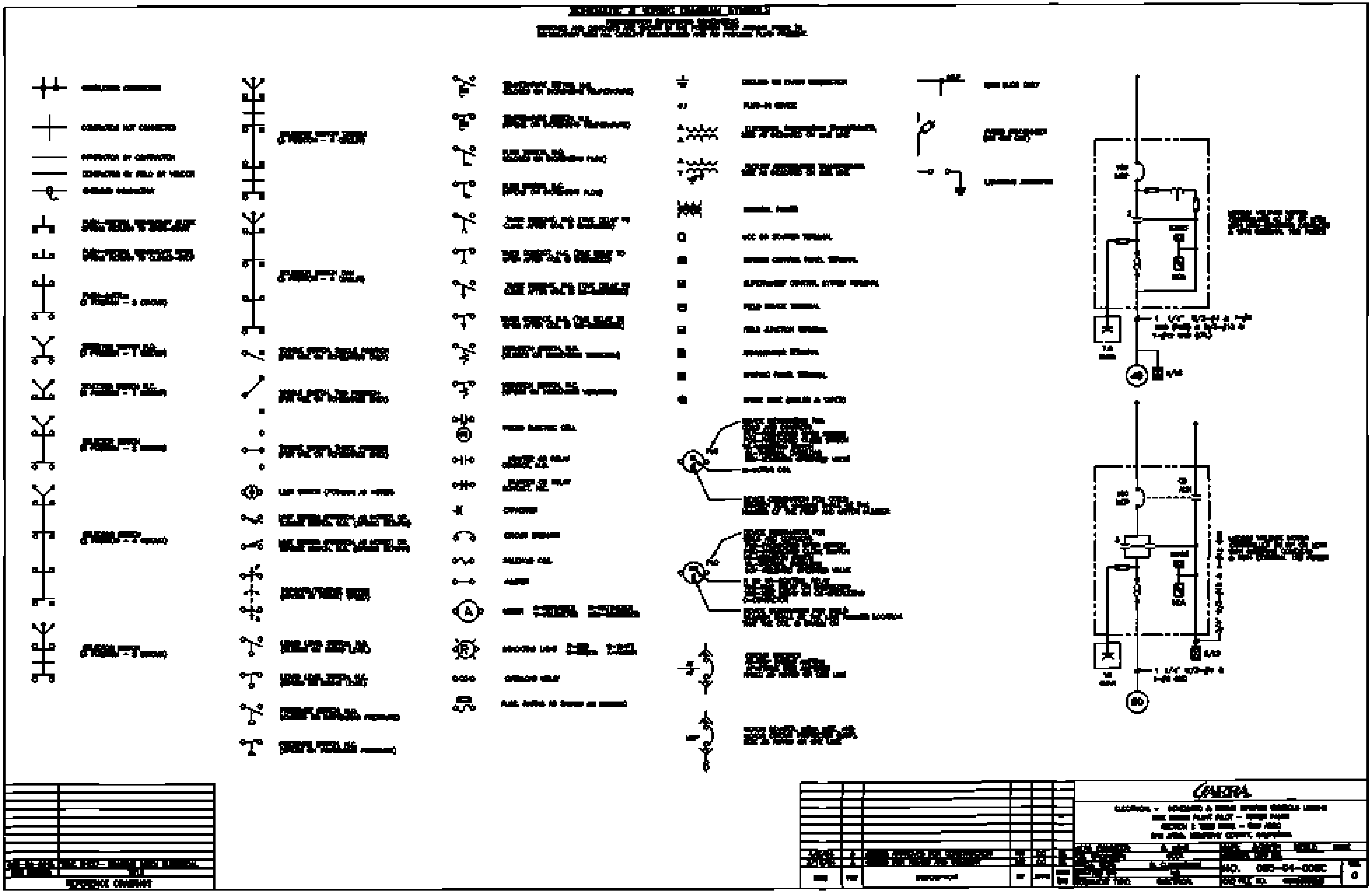
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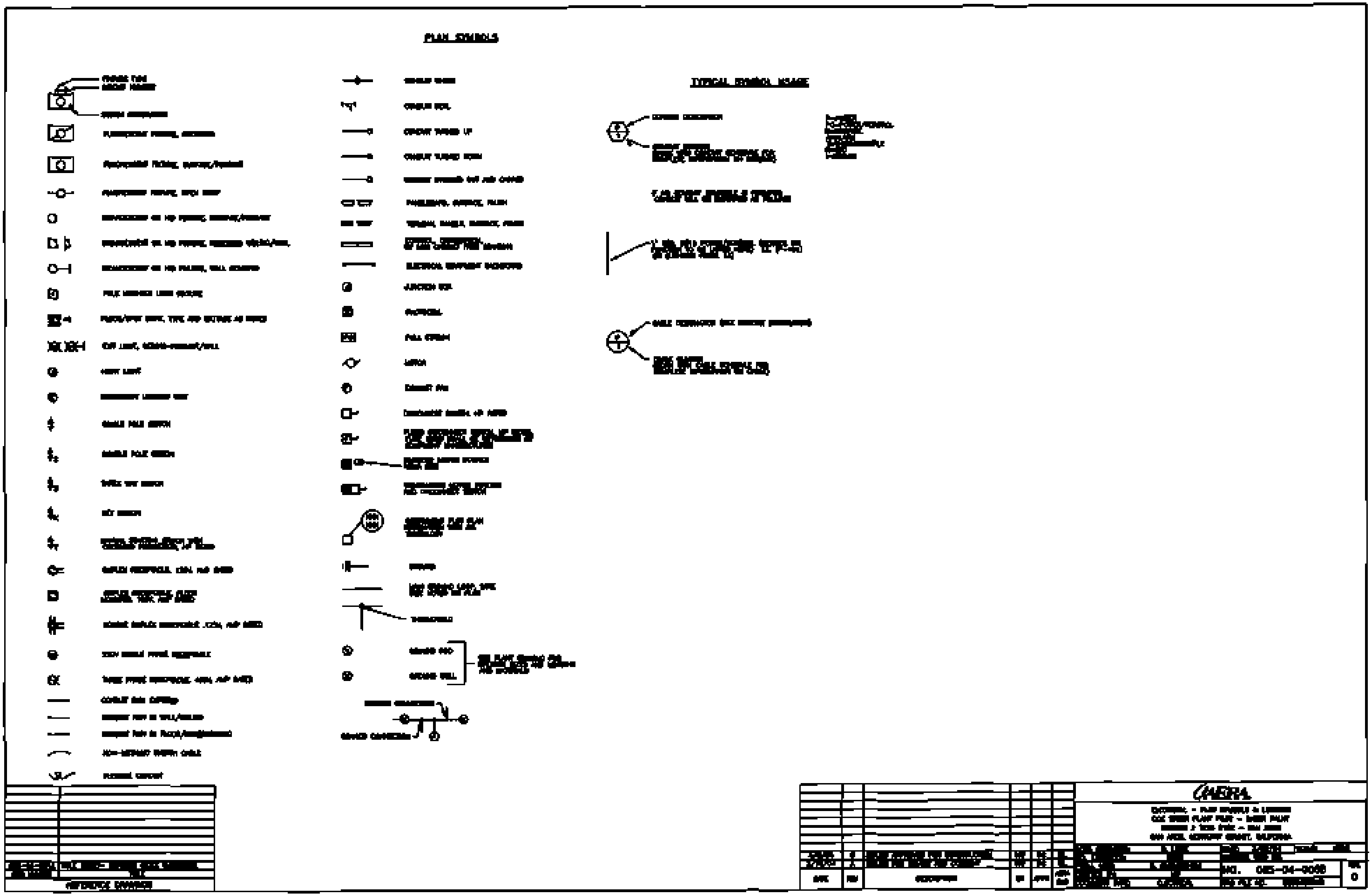
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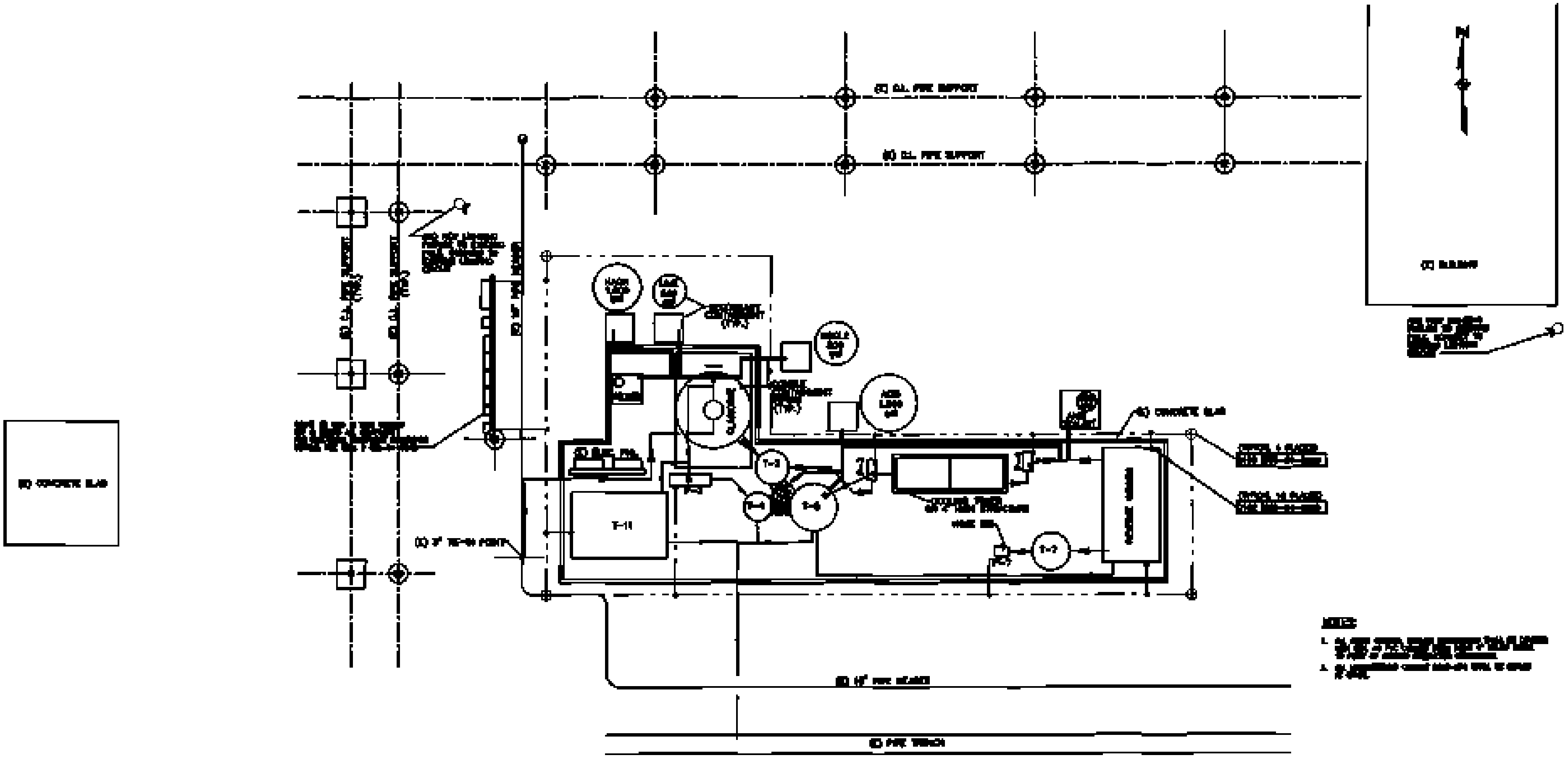

