

ICR Treatment Study Summary Report

Evaluation of Membrane Technology Using the Pilot-Scale Test For Compliance of the Information Collection Rule's; Grandfather of A Previously Conducted Study

Conducted during the period of July 19, 1989 through April 4, 1991

Prepared by:
The University of Central Florida
Environmental Systems Engineering Institute
Civil and Environmental Engineering Department
4000 Central Florida Boulevard
Orlando, Florida 32816-2450

In October 1997

For:
Pinellas County Utilities – PWS #: FL6521405
14 S. Ft. Harrison Avenue
Clearwater, Florida 34616
Ph. (813)-464-3438
FAX (813)-464-3944

Keller Plant 2, ICR # - 717

Attachments: 1 diskette containing the *Data Collection Spreadsheets and Summary Report*

Section I: Conclusions and Recommendations

Conclusions

1. Silt density indexes of groundwater from the Eldridge-Wilde well field were found to be less than three.
2. Four of ten spiral wound membranes tested in a single element membrane selection study reduced the THMFP below 50 µg/L as the species. Membranes with molecular weight cutoffs (MWC) below 400 and greater than 100 reduced the product stream hardness to less than 100 mg/L as CaCO₃ and more than 50 mg/L as CaCO₃. Consequently, several membranes met the membrane selection criteria. The FilmTec N-70 nanofilter was found to have the highest mass transfer coefficient (MTC) for water of any membrane that met the water quality criteria. TH and THMFP reduction was observed when the MWC of the membrane tested was 2000 or less. Membranes that had MWCs greater than 100 and less than 400 met all selection criteria.
3. The rate of MTC decline during preproduction studies using a single unit operated over an approximately one month period was predicted to be less than 15% over three months using conventional pretreatment. Consequently, acid addition and five micron prefiltration, which is conventional pretreatment, was determined to be adequate pretreatment for nanofiltration using groundwaters from the Eldridge-Wilde well field.
4. A two stage membrane pilot plant was operated at the Keller 2 water treatment plant using water from the Eldridge-Wilde wellfield and conventional pretreatment for a total of 9504 hours with 478 hours of downtime. The pilot unit was productive 95% of the time available for operation.
5. Operation with a balanced stage flux of 15 gsf/d and a system recovery of 60 % maintained the minimum membrane element flow velocity, decreased concentration polarization and improved water production. The predicted rate of membrane cleaning to maintain no more than a 15% MTC loss from an initial point of 0.35 gsf/d-psi would be approximately 6 to 9 months.
6. A black material was found on the prefilter cartridges and on the surface of an autopsied membrane. It was thought to be the major fouling material and indications were that it was ferric sulfide. The addition of oxygen into the source water by intermittent use of different wells could cause a reaction between hydrogen sulfide and iron that would foul the membranes. Elimination of this black material would very likely result in lower rate of MTC decline.
7. For the 11 sample periods conducted during operation using the source water to Keller 2. The average THM4 and HAA5 formation potential for the source water was 108 µg/L and 72 µg/L as the species, respectively. The final permeate stream concentrations

averaged 13 µg/L for THM4 and 7 µg/L for HAA5, resulting in a respective 87 and 91 % reduction. All permeate sample concentrations were below the proposed phase 2 DBP rule 40 and 30 µg/L concentrations. These results were determined from formation potential testing conditions of 96 hour incubation, 20 °C temperature, pH of 7.6 and chlorine doses of 12.5 mg/L for the feed and 5 mg/L for the permeate. The formation potential concentrations produced in the source water samples resulted in higher THMs than were normally recorded in the Pinellas County distribution system. Since the source water and distribution system represent similarly treated waters, the results from the membrane process monitoring would be expected to equal or be less than the actual DBPs found in a Pinellas County distribution system receiving a nanofiltered finished water.

8. The inorganic water quality produced by the membrane process using the Keller 2 source water averaged a total hardness of approximately 45 mg/L CaCO₃, an alkalinity of approximately 45 mg/L and a total dissolved solids of approximately 70 mg/L. The sodium concentration would be no more than 10 mg/L depending on whether lime or sodium hydroxide is used for alkalinity recovery. The remaining individual inorganic solutes will be less than 15 mg/L.

Recommendations

1. Any decision regarding the pursuit of a membrane process at Pinellas County should consider all benefits of the process. A nanofiltration process will produce high quality potable water in Pinellas County. The DBPFP will be low and will meet the proposed phase 1 and 2 DBP Rule MCLs for THMs and HAAs given a free chlorine residual is maintained in the distribution system. The reduction in TDS concentration in the finished water from a membrane process should provide a less corrosive water. The reduction in non-purgeable dissolved organic carbon will not only form fewer DBPs but will provide less chlorine demand and less nutrients for regrowth in the distribution system. Consequently the DBPs and the bacterial quality in the distribution system will be improved and the corrosiveness will be reduced.
2. Concentrate disposal options should be investigated thoroughly before a membrane process is chosen for water treatment. The cost of concentrate disposal is effected significantly by option. There are five basic options and many combinations of these options for concentrate disposal. The five options are sewer discharge, surface water discharge, land spreading or irrigation, rapid infiltration basins and deep well injection. The cost of these options generally varies from \$0.02/Kgal to \$0.10/Kgal and is generally less than the cost of membrane replacement. Consequently the cost although significant is not prohibitive; however the permitting process is far from standard. Currently concentrates are classified as industrial wastes and significantly scrutinized by FDEP. There has not been a proposed membrane process stopped for lack of a permit for concentrate disposal to the author's knowledge. However the attainment of a permit can and will probably be an arduous path. A method of concentrate disposal should be attained before any detail design is initiated.

Section II: Background Information

Treatment plant description

The following section will describe the existing treatment process used by the Pinellas County Utilities Keller 2 water treatment plant (WTP). Figure 1 presents the process schematic of the Keller 2 WTP.

The membrane studies were conducted at the S. K. Keller Water Treatment Facility located in the northeast corner of Pinellas County near Tarpon Springs, Florida. The water used for the pilot studies was the raw groundwater source to the Keller Plant 1 (ICR-ID No. 317) and the Keller Plant 2 (ICR-ID No. 717). Both of the Keller Plants use the Eldridge-Wilde well field which pumps water from the Floridan aquifer. Though the two plants have a separate well and source water collection system, the wells for each plant are located adjacent to each other and have similar water quality. The water treatment process for the two plants consists of aeration, free chlorine disinfection, pH stabilization using sodium hydroxide and additional corrosion control using an ortho/poly-phosphate blend. The two Keller Plants are located adjacent to each other and are essentially the same except for age and the mode of aeration. The Keller Plant 1 uses induced draft and the Keller Plant 2 uses cascade aeration.

