

Project Report Implementation of Advanced Water Purification Facility Extended Testing





Pasadena | San Diego | Oakland

Implementation of Advanced Water Purification Facility Extended Testing

Project Report

Prepared for the City of San Diego

By

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- City of San Diego North City Water Reclamation Plant
- City of San Diego Water Quality Laboratory
- City of San Diego Pure Water Program

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EXECUTIVE SUMMARY

This report presents the results of the Extended Testing project that was executed with funding from Proposition 50 Funds through the California Department of Water Resources on behalf of the City of San Diego's Public Utilities Department. The primary goal of this project was to design, install, commission, and test a 1.5 MGD ozone and biological activated carbon (BAC) pretreatment facility to the full advanced treatment train that was constructed for the City of San Diego's Demonstration Project to the San Vicente Reservoir. Full advanced treatment consists of membrane filtration (MF), reverse osmosis (RO), and advanced oxidation process (AOP). The primary goal of the additional pretreatment is to enhance reliability through treatment redundancy and robustness such that a future potable reuse project may not be subject to a dilution water requirement.

The Demonstration facility was tested for 22 months with more than 19,500 laboratory analyses performed in this study. The first 14-months consisted of routine operations and sampling without the ozone/BAC pretreatment system in service. These data provided a baseline of comparison to the performance once the ozone/BAC system was providing pretreatment. The ozone/BAC system was tested for the last 8-months of this project and served as pretreatment to the MF/RO/AOP train for the duration of this testing period, which concluded in January 2015. The ozone/BAC processes consistently reduced the total organic carbon (TOC) concentration by 40% after the initial 2-months of operation which demonstrated greater TOC removal until the activated carbon was exhausted. On average, the influent TOC concentration of 7 mg/L was reduced to 4 mg/L after the ozone/BAC pretreatment process. The reduced TOC concentrations provided enhanced RO product water quality with average permeate TOC concentrations being reduced from 60 μ g/L without pretreatment to 40 μ g/L with pretreatment. Regardless of whether the pretreatment was in service or not, eight (8) rounds of sampling for more than 90 different constituents of emerging concern (CEC) resulted in concentrations below the detection limit for the final product water. These results highlight the effectiveness of full advanced treatment to remove and destroy organic contaminants in recycled water. The ozone/BAC process demonstrated significant CEC removal and reduced many constituents to below the detection limit before reverse osmosis and AOP. In addition. the CECs and other organics were significantly reduced in the RO concentrate that must be ultimately discharged to the ocean when the ozone/BAC pretreatment was in service.

The ozone/BAC pretreatment enhanced the downstream membrane filtration performance. Operating at a flux rate of 41 gallons/ft²/day (gfd), the membrane cleaning interval went from 1-month to >4-months after the ozone/BAC

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pretreatment was put in service. Observations in water quality identified that the pretreatment process reduced fluorescence of the water for wavelength regions that are typically associated with membrane fouling materials. Additionally, manganese, another common membrane foulant other than organics, was effectively oxidized by ozone and filtered out by the BAC process. The enhanced water quality produced by the ozone/BAC pretreatment will reduce the capital cost of a future membrane filtration facility by 33% due to the improved membrane performance. Although this helps reduce the capital cost of these facilities, the ozone/BAC/MF/RO/AOP treatment train is still estimated to cost \$193M compared to \$170M without pretreatment. These costs are only for the advanced water purification facility (AWPF) and do not include other necessary facilities or conveyance. Although this project also demonstrated lower pressures and reduced cleaning intervals with ozone/BAC pretreatment, the O&M cost for the AWPF with or without ozone/BAC pretreatment was determined to be similar at this time with an annual cost of around \$20M. Continued operation to demonstrate long-term performance at the higher flux with ozone/BAC pretreatment would allow guantification of the O&M cost savings.

In addition to testing the ozone/BAC pretreatment, the UV AOP system was challenged with 1,4-Dioxane to determine removal rates as required by the 2014 Groundwater Replenishment Reuse (GRR) regulations. The UV system was evaluated with two different oxidants, hydrogen peroxide and sodium hypochlorite. Both oxidants demonstrated excellent removal with all results exceeding the 0.5-log removal required by the Division of Drinking Water (DDW). In fact, the lowest demonstrated removal was 1.2-log and removals approached 2.4-log, which is excellent performance. The importance of this testing was to confirm industry research for UV AOP and highlight the potential for UV/HOCI to drive the advanced oxidation process for a future full-scale facilities. These results demonstrated that UV/HOCI can provide similar log removals of 1,4-Dioxane at approximately equivalent chemical cost. Sodium hypochlorite is more common and less hazardous chemical than hydrogen peroxide. Additionally, the remaining HOCI residual after UV AOP would ensure that the breakpoint reaction continues to completion to remove the chloramines used for biofouling control, which will lower the total nitrogen of the final product water by approximately 0.5 mg/L-N. The HOCI residual can also be monitored in the pipeline to provide 6-log virus inactivation that will provide an additional barrier to ease monitoring and response requirements by DDW for the full-scale AWPF.