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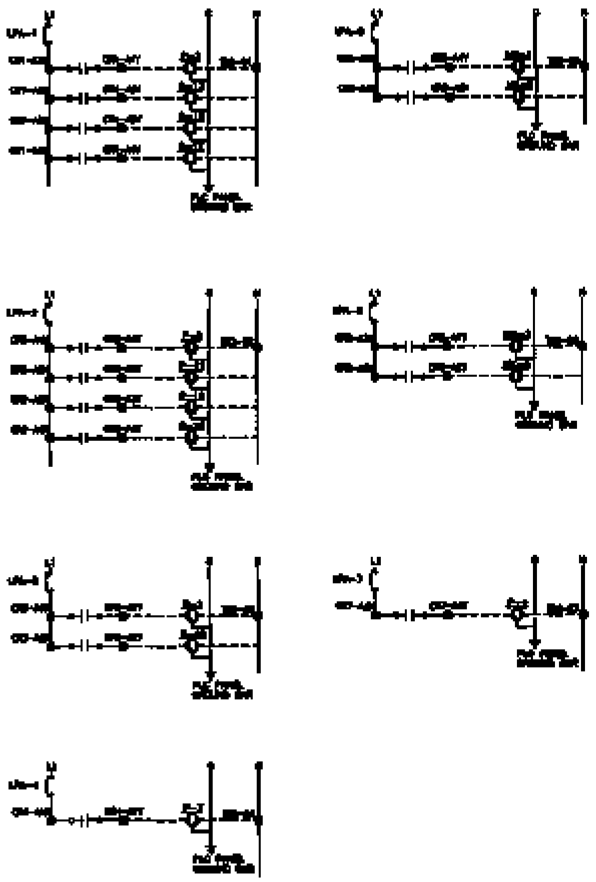

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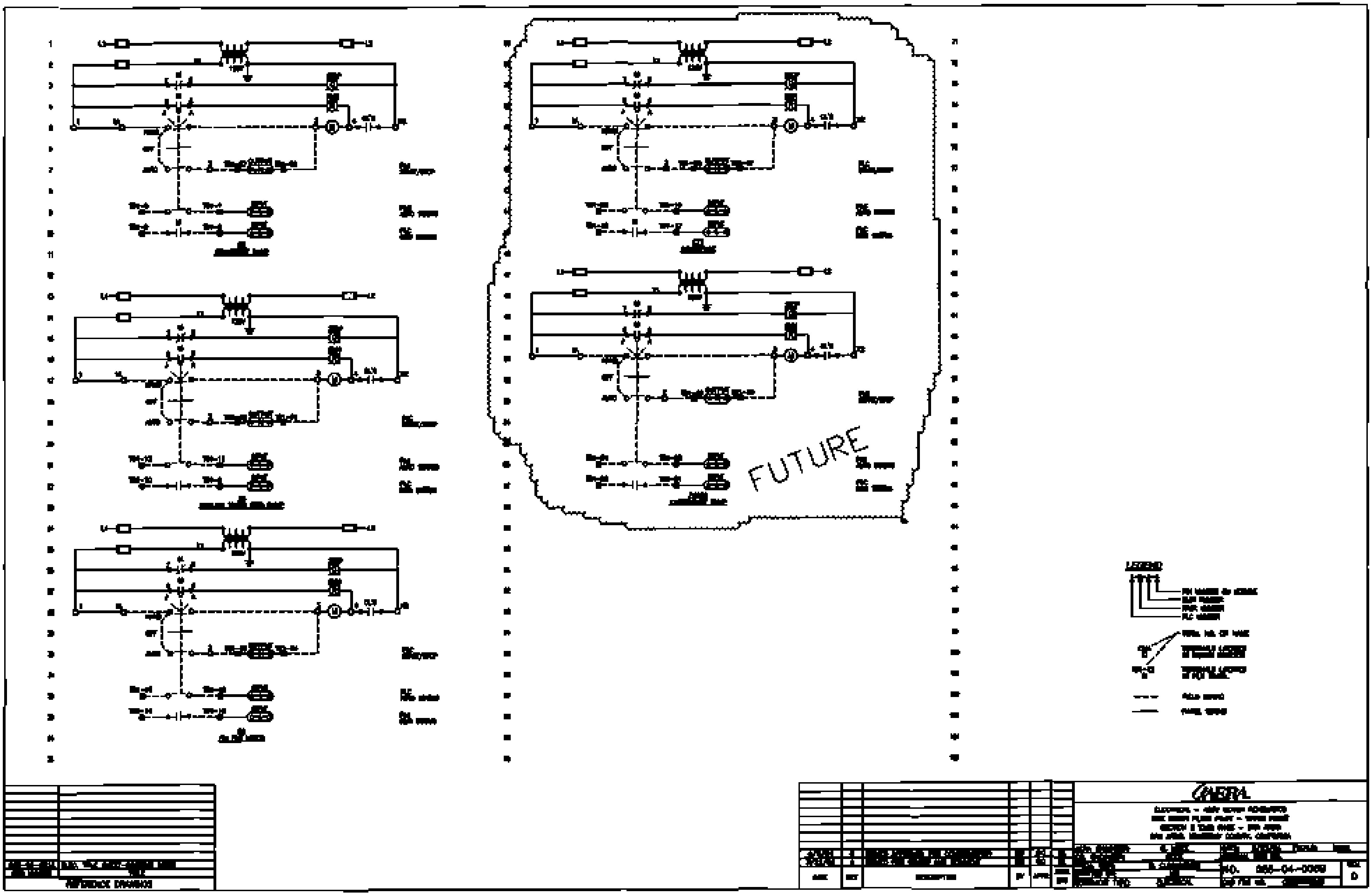
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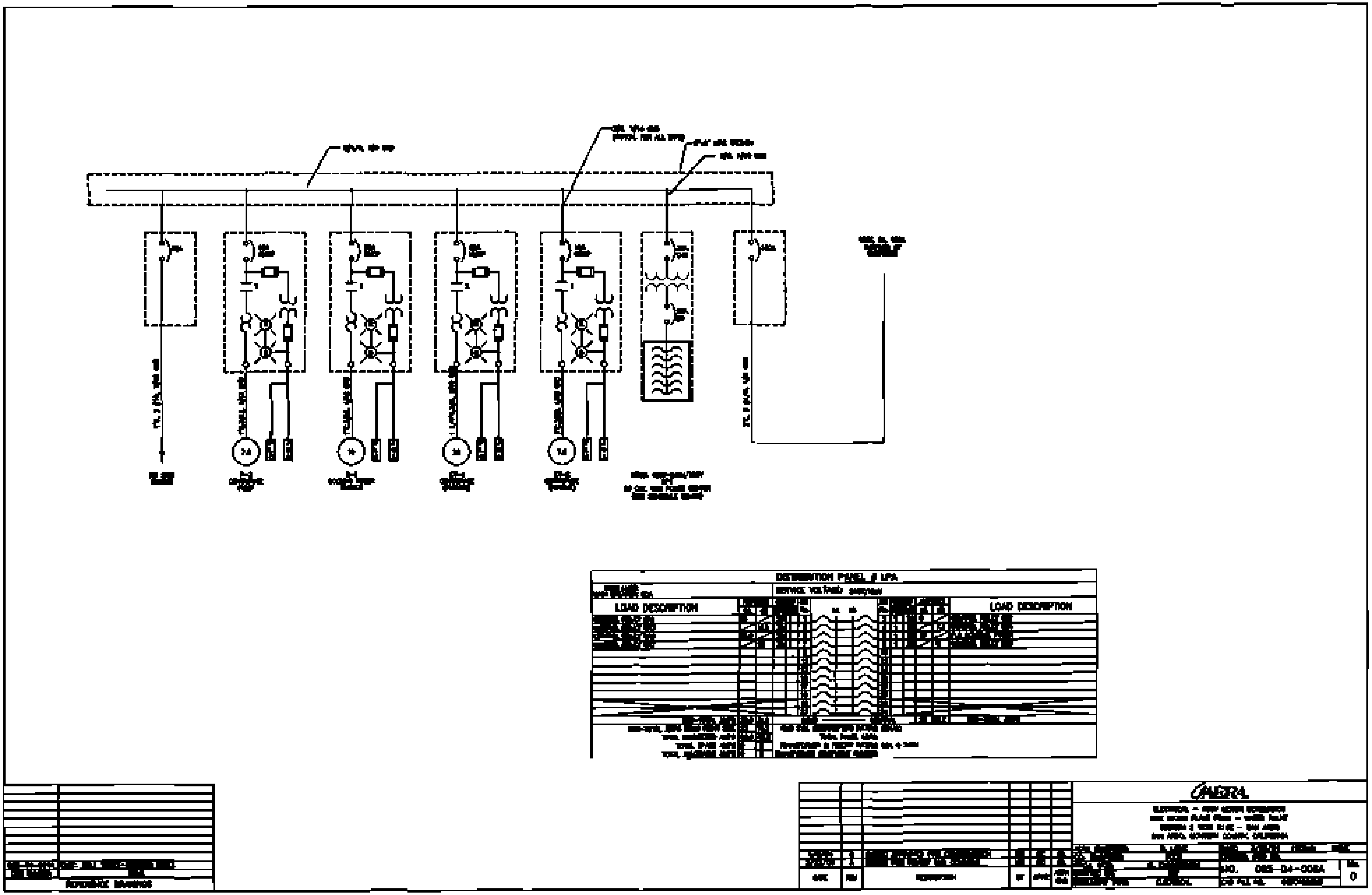
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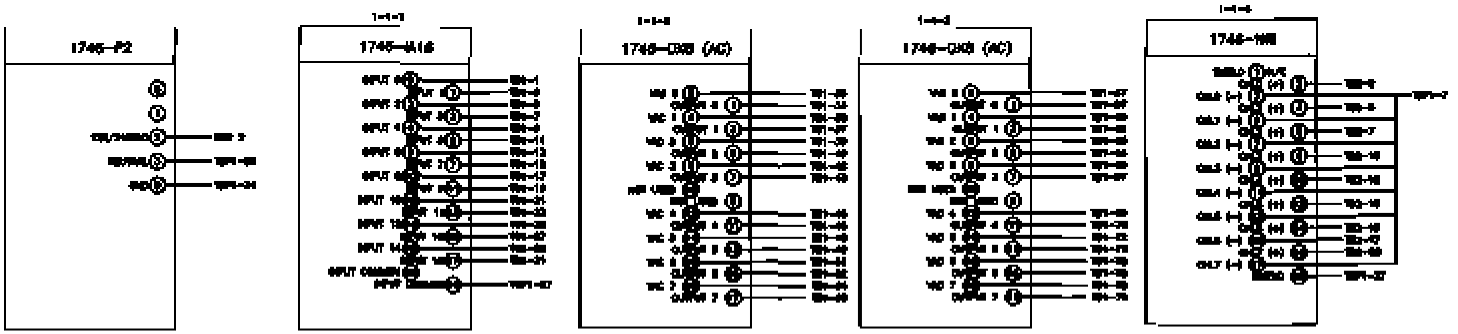