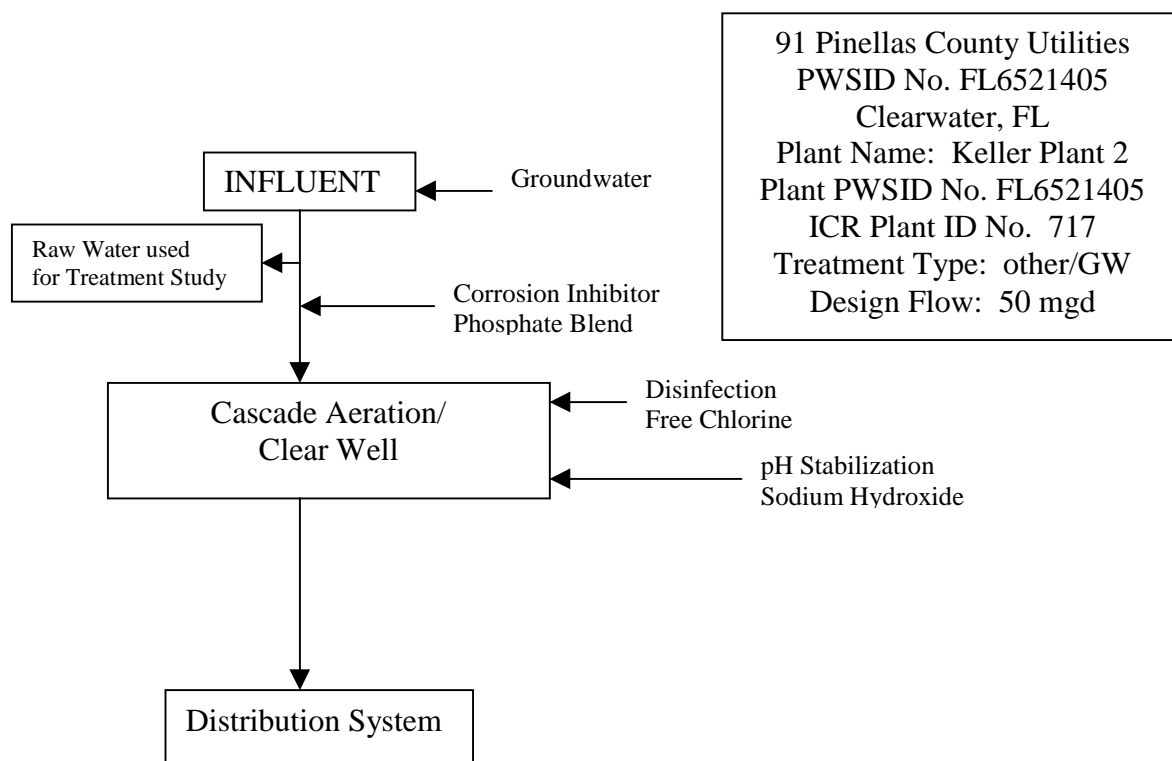


Figure 1: Process Schematic For Keller Plant 2

Table 2 presents the Keller Plant 2 process design and chemical addition parameters which were also documented in report forms A2 and A3 from the *ICR Sampling Manual* and

submitted for the *ICR Water Utility Database System*. The major challenge facing the utility will be meeting the proposed phase 1 and phase 2 DBP Rules using free chlorine. The Utility's water source and treatment facilities are located in the northern end of the county and it must distribute finished water through a very long system. Transmission of water through the entire length of the system requires numerous storage, repump and rechlorination facilities. In addition, approximately half of the water the county distributes is supplied by the West Coast Regional Water Supply Authority (WCRWSA). This Authority supplies chlorinated groundwater from well fields located in Pasco County, FL. This facility is north of Pinellas County and increases the length of time in the distribution system. To meet the proposed DBP Rules the Utility will have to use advanced treatment to remove DBP precursors and/or switch to an alternative disinfectant such as chloramines. To accomplish these alternatives coordination with the WCRWSA and their client utilities will have to be obtained.

Table 1: Keller Plant 2 Process Design and Chemical Addition Parameters

Unit Process	Process Description	Quantity
Plant Information		
	Treatment Plant Name	Keller Plant 2
	ICR Treatment Plant ID	717
	Treatment Plant PWS ID	FL6521405
	Treatment Plant Category	Other/GW
	State Approved Plant Capacity	40 MGD
	Historical Min. Water Temp.	24 deg. C
	Installed Sludge Handling Cap.	0.00 (gpd)
	Blending Indicator	N
Water Source		
	Water Source Name	Eldridge-Wilde Wellfield
	Water Resource Type	Groundwater
	Intake Name	Keller Plant 2 Influent
	Wellhead Protection	Yes
	Hydrologic Unit Code	Lat. +28°9'7" (deg.,min.,sec.)
		Long. -82°40'27" (deg.,min.,sec.)
Clear Well		
	Aeration	Cascade
	Surface Area	4,425 ft ²
	Liquid Volume	430,287 gal.
	Baffling Type	AV
	Short Circuiting Factor	N/A
Disinfection		
	Chlorine Gas	12 mg/L as Cl ₂
Corrosion Control		
	pH Stabilization	16 mg/L as NaOH
	Corrosion Inhibitor	1 mg/L as Product (ortho/poly phosphate)

Summary of source and finished water quality

The following section will present in tabular form the source and finished water quality of the Keller Plant 2. Table 2 presents the source water and Table 3 presents the finished water. The water quality analysis represents sample monitoring from November 1996 through September 1997. A monthly average DBP concentration was determined from the results of four monitoring sites. The monthly averages were used to develop the DBP results shown in Table 3. The DBPs were analyzed using USEPA methods 551.1 and 552.2. The monitoring period represents the most recent and complete parameter list and corresponds to sampling required by the ICR. Notification to monitor source water for bromides and uv-254 for one year was received in February of 1997.

Table 2: Source Water Quality Summary For Keller Plant 2

Water Quality Parameter	Average Yearly Concentration	Standard Deviation	Maximum Yearly Average	Minimum Yearly Average
Temperature (°C)	24.9	0.7	26.4	24.1
pH	7.51	0.08	7.68	7.45
Turbidity (ntu)	0.20	0.07	0.31	0.12
Alkalinity (mg/L CaCO ₃)	212	9	227	203
Calcium Hardness (mg/L CaCO ₃)	192	8	207	183
Total Hardness (mg/L CaCO ₃)	219	13	243	205
TOC (mg/L C)	4.0	0.4	4.8	3.5
UV-254 (cm ⁻¹)	0.112	0.008	0.120	0.098
Bromide (µg/L)	0.039	0.006	0.048	0.034

Table 3: Finished Water Quality Summary For Keller Plant 2

Water Quality Parameter	Average Yearly Concentration	Standard Deviation	Maximum Yearly Average	Minimum Yearly Average
Temperature (°C)	25.5	0.9	27.3	24.2
pH	7.78	0.09	7.94	7.62
Turbidity (ntu)	0.34	0.09	0.46	0.22
Alkalinity (mg/L CaCO ₃)	215	10	235	205
Calcium Hardness (mg/L CaCO ₃)	194	10	209	171
Total Hardness (mg/L CaCO ₃)	216	8	232	208
TOC (mg/L C)	4.0	0.5	4.9	3.5
UV-254 (cm ⁻¹)	0.191	0.259	0.720	0.079
TOX (mg/L Cl)	0.21	0.06	0.28	0.13
Distribution System THM4 (µg/L)	75	8	86	63
Distribution System HAA5 (µg/L)	51	10	65	41

Section III: Methods and Materials

Pretreatment Processes to the Advanced Treatment Process

The membrane treatment study was conducted using the raw groundwater supplied to Keller Plant 2. From a tap in the raw water collection main, prior to entry into the plant the water was pumped to the membrane pilot unit trailer. The raw water pump was used to maintain a pressure of approximately 30 psi to the membrane pilot unit prefilter. The raw water was pretreated with either Flocon 100 anti-scalent or sulfuric acid addition. Prefiltration consisted of two parallel cartridge filters with a nominal pore size of 5 microns. Figure 2 in the following Advanced Treatment Section presents a process diagram that shows the location of chemical addition and prefiltration. Table 4 presents the pretreatment processes and design parameters.

Table 4: Membrane Pilot Unit Pretreatment Design Parameters

Unit Process	Process Description
Scale Control (Pilot-Scale)	Chemical Type: Sulfuric Acid
	Adjust pH: 5.9
	Dose Rate (mg/L): 110
	Or : Flocon 100
	Dosed at 2 mg/L
Cartridge Filtration (Pilot-Scale)	Total Surface Area (ft ²): 2.2
	Nominal Pore Size (µm): 5
	Filter Material: Wrapped Polypropylene Yarn
	Filter Life (gal. of raw water): 10 ⁶

Advanced Treatment Process

The following section will present the membrane pilot plant design and the specification of the membrane elements. Figure 2 presents a flow diagram of the membrane pilot plant. Raw water was pumped from the Keller Plant 2 collection main to the membrane pilot plant trailer. Prior to passage through the prefilter, concentrated sulfuric acid was injected to reduce the pH and prevent calcium carbonate from precipitating. When the acid feed system failed Flocon 100 anti-scalent was added at 2 mg/L to prevent scaling. The chemically treated water then passed through (2)-20 inch long cartridge filters configured in parallel. The cartridge filters had an individual surface area of 1.1 ft², for a total surface area of 2.2 ft². These cartridge filters had a nominal pore size of 5 µm. After the prefilter the water passed through a high pressure feed pump which boosted the pressure to approximately 150 psi and passed the water through the membrane process.

The pilot plant utilized a 2-stage christmas tree configuration identical to the ICR pilot unit design described in the “*ICR Manual for Bench- and Pilot-Scale Treatment Studies*”. The first stage consisted of two pressure vessels in parallel, which in turn fed concentrate to a single pressure vessel in the second stage. It incorporated three 4040 elements per pressure vessel for a total of nine elements.