In summary, this report documents the impacts of ozone/BAC pretreatment on the AWPF at the Demonstration facility. Feedwater quality was enhanced and these improvements were quantified through an extensive sampling program. The addition of the ozone/BAC pretreatment process demonstrated additional contaminant attenuation as well as enhanced membrane performance that offsets some of the additional cost associated with the pretreatment processes.

1 INTRODUCTION

The City of San Diego has successfully developed a potable reuse project for reservoir augmentation through the design, installation, operation, and testing of the 1 million gallon per day (MGD) Advanced Water Purification (AWP) Facility. The AWP Facility was operated and tested for one year, resulting in a final report summarizing the treatment performance, multiple barrier concepts, reservoir modeling, and water quality results, which culminated in a conceptual approval letter form the California Department of Public Health (CDPH) available on the City of San Diego's website¹. The function of CDPH was switched to the California Division of Drinking Water (DDW) in 2014. While the results of this study were successful, a primary challenge for full-scale implementation of reservoir augmentation is the substantial cost and time of pipeline construction necessary for product water conveyance to the San Vicente Reservoir. The primary goal of this project was to test a treatment train that provides additional redundancy and robustness to enhance the reliability of the full advanced treatment train with the potential to eliminate the need for an environmental buffer in potable reuse.

1.1 **PROJECT OBJECTIVES**

The primary objective of the Extended Testing study at the City of San Diego's Demonstration Facility is to provide data on the effects of additional treatment barriers for pathogens and organics. The secondary objective is to quantify the effects of the additional treatment barriers on the performance of the Full Advanced Treatment (FAT) train already approved for reservoir augmentation. Ultimately, the additional treatment processes are being provided to enhance the treatment train's water quality reliability enough to allow the DDW to eliminate the requirement for dilution water altogether.

1.1.1 Pathogen Removal

The additional barrier provided in any direct potable reuse system must deliver substantial pathogen inactivation with a focus on virus and protozoa (*Giardia* and *Cryptosporidium*). Ozone disinfection has been selected as an additional disinfection barrier because it is extremely effective against virus and *Giardia* with some ability to inactivate *Cryptosporidium* as well. A biological filtration process using activated carbon as media, commonly referred to as biological activated carbon (BAC) will follow ozone disinfection as part of the pretreatment process. Although pathogen removal is likely to occur through the filtration

¹ http://www.sandiego.gov/water/waterreuse/demo/projectreports/

process, the primary purpose of the BAC is to address the oxidation byproducts produced by the ozonation process.

The inclusion of ozone disinfection as pretreatment to the AWP Facility will provide significantly higher cumulative log removals of pathogens that will greatly increase the overall reliability of the process train. The use of redundant, multiple barriers significantly reduces the risk of purified water being out of specification and thus provides greater public health protection. Figure 1-1 presents the multiple barriers process proposed for source water augmentation.



Water Purification Process

Figure 1-1 Multiple barriers provided for source water augmentation

1.1.2 Organics Removal

Ozone is a powerful oxidant that effectively oxidizes and inactivates disinfectantresistant pathogens, such as viruses, bacteria, spores and cysts (Peeters, et al. 1989; Rennecker, et al. 1999; von Gunten, et al. 2003b; Burns, et al. 2007; Talbot, et al. 2012; Gamage, et al. 2013). Ozone also oxidizes many organic molecules and trace organic contaminants present in treated wastewater, such as caffeine (von Gunten, 2003a; Wert, et al. 2009; Lee, et al. 2010; Pisarenko, et al. 2012; Gerrity, et al. 2012). Studies have also shown that the oxidation of organic matter with ozone converts the organic matter into more polar, less aromatic, and smaller molecular weight products (Buffle, et al. 2007; von Gunten, 2003a). Although BAC will not provide a barrier for pathogens, BAC has been shown to reduce the total organic carbon (TOC) concentration including organic byproducts from the ozonation process, such as aldehydes, ketones, and carboxylic acids (Gerrity, et al. 2011; Macova, et al. 2010; Farré, et al. 2011).