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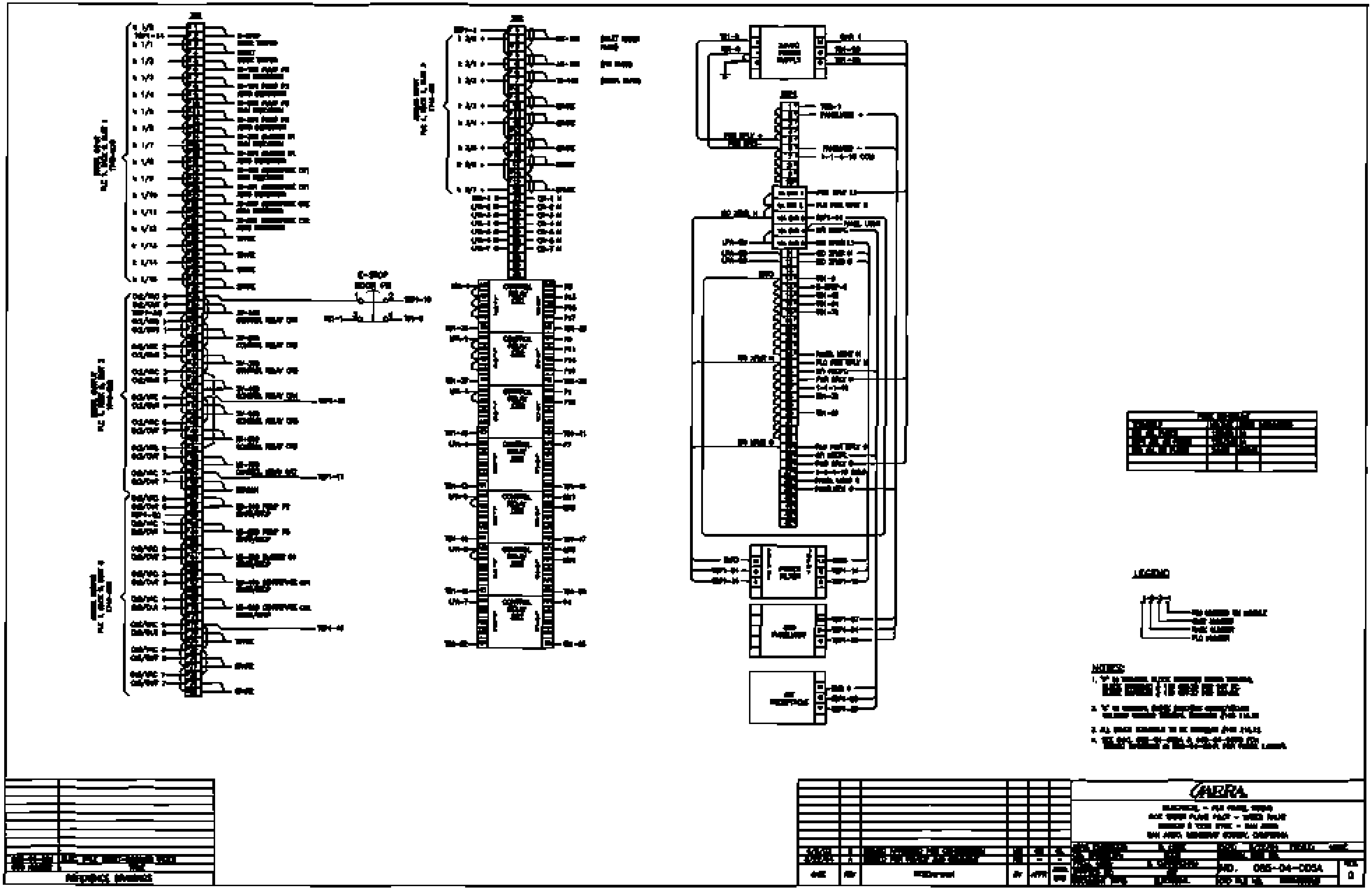E-STOP
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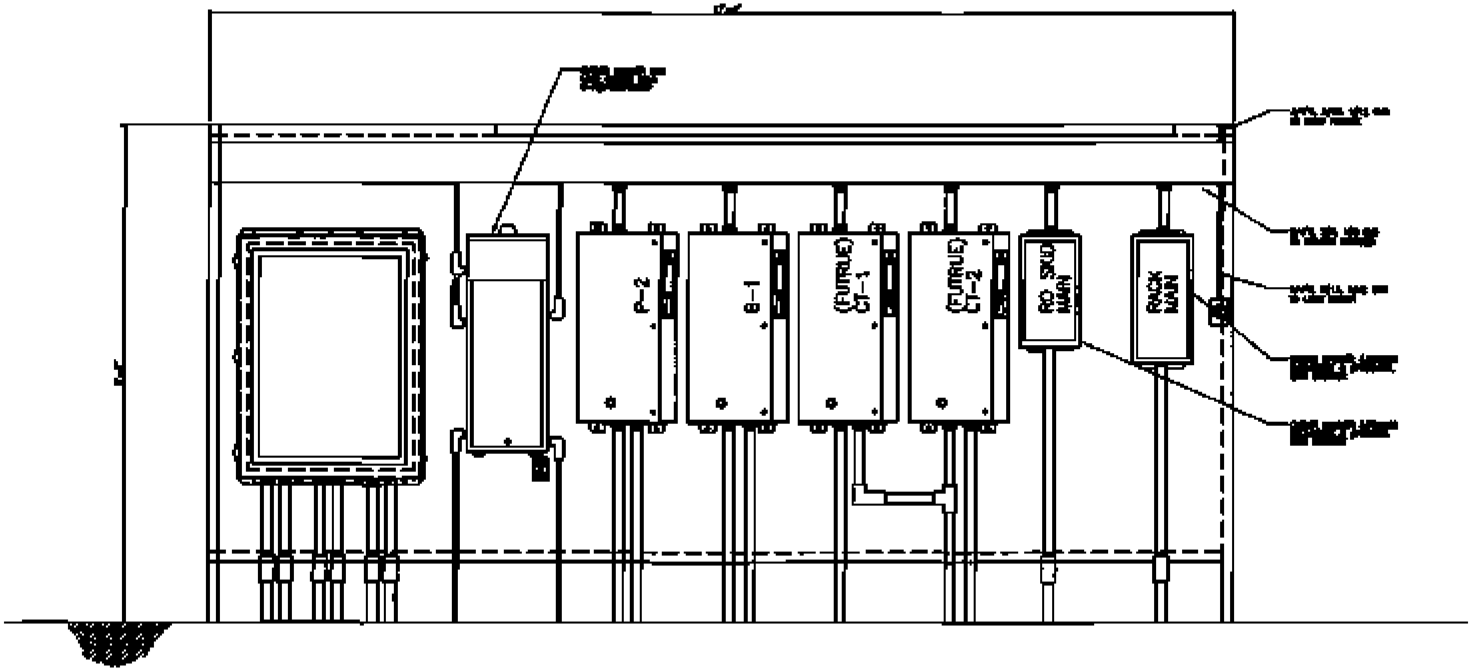