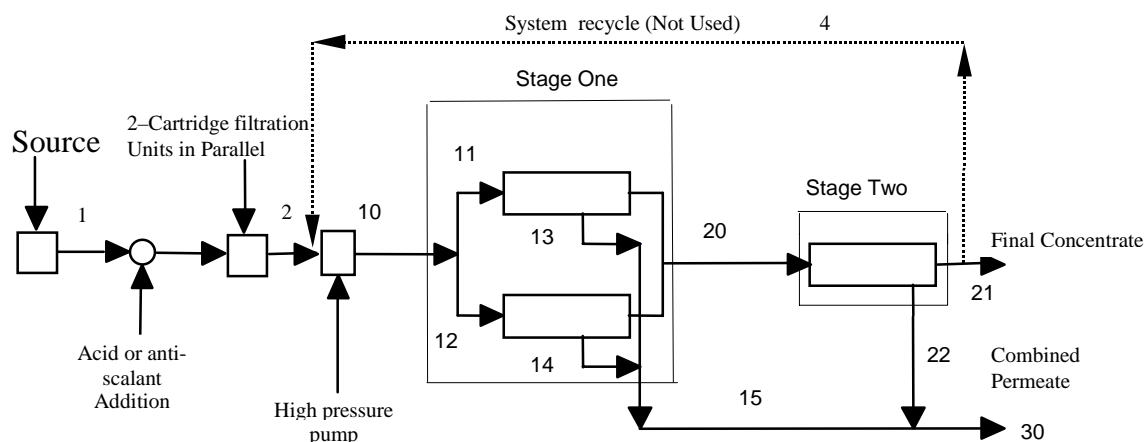


Figure 2: Membrane Pilot Unit Flow Diagram

Table 5 presents the information supplied by the manufacturer for the membrane elements used in the membrane pilot studies conducted at the Keller Plant 2. The initial single element testing was conducted using an element with approximately 70 ft² of membrane area. However, the elements used in the pilot study had an increased area of approximately 80 ft² due to a more efficient wrapping technique.

Table 5: Information Supplied by Membrane Manufacturer

Element	Dow U. S. A. (FilmTec)
Parameter	4040
Membrane	NF-70
Configuration	Spiral-Wound
Element Dia.	3.9"
Element Length	40"
Permeate Tube Dia.	0.75"
External Wrap	Fiberglass
Membrane Type	Thin film composite
Active Layer	Cross Linked Aromatic Polyamide
Functional Group	Amide
Backing	Polyester
Molecular Weight Cut	200
Charge	Negative
Ks (gsfd)	15 (Na)
Active Membrane Area	80 ft ²
Recovery	15 %
Permeate Flow	1700
Max. Feed Flow	16 gpm
Minimum Feed Flow	4.0 gpm
Water Flux	15-25 gfd
Water MTC	0.35 gsfd/psi
Max. Pressure	250 psi
PH (Long Term)	3-9
PH (Short Term)	1-11 @ 25 ⁰ C
Max. SDI	5
Membrane Life	5 yr
Max feed Turbidity	1 ntu

Experimental Design

The studies conducted at the Keller Plant 1 scheduled operation of the membrane pilot for six months with collection of 5 sample sets on a monthly basis. After the Keller Plant 1 membrane studies were completed the 2-stage pilot plant was connected to the source water of the Keller Plant 2.

The studies conducted at the Keller Plant 2 scheduled operation of the membrane pilot for approximately 12 months with collection of 12 sample sets on a monthly basis. However, the unit was actually operated for approximately 15 months with 11 sample events. Table 6 presents the experimental design of the membrane study. The unit was set to operate on a continuous basis after initiation with a system recovery of 60% and a stage and system flux of approximately 15 gsf. Limiting salt calculations and computer projections determined that SiO_2 would be the limiting salt at approximately 85% recovery. However, pump capacity and hydraulic characteristics of the pilot unit limited recovery to between 75 and 80 %. After operation at the Keller Plant 1 produced a cleaning frequency of once every 1.6 months the recovery was reduced to 60 % for operation at the Keller Plant 2. The reduced recovery would increase the velocity across the membrane element and reduce concentration polarization. The pretreatment consisted of acidification to control calcium carbonate precipitation and 5 μm prefiltration. If the acid feed system failed then equipment was available to add Flocon 100 anti-scalant at 2 mg/L. Recycle was not used during the pilot studies conducted at Keller Plant 2. The permeate streams from each stage were not restricted during initial operation which produced higher flux in stage 1 than in stage 2, similar to how full scale plants are presently operated. However, modifications were made that allowed for flow calibration and control of the individual stage flux. These modifications are explained in the Results and Discussion Section.

Table 6: Experimental Design of Keller 2 Membrane Studies

Season	Membrane	Pretreatment	System Flux (gsf)	Recovery (%)
Winter	NF-70	Conventional/Acid	15	60
Spring	NF-70	Conventional/Acid	15	60
Summer	NF-70	Conventional/Acid	15	60
Fall	NF-70	Conventional/Acid	15	60
Winter	NF-70	Conventional/Acid	15	60
Spring	NF-70	Conventional/Acid	15	60

Membrane Cleaning

There were several cleaning operations conducted on the membranes during the studies conducted during operation using the Keller Plant 2 source water. Cleaning of the membranes required two types of chemical combinations. For removal of calcium carbonate scaling, a 0.1 % solution of phosphoric acid and permeate water was used. This solution converts the carbonate ion to bicarbonate, and thereby dissolves calcium carbonate, removing the precipitate formed on the membrane. For biocleaning or removal of organic material, a mixture containing 0.1% solution of tetra-sodium salt of ethylenediaminetetraacetic acid (EDTA), 0.1% NaOH and permeate water was used. The solution produced a pH of

approximately 12. As is common in membrane facilities, permeate was used for preparing the cleaning solution in order to make the purest cleaning solution possible at the site.

During the cleaning of the membranes, the pilot plant was modified to form a closed loop system. The feed stream, permeate stream and concentrate stream valves were closed. The cleaning solution was made in a 30 gallon barrel and pumped through the two stage system by a 3/4 Hp centrifugal pump. A hose was connected to the feed line before the prefilters. Three-way valves were placed on the discharge line for the final concentrate and the combined permeate. These valves could be positioned to discharge the water out of the trailer or into the cleaning barrel for closed loop cleaning operation. The cleaning solution was pumped through the pilot plant to fill the membrane pressure vessels, the pumps were turned off and the membranes were allowed to soak for one to 24 hours. The cleaning solution could either be wasted or directed to the cleaning tank for recycling after soaking. The first flush of cleaning solution from the membrane pilot plant contained the highest concentration of foulants and was wasted for the first five to ten minutes of the cleaning procedure. After the initial flush, the cleaning solution was recirculated for one to two hours. A new cleaning solution was made and the procedure was repeated. Organic cleaning was conducted first followed by inorganic cleaning if necessary.

Analytical Methods

The following section presents a summary of the analytical methods used for the water quality analysis of samples collected during the membrane studies conducted for Pinellas County. Due to the broad scope of the water quality study conducted for the County in which the membrane study was one phase, analytical methods, material and quality control were included in a separate report. This report Titled *“Investigation And Analysis of Contaminants In The Potable Water Supply of Pinellas County: Laboratory Methods, Materials and Quality Control”* was forwarded to USEPA with the *“Request For Approval To Grandfather Data From A Previous Membrane Pilot Study To Meet The ICR Treatment Study Requirements For PWSID# FL6521405, Plant ICR # 717”*.

The DBP formation potential simulated the DBP formation in the distribution. The water is produced at the northeastern border of the county and is pumped, chlorinated and stored during distribution through the county. The distribution system is extensive and has a relatively long detention time. The conditions for DBP formation potential were selected to be a SDS formation for this system. These condition were set at an incubation pH of 7.6, temperature of 20⁰C, a reaction time of 96 hours at doses of 5 mg/L for the permeate samples and 12.5 mg/L for the feed stage 1. The free chlorine residuals after the 96 hours for the raw and total permeate samples were no less than 0.2 mg/L CL₂. For the total permeate samples residuals ranged from 0.2 to 2.1 and the raw water samples ranged from 1.3 to 4.5 mg/L CL₂. These formation conditions produced DBPs that were generally higher than what is measured in the distribution system.