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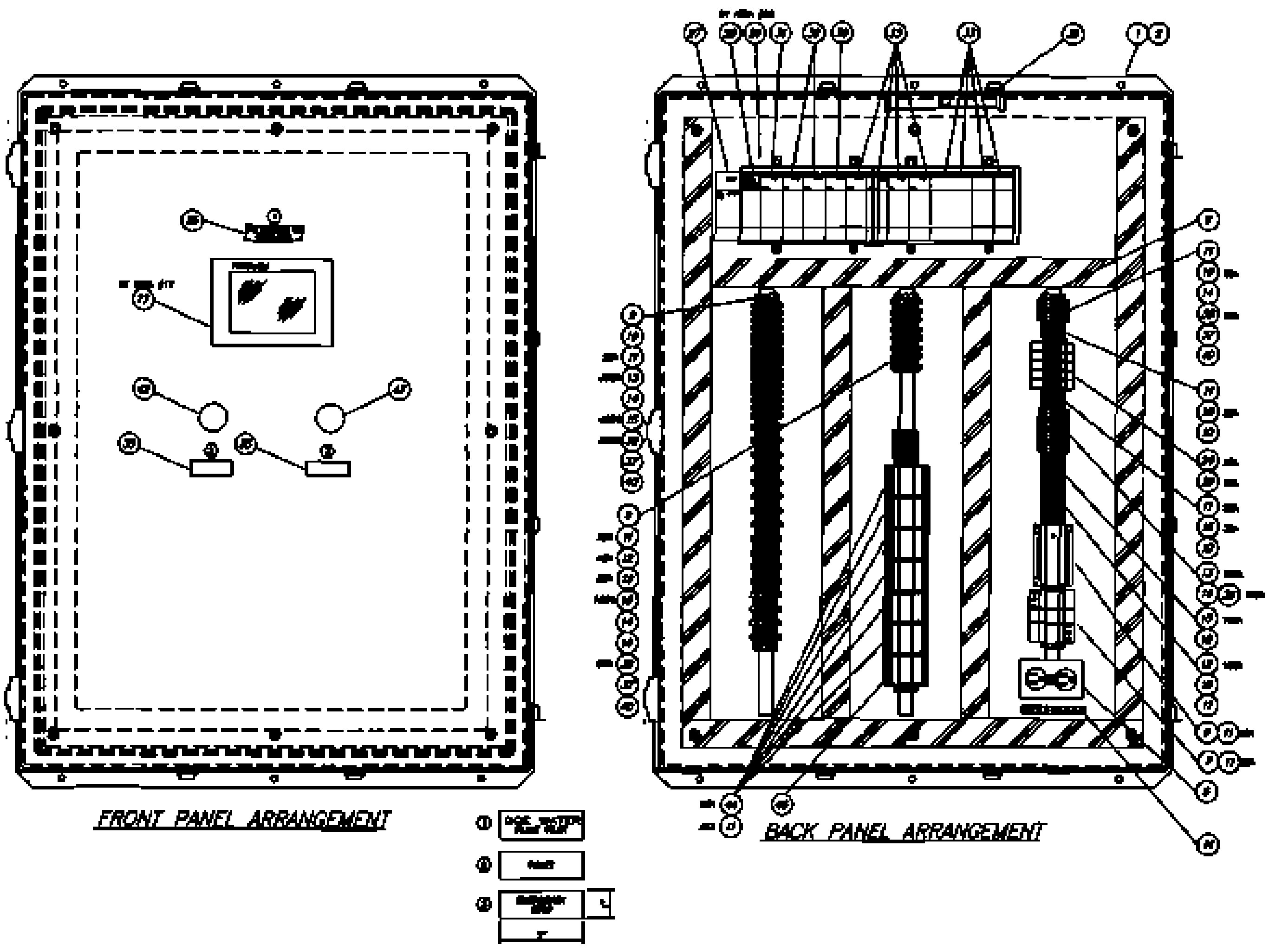

FRONT PANEL ARRANGEMENT

BACK PANEL ARRANGEMENT

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REV. 0

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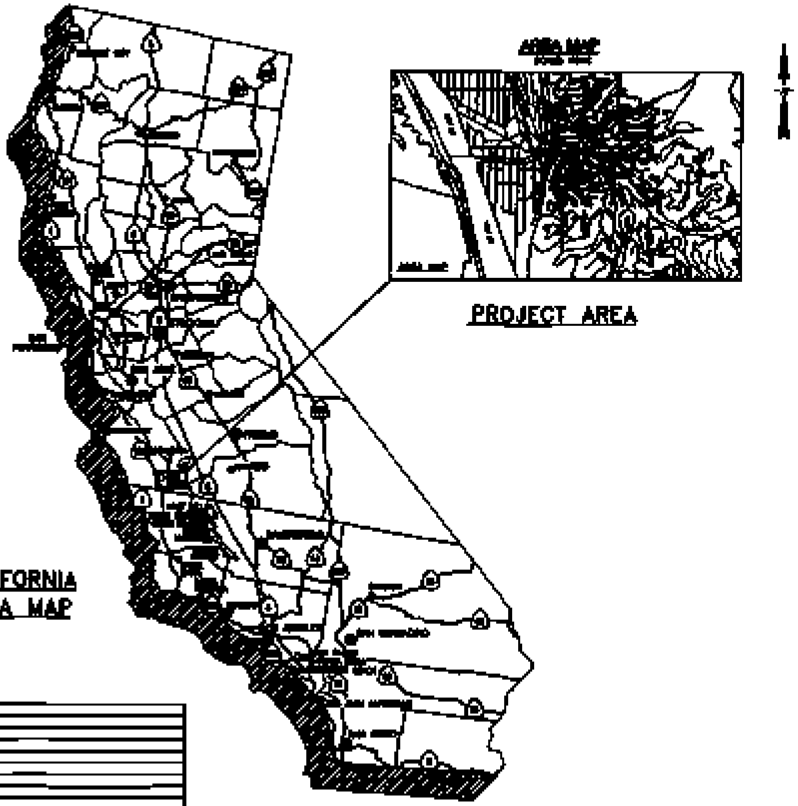

PROJECT AREA

CALIFORNIA AREA MAP

DRAWING INDEX

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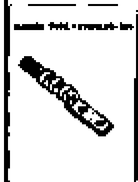
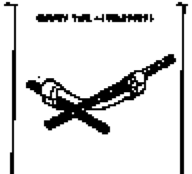
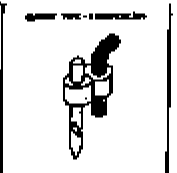
NO. 085-04-001A