The DBPs for the long term membrane pilot studies were measured using the USEPA 551 and 552 methods which included the measurement of 26 different compounds. The University of Central Florida was conducting membrane research for the USEPA titled *“Reduction of Disinfection By-Product precursors by Nanofiltration”*, (EPA/600/SR-92/023, April 1992) which required laboratory participation in the evaluation of the two analytical methods and the comparison of the THM4 methods EPA 501.2 and EPA 551. These studies were conducted in anticipation of the adoption of both EPA 551 and 552 methods. Included

with the request for approval to grandfather information was a paper Titled “*Comparison of THM Analyses by EPA Method 501.2 and 551*”. This paper was presented during an AWWA WQTC conference, (Orlando, 1992) and summarizes the results of the comparison of THMs by EPA 501.2 and 551. In addition, during the Pinellas County Water Quality Studies an extensive evaluation of the source waters was conducted by varying the formation parameters to produce statistical predictive models for chlorine and chloramine demand as well as the 26 DBP compounds. The THMs for this study were analyzed by both EPA 501.2 and 551 methods. The study produced THM formation curves from 0 to 96 hours at two chlorine doses and two temperatures for the Keller Plant 1 and 2 source waters and the permeate using the EPA 501.2 method. This study report titled “*Investigation And Analysis of Contaminants In The Potable Water Supply of Pinellas County: Disinfectant Residual and By Product Modeling*” can be provided at the USEPA’s request.

The Pinellas County membrane study evaluated the water quality of the flow streams for more parameters than the ICR protocol requires. However there were 2 parameters that were not measured during this study that are required of a proposed ICR study, bromides and UV-254. In addition instead of measuring total organic carbon (TOC) this study analyzed for non-purgeable dissolved organic carbon (NPDOC). Historical analysis on the Floridan aquifer has shown that the purgeable fraction of carbon is negligible and these water samples were not filtered before the analysis, therefore for this groundwater TOC and NPDOC are essentially the same.

The UCF ESEI Laboratory conducted all of the analysis associated with the membrane studies conducted at the Keller Plant 2. The UCF ESEI laboratory as described in the “*Investigation And Analysis of Contaminants In The Potable Water Supply of Pinellas County: Laboratory Methods, Materials and Quality Control*” was certified by the State of Florida and participated in USEPA performance evaluations during these studies. Pinellas County Utilities Laboratory and Montgomery Laboratories are conducting the analysis associated with the ICR Monitoring requirements. Montgomery Labs are measuring TOX and Bromides. The sample analysis related to ICR monitoring was used to produce Tables 2 and 3, which present the most recent source and finished water quality for the Keller Plant 2.

A summary of the analytical methods and detection limits for the UCF ESEI Laboratory analysis associated with the membrane studies is presented in Table 7. The contact personnel and information for the three laboratories are presented in Table 8.

Table 7: Summary Of Analytical Procedures

Procedure	Description	Reference	Reporting Level
Alkalinity	Acid titration	SM 403	2 mg/L
Chloride	Argentometric	SM 407A	1 mg/L
Chlorine Residual	Amperometric titration DPD Ferrous titrimetric	SM 408C SM 408D	0.1 mg/L
Color	Spectrophotometric	SM 204B	0.5 cpu
Fluoride	SPADNS	SM 413C	0.05 mg/L
Hardness, Total Ca ⁺⁺	EDTA titration	SM 314B	2 mg/L
		SM 311C	2 mg/L
Metals, General	Plasma Emission	SM 305	Fe = 10 µg/L
PH	Meter	SM 429	N/A
Sulfate	Turbidimetric	SM 426C	1 mg/L
Total Dissolved Solids	Gravimetric	SM 209B	1 mg/L
Turbidity	Ratio turbidimeter	SM 214	0.05 NTU
Silica	Heteropoly Blue	SM ¹⁹ 4500-SiE	1 mg/L
Sodium	Plasma Emission	SM 305	1 mg/L
Non-purgeable dissolved Organic Carbon	Persulfate-Ultraviolet Oxidation	SM 505B	0.3 mg/L
Disinfection By-Products	Micro-extraction, GC-ECD	EPA551,552*	1 µg/L Individual
Trihalomethane	Liquid-Liquid extraction	EPA 501.2	1 µg/L Individual
Total Organic Halide	Adsorption-Pyrolysis, Titrimetric	SM 506	2 µg/L
Formation Potential	Chlorination followed by 501.2, 551, 552, and TOX Analysis	TEXT	N/A

*EPA 551 analyzed the base-neutral function, while EPA 552 analyzed the haloacetic fraction.

SM = 16th Edition of Standard Methods. SM¹⁹ = Referenced under 19 th edition of Standard Methods.

EPA = U.S. Environmental Protection Agency

Table 8: Laboratories Conducting Analysis For Report

Laboratory	ICR I.D.	Contact	Address	Phone
Pinellas County Utilities	FL-006	Robert M. Powell, Director	1620 Ridge Rd. Largo, FL 34648	Phone – (813)-582-2302 FAX – (813)-584-8623
Montgomery Watson	CA-013	James C. Hein	555 East Walnut St. Pasadena, CA 91101	Phone – (818)-568-6400 FAX – (818)-568-6324
UCF Environmental Systems Engineering Institute	N/A	Dr. James S. Taylor, Director	University of Central Florida CEE Department 4000 Central Florida Blvd. Orlando, FL 32816- 2450	Phone – (407)-823-2785 FAX – (407)-823 6562

Section IV: Results And Discussions

Operations Description

Time of operation is classified by the events that occurred during operation. Periods of operation are defined as the time increments between events that for this study were mainly caused by modifications to the membrane pilot unit. This section will report these periods of operation numerically in order of their occurrence. Table 9 lists the 5 periods for Keller Plant 2. The effects of these system changes on water production and quality will be described in subsequent sections.

Table 9: Membrane Pilot Plant Periods Of Operation

PERIOD	DATE	TIME (hours)	REC. (%)	CHEM. FEED	COMMENTS
KELLER 2	2/6/90-4/25/91	9504			
1	2/6/90-2/22/90	0-365	75	F-100	High recovery with anti-scalent
2	3/05/90-5/29/90	368-2335	60	Acid	Cleaned membranes, balanced stage flux and recovery
3	5/30/90-9/20/90	2336-4515	60	F-100	Acid pump maintenance
4	9/21/90-10/25/90	4537-5342	60	Acid	Cleaned membranes, replaced acid pump
5	10/25/90-4/25/91	5342-9504	60	Acid	Replaced last membrane from stage 2 for inspection

On 1/10/90 the operation of the membrane system using the Keller Plant 1 source water was discontinued and the unit was prepared for operation using the Keller 2 water source. The membranes were cleaned with a high pH solution of EDTA for organic foulants, followed by a cleaning with a low pH phosphoric acid solution to remove inorganic precipitates.

Period 1 began when operation of the membrane pilot plant was started at Keller Plant 2. The pilot plant was operated at Keller Plant 2 for 9504 hours from 2/6/90 to 4/25/91. Five periods of operation were identified during the Keller Plant 2 membrane pilot plant studies. The first of these, period 1, ran from 0 to 368 hours of operation. During this period the system was operated at approximately 78% recovery and used the anti-scalent, Flocon F-100, for inorganic fouling control. On 2/22/90 (360 hours) the system operation was discontinued due to a pressure gauge leak. The pilot unit was not flushed before system operation was discontinued which resulted in membrane fouling. The membranes were cleaned for organic as well as inorganic fouling before restarting operation on 3/5/90.

The next period of operation, period 2, spanned from 368 to 2335 hours. The system recovery was decreased from 75 % to 60 % to reduce concentration polarization. The per

element recovery was approximately 10 %, which resulted in an approximate flux of 13.5 gsfd. Valves on the permeate stream from each pressure vessel were used to restrict flow which increased the permeate back pressure and decreased the net driving force. The result of controlling the permeate flux was to increase the mass transfer coefficient from approximately 0.30 to 0.40 gsfd after cleaning. Sulfuric acid addition was reintroduced as control for calcium carbonate precipitation. Sulfuric acid was used until 5/30/90 (2335 hours) when the chemical feed pump failed and ended the period.