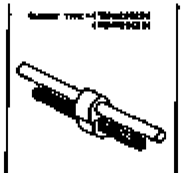
0

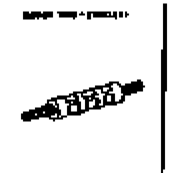

GROUND TERMINAL
DETAIL 1


GROUND PLATE
DETAIL 2

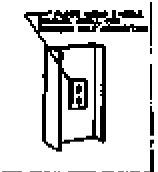

CROSS CONNECTOR
DETAIL 3

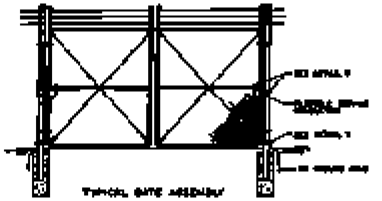

GROUND ROD TO CABLE
DETAIL 4

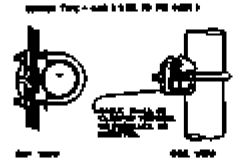

REINFORCING STEEL TO CABLE
DETAIL 5


SPLICE
DETAIL 6


CONNECTOR CABLE TO CABLE
DETAIL 7


STRUCTURAL STEEL TO CABLE
DETAIL 8

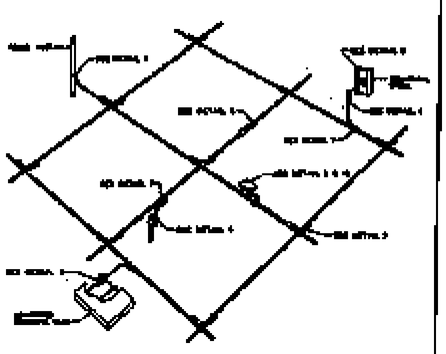

TYPICAL GATE ASSEMBLY


METALLIC POST TO CABLE
DETAIL 9


TYPICAL GROUNDING PLATE INSTALLATION
DETAIL 10

NOTES:

1. [illegible]
2. [illegible]
3. [illegible]
4. [illegible]
5. [illegible]
6. [illegible]
7. [illegible]


TYPICAL COMPRESSION GROUND SYSTEM

NOTE:
1. [illegible]

085-D4-2576

Appendix F: Membrane Autopsy Report for the Boron Rejection RO Membrane

HYDRANAUTICS
www.membranes.com
A Nitto Denko Company

RETURNED GOODS REPORT

Customer :	Kennedy Jenks	**RGA # :**	3058
Contact:	Ganash Rajagopalan	**Product Type :**	SWC4-4040
Fax # :	949-261-2134	**Quantity :**	3
End User :	Aera Energy, LCC	**RGA Assigned To :**	A. Miller
Sales Person :	John Kutilek	**Valid Warranty Claim :**	YES ☐ NO ☒
VP – Application Technology :	Craig Bartels	**Date :**	6/16/05
Technical Service Manager :		**Date :**	

CUSTOMER CLAIM/PROBLEM STATEMENT

Low permeate flow; retest (3) and dissection (1) for foulant determination requested by consulting engineer Kennedy Jenks.

ACTION REQUIRED/TAKEN BY TECHNICAL GROUP

Vacuum Test	YES ☒ NO ☐	Bubble Test	YES ☒ NO ☐
Standard Re-Test	YES ☒ NO ☐	Dye Test	YES ☐ NO ☒
Autopsy	YES ☐ NO ☒	Dissection	YES ☒ NO ☐
Weight Loss On Ignition (WLOI)	YES ☐ NO ☒	SEM/EDAX	YES ☒ NO ☐
Membrane Cell Test	YES ☐ NO ☒	Cleaning	YES ☐ NO ☒

EVALUATION

Serial Number	Shipping Material Inspection	Element Visual Inspection	Element Weight*
S4X90094	Shipping box damaged; bag unsealed; not leaking	Feed end core tube marked 2-3. No debris observed under seal carrier. Some discoloration, overall appearance fair, no odor.	8.58

S4X90024	Shipping box damaged; bag unsealed; not leaking	Feed end core tube marked 2-1. No debris observed under seal carrier. Some discoloration, overall appearance fair, no odor.	9.30
S4X90104	Shipping box damaged; bag unsealed; not leaking	Feed end core tube marked 2-2. No debris observed under seal carrier. Some discoloration, overall appearance fair, no odor.	8.26

* The normal weight of an unused wetted element is 8 lbs (± 1 lb).

- **Vacuum and Bubble Testing-** Vacuum (Dry) and Bubble (Wet) test were conducted to inspect integrity of the element. No leaks were detected on any of the elements during bubble testing. Two of the returned elements passed the vacuum test. Determination of source of vacuum failure in element S4X90094 would require an autopsy (not requested).

Serial Number	**Bubble Test**		**Vacuum Test**	
	Feed End	**Feed End**	**Start**	**Finish**
S4X90094	No Leaks	No Leaks	20.9	9.9
S4X90024	No Leaks	No Leaks	20.9	20.5
S4X90104	No Leaks	No Leaks	20.9	19.4

- **Standard Re-test-** The re-test of the elements (see table below) revealed an overall reduction in flow. Nominal rejection and flow values for this element were used for comparison to evaluate retest data and determine which element to dissect. Element S4X90094 did show increased salt passage but had the lowest delta P and highest flow of the three returned elements. The other two elements tested above nominal for rejection but demonstrated a significant decrease in flow.

STANDARD RE-TEST PERFORMANCE DATA							
SERIAL	Nominal		RE-TEST			% CHANGE	
NUMBER	Rejection	Flow (GPD)	Rejection	Flow (GPD)	DeltaP*	Salt Passage	Flow (GPD)
S4X90094	99.8	1150	99.3	1003	4.8	+248	-13
S4X90024	99.8	1150	99.9	945	5.1	-50	-18
S4X90104	99.8	1150	99.9	871	5.2	-50	-24

* Maximum allowable delta P is 10 psi.

- **Dissection** – Element S4X90104 tested the highest for delta P and the lowest for flow (an indication of heavy fouling) thus it was selected for dissection. A sample was collected from the element for SEM/EDAX analysis.
- **Scanning Electron Microscope -** The sample collected tested negative for carbonates (see attached data). There were ridges several inches long (photo #1) parallel to each other along side some of the brine spacer lines. The membrane appeared undamaged on the ridges. Most of the membrane was covered with a thin layer of foulant similar to the photo (#2) below. There were some scattered sphere shapes (probably cells) similar to the sphere on the photo (#1) below.

Photo #1

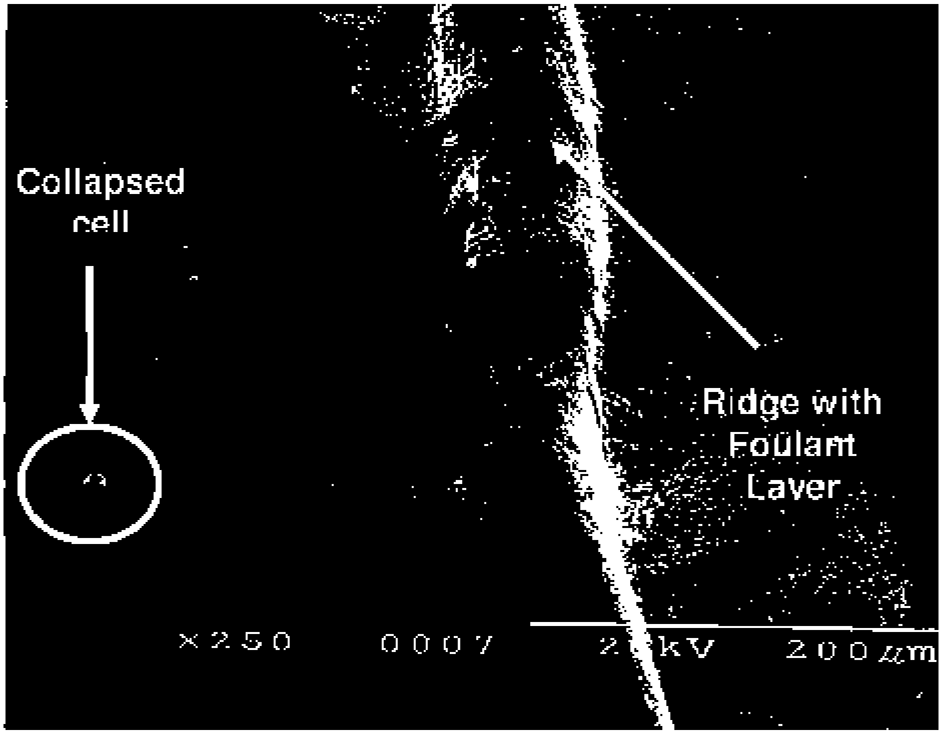
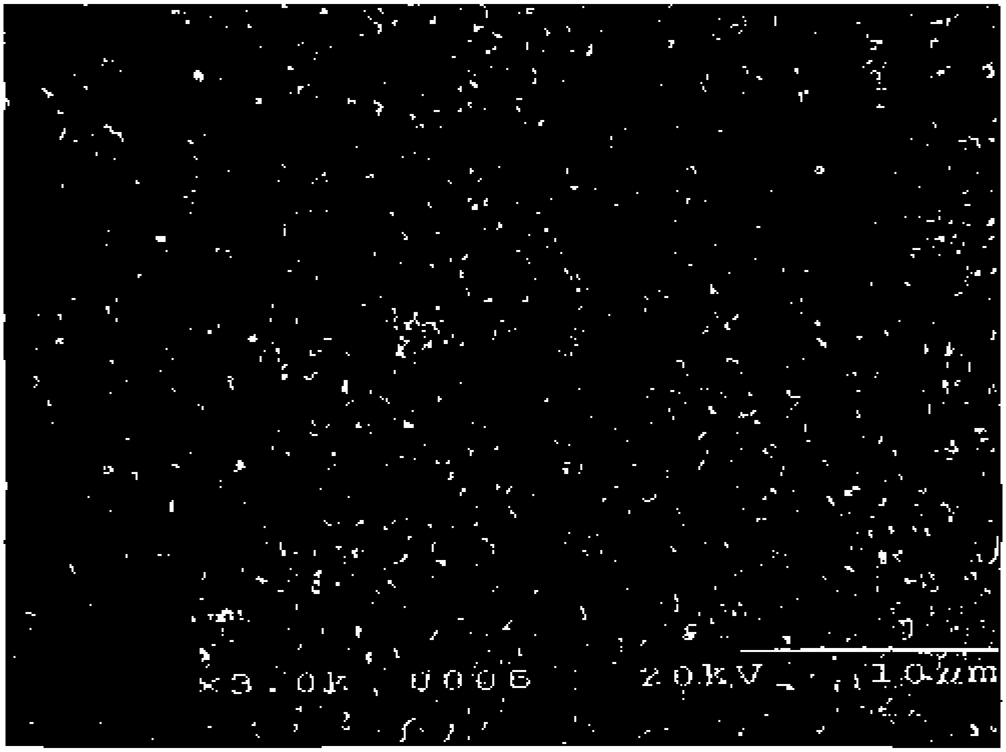