The Flocon 100 anti-scalent was used from 2336 hours until 4515 hours, which was designated as period 3. Two fouling events took place during this period because of power failures caused by thunderstorms. Because the concentrate stream was not flushed from the array, inorganic salts precipitated and fouled the membranes. The first fouling event occurred on 7/10/90 (3260 hours) and the second occurred on 7/19/90 (3375 hours). On 7/24/90 (3378 hours) the system was cleaned with a solution of phosphoric acid to remove the inorganic scale. Because flow and pressure values returned to levels recorded prior to fouling, organic cleaning was not conducted. Period 3 continued until 9/20/90 (4515 hours) when the system was shut down for cleaning. This was done to evaluate the ability of organic and inorganic cleanings to restore the membrane water production or MTCs to levels recorded at the start of period 2.

Period 4 began on 9/21/90 at 4537 hours of operation and continued to 10/25/90 at 5342 hours of operation. This period started after the cleaning regime and under the same conditions as period 2 which was also identical to period 3 except that acid was used instead of anti-scalent to control scaling. This period was ended when the last membrane of the third stage was replaced with a new membrane. The replaced membrane was sent to the manufacturer, FilmTec, for examination to identify foulants. This material was never positively identified but was thought to be an iron sulfide precipitate.

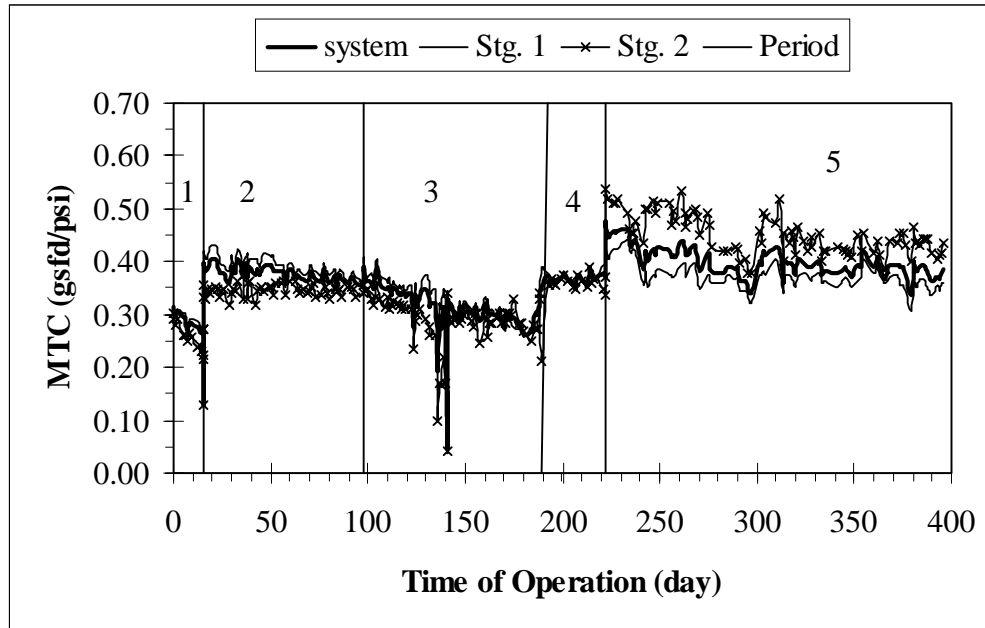
Period 5 began following the replacement of the membrane on 10/25/90 at 5342 hours of operation. The replacement membrane element in stage increased the permeate flow which when controlled to a flux of 13 gsfd increased the back pressure and decreased the net driving force. The result was an increase in mass transfer coefficient. This period ended with the termination of pilot plant operation on 4/25/91 at 9504 hours of operation.

Water Production

The 2 stage membrane pilot plant was operated at the Keller 2 water treatment plant using water from the Eldridge-Wilde well field and conventional pretreatment for a total of 9504 hours with 478 hours of downtime. The pilot unit was productive 95% of the time available for operation.

Figure 3 presents a plot of the MTCw(Tavg oC) generated from the *Data Collection Spreadsheets*. The stage 1 and stage 2 MTCw were taken directly from the Data Collection Spreadsheets but the MTCw for the system was modified. The system MTCw developed by the spreadsheet incorporates the mechanical head loss of valves and piping between the stages and therefore produces a higher net driving force than the individual stages. This in turn produces a MTCw lower than either of the stages. The system MTCw developed for Figure 3 and the rates of decline were calculated by summing the flow weighted stage 1 and 2 MTCw.

Figure 3: Membrane Pilot Plant Water Production



Using linear regression techniques on the data presented in the graph, a water production decline rate was determined for each period. Table 10 presents the rate of decline and cleaning frequency for each period. The cleaning frequency was calculated using the individual rate of decline and a common initial manufacturer specification MTC of 0.35 gsfd and a 0.15 % decline.

Table 10: Predicted Cleaning Frequency For Keller Plant 2 Membrane Operations

Period (#)	Operational Condition	Equation $MTC_w = MTC_o - M(\text{time})$ MTC (gsfd/psi); Time (day)	Cleaning Frequency ¹ (Months)
1	Chem., Recovery		
1	Anti-scalent, 80%	$MTC = -0.0033T + 0.31$	0.5
2	Acid, 60%	$MTC = -0.0002T + 0.38$	8.7
3	Anti-scalent, 60%	$MTC = -0.0010T + 0.36$	1.7
4	Acid, 60%	$MTC = 0.0003T + 0.36$	Non-fouling
5	Acid, 60%	$MTC = -0.0003T + 0.43$	5.8

1 – Calculated with MTC_o at 0.35 gsfd/psi and 15% decline

Table 10 shows that period 1 when the pilot unit was operated with anti-scalent and a recovery of 80% had the highest cleaning frequency at 0.5 months. During period 3 when the unit was operated with anti-scalent and a lower recovery of 60 % the cleaning frequency decreased to once every 1.6 months. This indicated that concentration polarization at the higher recovery was having an adverse effect on water production. This is reinforced when the periods 2, 4 and 5 are compared to the results obtained from operation using the Keller Plant 1 source. Periods 2, 4 and 5 used a recovery of 60% during the operation on the Keller Plant 2 source and the Keller Plant 1 operation used 80% recovery. Both included 5 micron filtration and acid addition. The Keller Plant 2 operation predicted cleaning frequencies were

much lower at once every 4.4, 5.8 months and non-fouling than the once every 1.6 months predicted while operating using the Keller Plant 1 source water.

Comparison of the Keller Plant 2 periods also indicates that the use of anti-scalent by itself was not as effective in maintaining water production as pH control with sulfuric acid.

There appeared to be no adverse effects on water production from seasonal changes in climate. The pilot plant operation was initiated in the winter (February 1990) and ended Spring (April 1991).

Water Quality Data

The following section will present a summary of the water quality data collected from the membrane pilot studies conducted at the Keller Plant 2 WTP. Water quality samples were collected approximately once a month after the pilot plant was set to operate at 60 % recovery and balanced stage flux. The first sample set was collected in the winter (March 1990) with a total of 11 sample sets collected over the 14 months of operation. There appeared to be no seasonal effect on the water quality of samples collected during this study.

Source Water Quality

Table 11 presents the source water quality of samples collected during operation of the membrane pilot unit at the Keller Plant 2 WTP. The water samples were collected from a sample port located on the well field collection main at the tap for the pilot unit. These samples represent the raw water from the well field prior to any pretreatment.

Table 11: Source Water Quality For Keller Plant 2 Membrane Pilot Studies

Parameters	Units	High	Low	Avg.	Std. Dev.
PH		7.5	7.2	7.4	0.1
TDS	mg/L	260	220	247	13
Alkalinity	mg/L CaCO ₃	280	210	234	22
Total Hardness	mg/L CaCO ₃	220	200	209	7
Calcium Hardness	mg/L CaCO ₃	200	180	188	6
Chlorides	mg/L Cl ⁻	9.3	7	8.3	0.8
Sulfates	mg/L SO ₄	1.9	1	1.2	0.3
Sodium	mg/L Na	7	4.4	6.2	0.7
Iron	µg/L Fe	170	36	77	37
Turbidity	NTU	1	0.1	0.3	0.3
Fluoride	mg/L F	0.29	0.09	0.16	0.06
Silica	mg/L SiO ₂	16	13	14.6	1.3
Color	CPU	24	10	14	4
NPDOC	mg/L C	3.4	2	2.9	0.4
SDS-THM	µg/L	170	43	108	34
SDS-HAA5	µg/L	113	18	72	32
SDS-TOX	µg/L Cl ⁻	580	280	438	82

Water Quality of Pretreated Influent

Table 12 presents the feed water quality of samples collected during operation of the membrane pilot unit at the Keller Plant 2 WTP. The water samples were collected from a sample port located on the pilot unit between the pretreatment processes and the high-pressure pump that fed the membrane elements of stage 1. These samples represent the influent water to the membrane process after either acidification with sulfuric acid or anti-scalent addition and 5 micron filtration. Three sample sets were collected when anti-scalent was used for pretreatment. These sample analyses were excluded from the data analysis summary in Table 12 for TDS, pH, Alkalinity, Fluoride and sulfate. The anti-scalent did not appreciable change the source water concentrations of the parameters measured for this study. However, sulfuric acid did have an effect on TDS, fluoride, pH alkalinity and sulfates.

The major difference between the water quality of the source or raw water and the pretreated influent to the membrane process is the effects of the addition of sulfuric acid for scaling control. In general, the pH and alkalinity decreased while sulfates and TDS increased following acid addition. The source water had relatively low sulfates averaging 1.2 mg/L SO_4 . The acid addition raised the sulfate on average to 115 mg/L SO_4 . On average fluoride concentration increased from 0.16 to 0.33 mg/L F with the addition of sulfuric acid. The DBP formation potentials were conducted on the source water and not the feed stream to the membrane pilot unit.

Table 12: Influent Water Quality For Keller Plant 2 Membrane Pilot Studies

Parameter	Units	High	Low	Avg.	Std. Dev.
PH		6.6	5.8	6.1	0.2
TDS	mg/L	350	310	326	13
Alkalinity	mg/L CaCO_3	160	76	107	30
Total Hardness	mg/L CaCO_3	230	200	213	10
Calcium Hardness	mg/L CaCO_3	240	180	199	18
Chlorides	mg/L Cl^-	9.8	6.8	7.8	0.9
Sulfates	mg/L SO_4	140	88	115	19
Sodium	mg/L Na	7	4.4	6.2	0.7
Iron	$\mu\text{g/L}$ Fe	100	32	58	23
Turbidity	NTU	4.3	0.1	0.9	1.5
Fluoride	mg/L F	0.42	0.18	0.33	0.08
Silica	mg/L SiO_2	18	13	14.6	1.3
Color	CPU	23	10	15	4
NPDOC	mg/L C	5	2.1	3.3	0.8

Finished Water Quality

Table 13 presents the combined permeate water quality of samples collected during operation of the membrane pilot unit at the Keller Plant 2 WTP. The water samples were collected from a sample port located on the pilot unit after permeate from stage 1 was combined with permeate from stage 2. These samples represented the finished water from

the membrane process. This data shows that the NPDOC was reduced below 0.5 mg/L C and the THM4 and HAA5 formation potentials were below the proposed phase 2 limits.

Table 13: Keller Plant 2 Membrane Pilot Plant Finished Water Quality

Parameter	Units	High	Low	Avg.	Std. Dev.
PH		6.9	5.4	6	0.6
TDS	mg/L	82	55	71	10
Alkalinity	mg/L CaCO ₃	59	28	44	11
Total Hardness	mg/L CaCO ₃	58	35	46	8
Calcium Hardness	mg/L CaCO ₃	52	29	40	7
Chlorides	mg/L Cl ⁻	4.5	2.8	3.7	0.6
Sulfates	mg/L SO ₄	11	10	6.7	3.9
Sodium	mg/L Na	3.3	2.4	2.9	0.3
Iron	µg/L Fe	24	10	13	4
Turbidity	NTU	0.4	0.1	0.2	0.1
Fluoride	mg/L F	0.16	0.05	0.08	0.03
Silica	mg/L SiO ₂	8.2	6.8	7.4	0.5
Color	CPU	11	1	3	4
NPDOC	mg/L C	0.5	0.2	0.3	0.1
SDS-THM	µg/L	39	4	13	10
SDS-HAA5	µg/L	20	2	7	6
SDS-TOX	µg/L Cl ⁻	140	21	50	35

Table 14 presents the average percent rejection of solutes from the finished water during the membrane studies. The reference concentration was the pretreated influent water quality. In general, the organic parameters were reduced by 80 to 91 %.

Table 14: Rejection of Solutes For Keller Plant 2 Membrane Studies

Parameter	Rejection (%)
TDS	76
Alkalinity	66
Total Hardness	78
Calcium Hardness	80
Chlorides	53
Sulfates	92
Sodium	53
Iron	76
Fluoride	69
Silica	49
Color	80
NPDOC	91
SDS-THM	87
SDS-HAA5	91
SDS-TOX	89

Impact of Seasonal Variability

The water quality and production data indicates that there are no impacts associated with the season of the year on the membrane process. Because the source to the Keller Plant 2 comes from a relatively deep aquifer the source water quality remains relatively constant. Relatively small changes in the source water quality are associated with the individual water quality of each well and the combination of wells that are operated at a given time.

Cost Information

This section outlines cost estimates for building and operating a membrane softening system for a 10 and 50 mgd groundwater nanofiltration plant at Pinellas County. The cost estimates are not exact and should be used for comparative purposes only. A much more exact estimate would have to be completed for actual cost estimates for financing. The cost estimate is adequate for general cursory cost comparisons to other water treatment processes. The groundwater cost estimate details cost for building and operating a membrane softening plant with conventional pretreatment of acid feed and prefiltration at 85 % recovery and 150 psi. The estimated capital cost for a 10 and 50 million gallon per day (MGD) membrane softening operation using a groundwater source at Pinellas County is shown in Table 14. The operation-maintenance (O & M) costs for the membrane softening operation are also summarized in Table 15. References for both O & M costs and capital costs were taken from several different sources (EPA 1979, Taylor 1989, Goigel 1990) and updated by the Engineering News Record Construction Cost Index to 1991.

The capital cost estimated consisted of land, site work, buildings, process equipment, process piping, instrumentation, high service pumps and capital costs associated with deep well injection. No cost for on site finished water storage tanks was estimated as these costs are common to all treatment processes and should be separated from the costs used for comparison of different processes. Using the references mentioned above, the capital cost of a 10 MGD and 50 MGD membrane softening plant was estimated as \$15,874,250 and \$65,040,500 respectively. The amortized cost over 20 years at 10% is \$0.51/Kgal for the 10 MGD plant and \$0.42/Kgal for the 50 MGD plant for finished water. The total O & M cost for the 10 and 50 mgd plant was estimated to be \$2,102,700 and \$9,348,500 or \$0.58/Kgal and \$0.51/Kgal respectively.

Both the 10 and 50 mgd plants were sized on a array basis. A three stage array with 4 pressure vessels in stage one, 2 pressure vessels in stage two and one pressure vessel in stage three was assumed. Each pressure vessel contained six membrane elements which had an 8" diameter and 350 sf. A system flux of 15 gsf/d was assumed at a system pressure and recovery of 150 psi and 85 %. Each array contained 42 membrane elements and would produce 220,500 gpd and 46 arrays would be required to produce 10 mgd. Increasing the number of arrays to 230 would supply 50 mgd and was the basis for developing the 50 mgd cost estimate.

The building for the 10 mgd plant was estimated to have 20,000 sf of area and was priced at \$70/sf for a total estimated cost of \$1,400,000. The estimated building cost for the 50 mgd plant was \$6,500,000. Since the building costs was only for the membrane facility very little economy of scale was realized. The control room area was only doubled for the 50 mgd plant from that of the 10 mgd plant, so a savings of \$500,000 was realized. The remaining building costs for the chemical feed and storage buildings, chlorine feed buildings, clearwell,

administration and power vault buildings were taken from the EPA cost manuals and updated to 1991 costs using the ENR index.