Photo # 2



- **Energy Dispersive X-Ray Microanalysis** – The foulant layer was examined to determine composition. The foulant layer consisted of primarily silica, magnesium and iron. There was also a small amount of phosphorus.
- **Cleaning**- N/A

CONCLUSION

Based on the data above foulant is the cause of the reduction in flow. The ridges noted and photographed under SEM are probably caused by an accumulation of foulant at the brine spacer lines. The ridges on the sample extracted from element S4X90104 appear undamaged and there is no corresponding increase in salt passage on retest. The failed vacuum test of element S4X90094 and subsequent increase in salt passage is likely due to some damage to the membrane (perhaps more significant and damaged ridges). Without an autopsy cause of increased salt passage can not be accurately determined.

RECOMMENDATIONS

Hydranautics recommends investigating targeting the specific foulants identified above with pre-treatment and increasing element cleaning frequency to prevent accumulation of foulant at the brine spacer lines sufficient to create ridges.

HYDRANAUTICS
High Performance Membrane Products
A NITTO DENKO CORPORATION

SEM / EDAX REPORT

To: A. Miller	**Date:** May 17, 2005
Cc: D. Carlton	**Log** 05-193
Membrane Type: SWC4	**Sample ID:** RGA 3058 serial number S4X90104 Returned from use on softened water from an oil field at Kennedy Jenks
Original Photos Wanted? YES ☐ NO ☐	**Analyzed By:** JR
Analytical Manager: Deborah Carlton	Date: 5/17/05

PURPOSE FOR STUDY

To look for the cause of the reduced flow.

ACTION REQUIRED/TAKEN BY ANALYTICAL GROUP

The untouched returned membrane and a control piece were dried, mounted and gold coated for SEM. To check for carbonates a piece of returned membrane is placed in HCl.

SEM / EDAX EVALUATION RESULTS

SEM Photos-
1 The control piece is seen at 3,000X.
2 The returned membrane is seen at 3,000X.
3 A ridge is shown on the returned membrane at 250X.
4 The top of the ridge is seen at 3,000X.

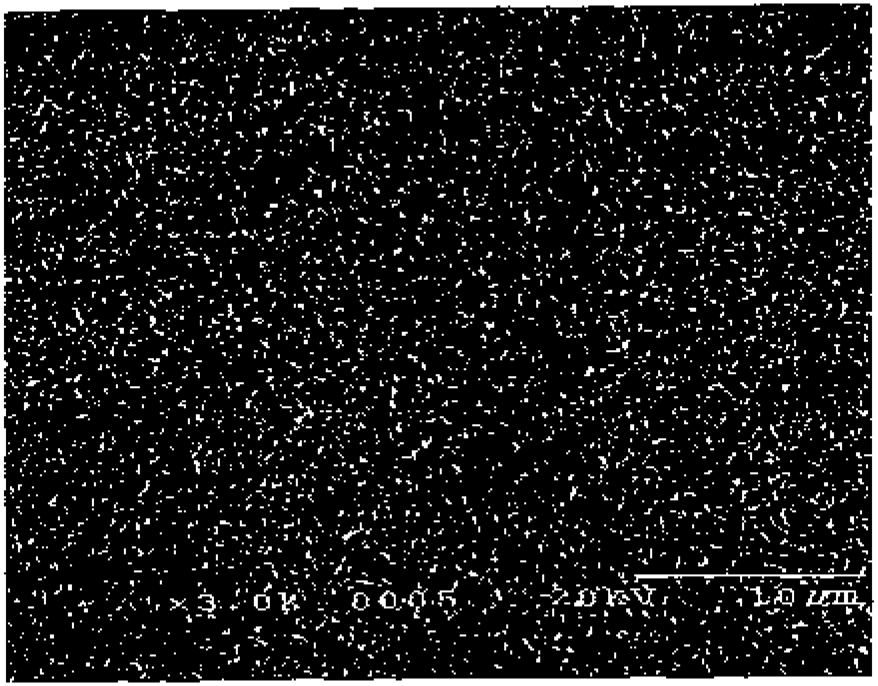
EDAX Scans-
1 The composition of the control sample is seen.
2 The composition of the returned membrane is seen.
3 The composition of a spot on the returned membrane with thick foulant near the brine spacer is seen.

ANALYTICAL GROUP OBSERVATIONS/NOTES

The returned membrane did not bubble in HCl so carbonates were very low or absent. There were ridges inches long parallel to each other on some of the brine spacer lines. The membrane appeared undamaged on the ridges. The cause of the ridges was not determined. Most of the membrane was covered in thin foulant similar to that seen on photos two and four. Scattered isolated probable cells were seen. The collapsed sphere shape on the left side of photo three is one of the probable cells.