Table 15: Cost Estimate For Pinellas County Nanofiltration Plant

Category	Cost	
	10 MGD	50 MGD
<u>Capital</u>		
Land	\$35,000	150,000
Site work	\$300,000	500,000
Buildings		
Membrane	\$1,400,000	6,500,000
Chemical Feed	\$224,000	560,000
Bulk Chemical Storage	\$168,000	630,000
Chlorine Feed	\$168,000	785,000
Clearwell and pumps	\$244,000	1,220,000
Administration and Lab	\$140,000	420,000
Power Vault	\$15,000	75,000
Process Equipment		
Membranes and pumps	\$6,000,000	\$27,000,000
Chemical Feed	\$115,000	\$517,500
Chlorination	\$100,000	\$160,000
Aerator	\$400,000	\$1,200,000
Process Piping	\$1,323,000	\$6,600,000
Instrumentation and electrical	\$992,250	\$3,473,000
High Service Pumps	\$200,000	\$1,000,000
Deep Well		
Injection Well	\$3,000,000	\$11,250,000
Unlined Lagoon Back-up System	\$200,000	not required
Transport Pipeline	<u>\$850,000</u>	<u>\$3,000,000</u>
Total:	\$15,874,250	\$65,040,500
\$/Kgal (20yrs at 10%)	\$0.51	\$0.42
<u>O & M (per year)</u>		
Wages	\$195,000	\$545,000
Power	\$600,000	\$2,850,000
Chemical Supplies	\$713,700	\$3,568,500
Maintenance	\$515,000	\$2,030,000
Telephone	\$12,000	\$30,000
Deep Well	\$15,000	\$75,000
Other	<u>\$52,000</u>	<u>\$250,000</u>
Total:	\$2,102,700	\$9,348,500
\$/Kgal	\$0.58	\$0.51
<u>Total Cost</u>		
\$/Kgal	\$1.09	\$0.93

Forty-six membrane arrays were required for the 10 mgd plant. The arrays would be distributed among ten skids, each of which would produce approximately 1.2 MGD. Membrane flux can be varied to suit actual needs so exact flux is not required for accurate cost estimates. There would always be one skid available for immediate utilization for the 10 mgd design. Five skids would be available for immediate use for the 50 mgd design. Each skid has an estimated capital cost of \$600,000 or \$6,000,000 for 10 skids in the 10 mgd plant.

Some slight savings of scale was assumed for the 50 mgd design due to lower unit costs of materials. The capital cost for membrane process equipment was estimated at \$27,000,000. The remaining process equipment cost was estimated from EPA cost manuals and adjusted to 1991 cost using the ENI index. These costs are based on chemical dosing rates that are listed in the O&M cost section. There was very little economy of scale associated with the chemical feed equipment for the 50 mgd design. However, significant economy of scale was realized for the chlorination and aeration process equipment. The process piping is the interconnecting piping for each of the arrays, skids and system. Very little economy of scale was realized for the process piping or the high pressure pumps because the same amount of this type of equipment is required on a unit flow basis. Some electrical and instrumentation savings could be realized because of the reduction in unit cost of a central control facility for 50 mgd plant.

Deep well injection was chosen as the method of concentrate disposal because it appears to be the current method of choice. However significant cost savings could be realized if surface discharge could be realized. The cost for deep well injection was estimated using a UCF master thesis (Goigel, 1991). This cost was developed by assuming one deep well with a 2 mgd capacity for the 10 mgd plant. The capacity for the 50 mgd plant is 9 mgd. Actually less than 2 mgd is required for disposal at 85 % recovery but the cost savings associated with a 1.76 vs a 2.0 mgd well are not significant. These costs include storage of 6 mgd in a unlined lagoon as a backup system.

Four deep wells were selected with a capacity of 3 mgd each in order to have a available well on stand by for the 50 mgd system. No unlined lagoon is required here because of the extra well. A 10" diameter ductile iron pipe was used for the ten mile transport pipeline. There is only one deep well included in the estimated cost for the 10 mgd facility. A ten mile distance from the membrane plant was assumed for transport of the concentrate to the injection well. A maximum velocity of 6 feet per second was used for transport and injection. The cost for all deep wells was estimated, per Florida regulations, as a Class I injection well for industrial and municipal waste. Construction includes a tubing and packer system, in addition to the conventional casing and cement.

The estimated annual operation and maintenance cost were estimated at \$2,102,700 per year or \$0.58/Kgal of finished water for the 10 mgd plant. The labor required for the membrane plant was estimated to be one supervisor at \$30,000/year, one head operator at \$25,000/year, and seven operators at \$20,000/year each. The operators worked in three shifts; three on the day shift, three evening and one night. The yearly salary for all above employees includes benefits. This labor cost was increased to include two supervisors, two head operators and 22 shift operators for the 50 mgd plant. The power cost for the membrane operation was developed using a feed pressure of 150 psi, 85% recovery, pump and motors both 85% efficient, a power cost of \$0.075/kwh, and a water flux of 15 gsf/d. This power cost was calculated as \$445,300/year, which was increased to \$600,000 to cover other plant power for the 10 mgd plant. Some unit cost savings were assumed for the 50 mgd plant as the total power was estimated to cost \$2,850,000. The only power savings would have to be realized with other than the high pressure membrane pumps. High service pumping is not included in these costs. The total power costs account for 36% of the total O & M cost. The chemical supplies cost was calculated for doses of 143 mg/L H₂SO₄, 68 mg/L NaOH, 7.5 mg/L Cl₂, and 1 mg/L inhibitor at \$0.08/lb, \$0.10/lb, \$0.04/lb and \$1/lb, respectively. Cleaning chemicals were also added to this cost at \$3000/yr for quarterly cleaning.

The maintenance cost includes membrane replacement, professional controls and electrical maintenance contracts, prefilter replacement, and pump maintenance. Membrane replacement was estimated at \$445,300/yr for the 10 mgd plant based on a cost of \$1000/membrane and a five year life. A \$50,000/yr professional contract was estimated for controls and electrical maintenance. Prefilters were estimated to be replaced monthly at a cost of \$7,800/year. Pump maintenance was estimated at \$10,000/year. The total maintenance cost estimated was increased to \$2,030,000 for the 50 mgd plant.

Section V: QA/QC Summary

The following section will present a summary of the quality assurance and quality control results compiled during the membrane pilot studies conducted at Keller Plant 1 and Keller Plant 2.

Solute Mass Balances

Table 16 presents the solute mass balances for operation on the Keller Plant 2 source water. A mass balance was conducted around the membrane system for each sample period and the results summarized. The results show that the mass balances ranged on average from 84 to 106. These mass balances indicate the accuracy of the measurements of flow and water.

The following equation presents the mass balance calculation.

$$X = \frac{M_P + M_C}{M_F} = K \left[\frac{C_P Q_P + C_C Q_C}{C_F Q_F} \right] 100$$

Where:

X = Percent mass recovery of solute

M = Mass (lb/day)

C = Concentration (mg/L)

Q = Flow (gpm)

_{F,P,C} = System Feed, Concentrate, Permeate locations

K = 0.012, conversion Factor

Table 16: System Mass Balance For Keller Plant 2 Membrane Pilot Study

Parameter	High	Low	Average	Std. Dev.
TDS	107	89	97	6
Alkalinity	107	68	96	10
Total Hardness	106	90	98	5
Calcium Hardness	104	78	95	8
Sulfate	109	90	102	7
Chloride	116	87	106	10
Sodium	123	91	104	8
Iron	119	28	84	25
Fluoride	121	7	88	30
Silica	103	71	94	9
NPDOC	121	59	104	17

Precision

Precision was the reproducibility observed between duplicate analyses. Duplicates were two determinations of a given parameter for the same sample by repeating the analytical procedure. The precision was expressed as percent relative deviation for each pair of analyses and was calculated by the following formula:

$$\% \text{ RSD} = \left(\frac{S}{\bar{X}} \right) \times 100$$

where:

S = standard deviation

\bar{X} = mean (average for a pair)

The standard deviation (S) for a data pair was calculated using the following equation:

$$S = \sqrt{(X_1 - X_2)^2 / 0.89}$$

where: X_1 and X_2 were individual observations.

Precision of a given analytical method was continuously determined by using the mean range and variance determinations. The range was the difference between the two duplicates. The normalized mean range, \bar{R} , was calculated using the following equation:

$$\bar{R} = \frac{\sum_{n=1}^N R}{N}$$

where:

$\sum_{n=1}^N R$ = sum of the relative standard deviations

$n=1$

N = number of data pairs

The variance, S_R^2 , was calculated by:

$$S_R^2 = \frac{\sum_{n=1}^N R^2 - (N \bar{R}^2)}{(N-1)}$$

where:

$\sum_{n=1}^N R^2$ = sum of the relative standard deviations

$n=1$

\bar{R}^2 = square of the mean range

N = number of data pairs

The warning limits (WL) and control limits (CL) were calculated by the following equations:

$$WL = \overline{R} + 2S_R$$

$$CL = \overline{R} + 3S_R$$

where:

\overline{R} = mean range

S_R = square root of variance

Data was assessed by interpreting the mean range (also referred to as the central line), with regard to the warning and control limits. A graph of concentration versus sample occurrence or number was used to facilitate the interpretation. The mean range, WL and CL were shown as horizontal lines on the graph. The results of an individual paired duplicate analysis were entered on the graph and interpreted by where they fell within the boundaries on the graph. A minimum of twenty pairs of duplicate analyses were used to construct the graph.

Table 17 and 18 lists the compilation of the precision data obtained for the parameters monitored during the Pinellas County project and the percentage of the time that the data was within the ninety-five percent confidence interval.

Table 17: Precision For Organic Parameters

Parameter	Precision RSD	Std. Dev	Mean	UWL	UCL	%C.I.
Chloroform	0 - 23	6	4	12	18	98
Bromodichloromethane	0 - 16	5	3	9	14	100
Dibromochloromethane	0 - 44	10	4	20	30	93
Bromoform	0 - 16	4	3	8	12	80
Monochloroacetic acid	0 - 110	28	22	55	83	90
Monobromoacetic acid	0 - 95	24	18	49	73	98
Dichloroacetic acid	0 - 94	29	25	58	87	98
Dibromoacetic acid	0 - 48	15	14	29	44	93
Trichloroacetic acid	0 - 129	34	29	69	103	98
Color	0 - 9	3	2	6	9	100
NPDOC	0 - 14	4	4	8	12	98
TOX	0 - 15	4	6	9	13	98

Table 18: Precision For Inorganic Parameters

Parameter	RSD Precision	Std. Dev.	Mean	UWL	UCL	%C.I.
Alkalinity	0 - 4	1	1	2	4	100
Turbidity	0 - 17	4	6	9	13	93
TDS	0 - 13	4	4	8	12	98
Total Hardness	0 - 12	4	2	8	12	100
Ca Hardness	0 - 9	2	2	5	7	93
Chloride	0 - 11	3	2	7	10	93
Sulfate	0 - 75	20	8	41	61	93
Fluoride	0 - 16	5	4	11	16	100
Silica	0 - 8	3	1	5	8	100
Sodium	0 - 7	2	2	4	6	98
Iron	0 - 8	3	2	5	8	100

Accuracy

The data obtain through spike analyses was used as a measure of accuracy, the degree of difference between observed and known values. Known concentrations were added to samples and the following equation used to determine the recovery of the specific parameter:

$$\% \text{ Recovery} = \left(\frac{(Z - X)}{T} \right) \times 100$$

where:

Z = observed spike concentration

X = concentration of unspiked sample

T = True concentration of spike

The percent recovery, the mass of the spike, spiked and unspiked sample concentration were reported on quality control report forms. As with the duplicates, the mean, variance, warning and control limits were calculated using at least twenty data points. For the spikes, percent recovery was used instead of relative standard deviation; and as with the duplicates the mean, variance, warning and control limits were calculated using the previously cited equations. One additional difference between the presentation of the spike and duplicate data is that the warning and control limits were expressed in terms of plus or minus standard deviations. The upper limits were positive deviations. The lower limits were negative standard deviations. A graph of the data and the statistically calculated control were developed. This graph was used to access the acceptability of the data in the same manner as previously described for the duplicate analyses. Table 19 and 20 list the compilation of accuracy data for the parameters monitored in this study and the percentage of time that the data was within the ninety-five percent confidence interval.

In addition to the duplicate and spike data, purchased reference check samples were also used to assess analytical quality. The samples came with preparation instructions, a true value, and a ninety-five percent confidence interval that was computed by the manufacturer. These samples were used for the inorganic analyses, since most of the samples could be

maintained and reanalyzed on a daily basis for three months if refrigerated. Sample analysis was not to take place if the results of the reference analysis were outside the given confidence interval. Additionally some analyses made use of a check sample that was prepared by the laboratory staff to monitor analytical performance.

Table 19 Accuracy For Organic Parameters

Parameter	Accuracy	Std. Dev.	Mean	Warning Limit	Control Limit	% C.I.
Chloroform	52 - 104	15	83	±31	±46	98
Bromodichloromethane	76 - 112	8	91	±16	±24	100
Dibromochloromethane	76 - 178	15	96	±30	±45	93
Bromoform	83 - 128	9	93	±18	±27	80
Monochloroacetic acid	16 - 190	39	63	±79	±118	93
Monobromoacetic acid	25 - 180	41	74	±83	±124	98
Dichloroacetic acid	20 - 196	44	77	±87	±131	100
Dibromoacetic acid	22 - 230	42	68	±85	±127	95
Trichloroacetic acid	6 - 74	20	33	±40	±60	98
NPOC	86 - 110	7	98	±14	±21	100
TOX	90 - 120	10	108	±20	±30	100

% C.I. refers to % of time analysis is within 95% confidence interval.

Table 20: Accuracy For Inorganic Parameters

Parameter	Accuracy	Std. Dev.	Mean	Warning Limit	Control Limit	% C.I.
Alkalinity	92 - 111	5	100	±11	±16	100
Total Hardness	88 - 106	6	99	±11	±17	100
Ca Hardness	89 - 105	5	99	±10	±15	100
Chloride	88 - 112	6	101	±11	±17	100
Sulfate	89 - 127	10	106	±21	±31	100
Fluoride	106 - 128	9	113	±18	±27	100
Silica	92 - 110	6	101	±11	±17	100
Sodium	86 - 115	9	98	±17	±26	100
Iron	93 - 110	6	100	±13	±19	100

USEPA Performance Evaluation

Eight performance evaluation studies were performed during the course of the project. The results of the evaluations are summarized in Table 21.

Table 21: USEPA Performance Evaluation Summary

Parameter	Units	WS020	WS021	WS022	WS023	WS024	WS025	WS026	WS027
Chloroform	µg/l	19.6 56	13.1 76.6	44.9 24.3	37.5 45.1	9.9 67.8	83.8 28.7	6.7 51	87.3
Bromoform	µg/l	44 20.5+	67.1 27.8	56.7 25.7	70 15.9	11 60.8	49.4 10.2	16 92	25.5
Bromodichloromethane	µg/l	22.6 73	10.4 39.7	18.6 61.5	12 65.4	22.1 59.9	76.5 9.7	24 58	35.4
Dibromochloromethane	µg/l	63.7 30.2+	44.3 16.4	69 15.7	26.9 44.7	8.1 80.2	48.4 16.5	21 86	33.6
Total THM's	µg/l	149.9 179.7	134.9 160.5	189.2 127.2	146.8 171.1	51.1 268.7	258.1 65.1	67.7 287	181.8
Residual Free Chlorine	mg/l	0.64 1.42		0.31 1.13	0.35 1.26	0.7 1.18	0.54 1.47	0.89 0.27	0.36
Turbidity	NTU	4.4 0.7						5.83 1.28	0.99 0.7
Fluoride	mg/l			0.72 1.55	0.27+ 1.32	1.39 1.77	2.46 1.44	3.43 1.33	4.32
Calcium (as CaCO ₃)	mg/l	116		152				122	138
PH	Units	9.11						9.04	9.21
Alkalinity (as CaCO ₃)	mg/l	34.9		51.0+				40.6	37.9+
Sodium	mg/l							15.6	-15.3
Sulfate	mg/l							22.8 8.79	13.9
Dibromoacetic acid	µg/l								4.4
Dichloroacetic acid	µg/l								6.3
Monobromoacetic acid	µg/l								3.5
Monochloroacetic acid	µg/l								7.1
Trichloroacetic acid	µg/l								9.5

- = Value outside acceptable range on the low side

+ = Value outside acceptable range on the high side

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Appendix

Data Collection Spreadsheets