[illegible] Control

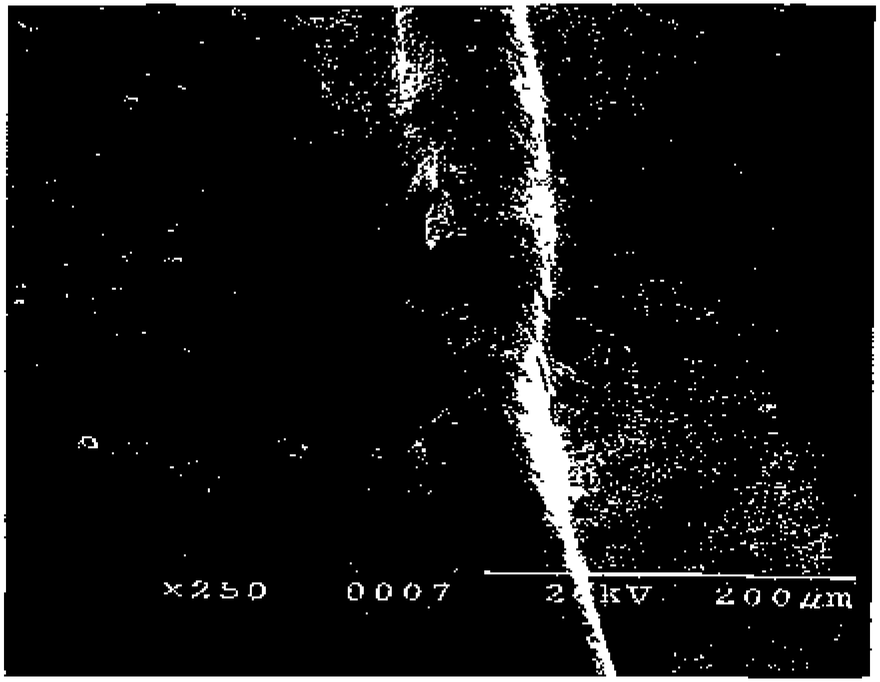
PHOTO#1



295-37-1

Kuhn

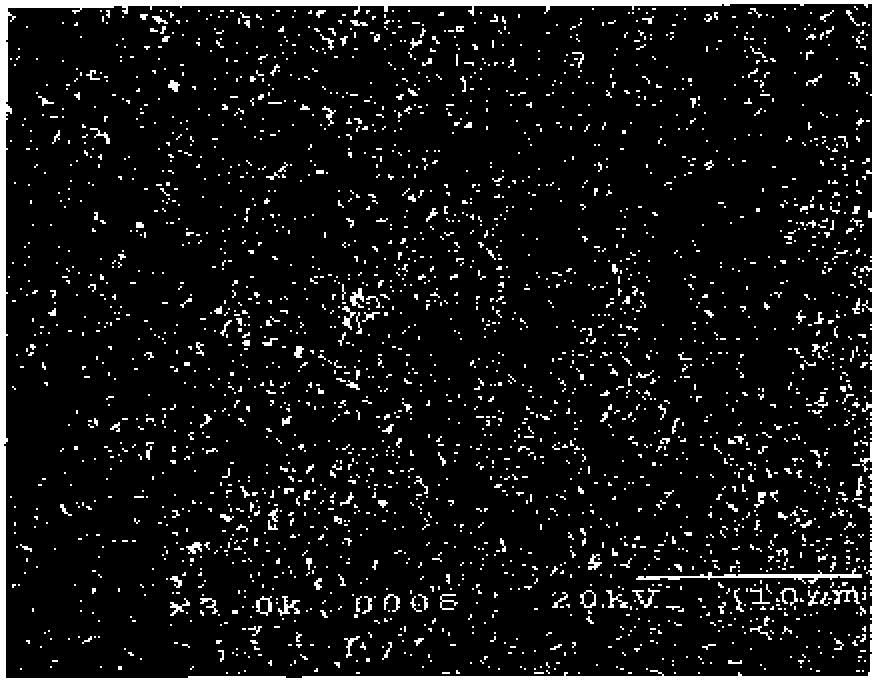
Photo #3



295-37-3

Membrane Away from Brass spacer

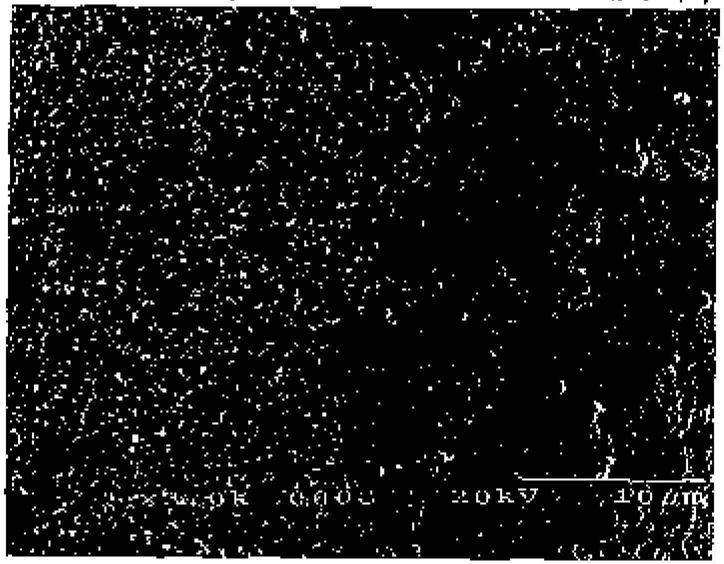
PHOTO #2



295-37-2

Top of the Ridge

PHOTO #4



295-37-

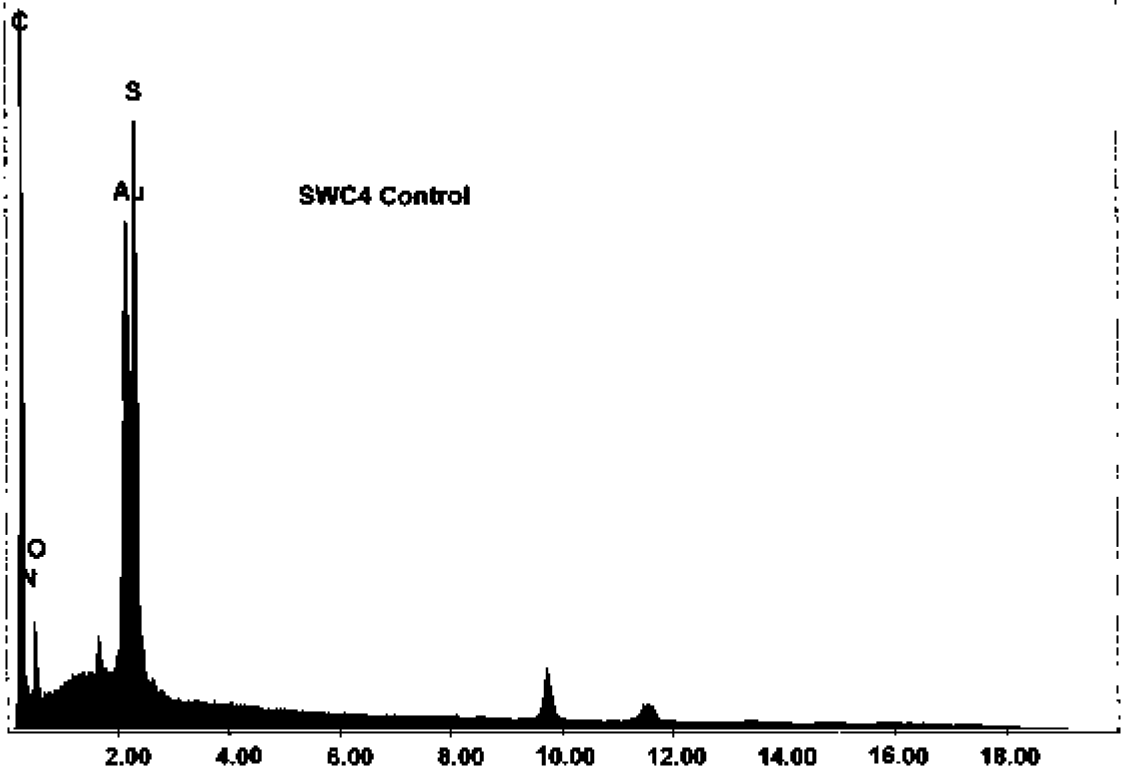
SCAN#1

Untitled:1

Label:Hydranautics Du Reinstal 4-15-05 JMendoza

kV:20.0 **Tilt:0.0** **Take-off:25.0** **Det Type:SUTW+** **Res:132** **Tc:40**

FS : 6989 **Lsec : 523** **17-May- 5** **11:55:10**



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
C K	49.64	73.10	0.1084	1.0618	0.2055	1.0001
N K	7.65	9.66	0.0080	1.0524	0.0999	1.0001
O K	7.93	8.76	0.0110	1.0439	0.1328	1.0000
AuM	23.20	2.08	0.2326	0.7090	1.4132	1.0007
S K	11.59	6.39	0.0752	0.9956	0.6514	1.0000
Total	100.00	100.00				

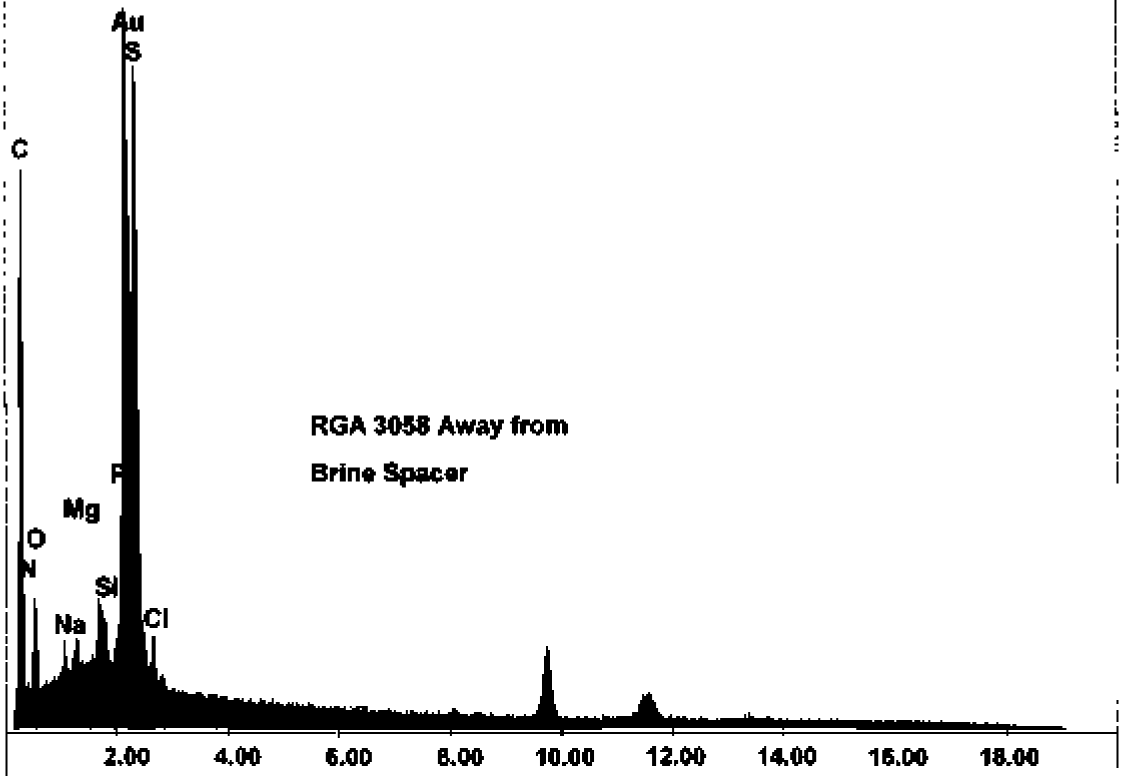
SCAN#2

Untitled:1

Label:Hydranautics Du Reinstal 4-15-05 JMendoza

kV:20.0 **Tilt:0.0** **Take-off:25.0** **Det Type:SUTW+** **Res:132** **Tc:40**

FS : 2562 **Lsec : 278** **16-May- 5** **16:50:55**



RGA 3058 Away from
Brine Spacer

EDAX ZAF Quantification (Standardless)
Element Normalized

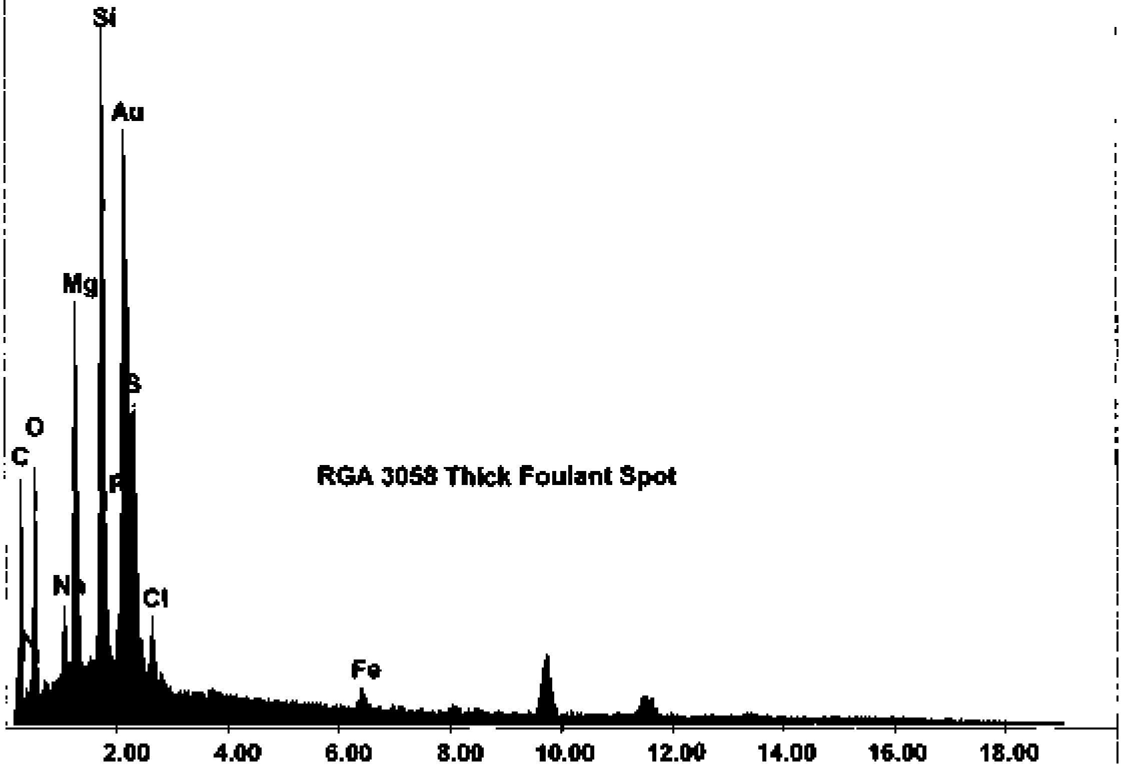
Element	Wt %	At %	K-Ratio	Z	A	F
C K	40.65	67.32	0.0767	1.0811	0.1745	1.0001
N K	6.98	9.91	0.0078	1.0715	0.1049	1.0001
O K	8.00	9.94	0.0116	1.0627	0.1365	1.0001
NaK	0.60	0.52	0.0021	0.9942	0.3453	1.0007
MgK	0.54	0.44	0.0026	1.0191	0.4708	1.0012
SiK	0.85	0.60	0.0063	1.0176	0.7240	1.0036
P K	0.68	0.44	0.0055	0.9908	0.8108	1.0056
AuM	28.85	2.91	0.2822	0.7246	1.3490	1.0007
S K	11.88	7.37	0.0705	1.0186	0.5821	1.0004
ClK	0.97	0.55	0.0058	0.9717	0.6138	1.0000
Total	100.00	100.00				

SCAN#3

Untitled:1

Label:Hydranautics Du Reinstal 4-15-05 JMendoza

kV:20.0	**Tilt:0.0**	**Take-off:25.0**	**Det Type:SUTW+**	**Res:132**	**Tc:40**
FS : 1991	**Lsec : 173**			**16-May- 5**	**16:42:10**



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
C K	22.19	43.36	0.0354	1.0970	0.1452	1.0002
N K	4.37	7.33	0.0060	1.0872	0.1258	1.0003
O K	15.06	22.08	0.0265	1.0783	0.1634	1.0002
NaK	1.80	1.83	0.0061	1.0086	0.3357	1.0022
MgK	6.84	6.60	0.0317	1.0338	0.4470	1.0023
SiK	9.74	8.14	0.0643	1.0322	0.6383	1.0021
P K	1.06	0.80	0.0069	1.0067	0.6497	1.0028
AuM	29.65	3.53	0.2416	0.7366	1.1057	1.0003
S K	6.49	4.75	0.0337	1.0360	0.5005	1.0007
ClK	1.63	1.08	0.0093	0.9880	0.5744	1.0001
FeK	1.16	0.49	0.0104	0.9251	0.9545	1.0133
Total	100.00	100.00				

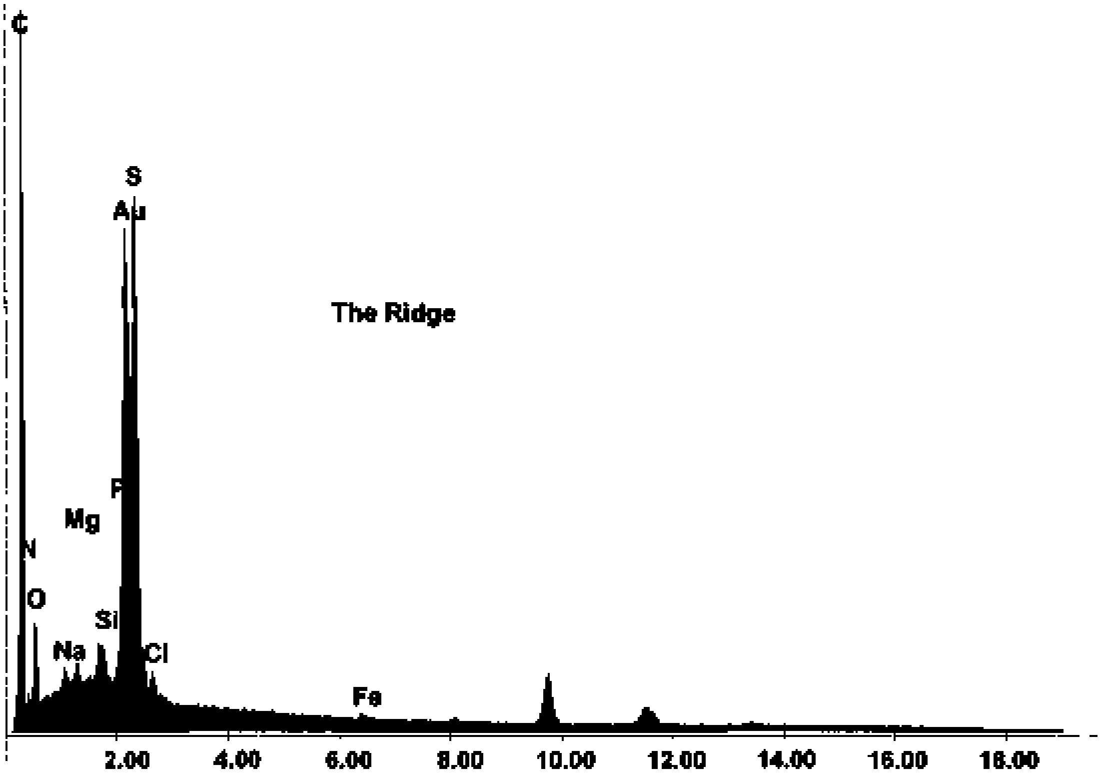
SCAN #4

Untitled:1

Label:Hydranautics Du Reinstal 4-15-05 JMendoza

kV:20.0 **Tilt:0.0** **Take-off:25.0** **Det Type:SUTW+** **Res:132** **Tc:40**

FS : 6646 **Lsec : 540** **16-May- 5** **16:59:03**



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
C K	50.06	73.78	0.1082	1.0619	0.2036	1.0001
N K	6.34	8.01	0.0066	1.0526	0.0992	1.0001
O K	8.00	8.86	0.0113	1.0440	0.1349	1.0001
NaK	0.53	0.41	0.0019	0.9769	0.3597	1.0006
MgK	0.37	0.27	0.0018	1.0014	0.4931	1.0011
SiK	0.61	0.38	0.0046	1.0002	0.7533	1.0034
P K	0.50	0.29	0.0041	0.9703	0.8403	1.0055
AuM	22.58	2.03	0.2232	0.7089	1.3939	1.0006
S K	10.09	5.57	0.0650	0.9955	0.6466	1.0003
ClK	0.61	0.31	0.0039	0.9504	0.6738	1.0000
FeK	0.30	0.10	0.0027	0.8906	0.9765	1.0132
Total	100.00	100.00				