The BAC filtration process will biologically reduce the total organic carbon (TOC) concentration by 30-50%, which includes the organic byproducts of ozonation, such as aldehydes, ketones, and small carboxylic acids. A lower level of TOC in the membrane feed will reduce associate organic fouling leading to longer intervals between membrane clean-in-places (CIPs) and also reduce TOC in the RO concentrate. Thefore, the additional pretreatment with ozone and BAC should result in the following benefits:

- 1. Reduce downstream membrane fouling of microfiltration and reverse osmosis
- 2. Reduce the concentration of trace organic contaminants that eventually make their way to the ocean in the RO concentrate

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3. Enhance the feedwater quality by eliminating most trace organics and substantially reducing pathogen concentrations

1.2 TEST PLAN OBJECTIVES

The primary objectives of the AWP Facility extended testing are:

- 1. Document ozone/BAC performance and improvements to water quality
- 2. Evaluate the ozone and BAC systems impact on downstream processes

2 DEMONSTRATION FACILITY DESCRIPTION

2.1 DESIGN CRITERIA

The feedwater to the ozone/BAC pretreatment system is the tertiary filtered water from the North City Reclamation Plant (NCWRP). The water undergoes primary sedimentation, secondary treatment (an activated sludge treatment), and tertiary filtration prior to being fed into the ozone system. The tertiary feedwater is of a relatively high water quality as presented in Table 2-1 and this is due to the significant biological treatment provided by the NCWRP with a high solids retention time (SRT), which is typically greater than 10 days. Additionally, the well-oxidized secondary effluent is filtered through seven feet of 1.0 mm anthracite, ensuring a low amount of suspended solids and colloidal material (i.e. turbidity).

| Parameter | Unit | Value |
|-----------|--------|------------|
| тос | mg/L | 6 - 8 |
| Turbidity | NTU | 0.15 - 0.3 |
| Nitrate | mg/L-N | 12 |
| Ammonia | mg/L-N | 0.1 |

Table 2-1 Typical Feedwater Quality

2.2 SYSTEM DESCRIPTION

2.2.1 Ozone System Installation and Start-Up

The ozone container, provided by WEDECO (Charlotte, NC), was commissioned in June 2014. The contained system consists of an oxygen generator, ozone generator, two ozone dissolution systems (1,100 gpm and 550 gpm), ozone destruct system (located outside of container), alarms, generator cooling water system (outside of container), exhaust fan, and respective instrumentation and controls. The ozone system has a generator capable of generating up to 190 lbs/day at 10% ozone by weight. The maximum applied dose to the side stream ozone system is 14.3 mg/L for a water flow of 1,100 gpm or 1.58 MGD. The complete installation and system components can be seen in Figure 2-1.



Figure 2-1 Layout of Ozone System and Sample Points

The ozone contactor was constructed with 24-inch diameter pipeline following ozone dissolution and provided > 7 minutes of contact time over a length of 360 feet. The ozone contactor consists of 6 segments arranged in a serpentine configuration, flow straighteners at every entrance and exit to achieve plug flow, and a degassing installation to prevent contactor water volume loss to gas. Gas removed is routed to a destruct system, which converts ozone to oxygen gas, and is released to the atmosphere. An ozone quenching system consisting of sodium bisulfite was installed for operation with higher ozone residual. Figure 2-2 shows the installed ozone contactor. The ozone contactor's design basis and is shown in Table 2-2.



Figure 2-2 Ozone Contactor

| Table 2-2 | Ozone | Contactor | Design | Basis |
|-----------|-------|-----------|--------|-------|
|-----------|-------|-----------|--------|-------|

| Parameter | Value |
|------------------------------|---|
| Pipeline Diameter | 24 inches |
| Pipeline Length | 6 x 61.58 ft segments |
| Total Volume | 7800 gallons |
| T _{Modal} @ 1.5 MGD | 7.5 min |
| Applied O ₃ Dose | up to 14 mg/L |
| Baffling Efficiency, % | 95% T ₁₀ /T _{Modal} |
| T ₁₀ | 7.25 min at 1075 gpm |

2.2.2 BAC Filter System Description

Leopold (Zelienople, PA) provided the BAC filter units with blowers, pumps, control panels, and backwashing capabilities. Two steel container filter structures with a filtration area of 180 ft² each and 6.5 feet of granular activated carbon (GAC) depth. Calgon Carbon provided 31 tons of Filtrasorb 820-M—a coal based carbon that is more dense and durable than conventional coal GAC due to additional processing (reagglomeration). The complete installation and system components can be seen in Figure 2-3.

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Figure 2-3 BAC Filter

Table 2-3 BAC Filter Specifications

| Parameter | Value |
|---------------------|---|
| Number of Filters | 2 |
| Area per Filter | 180 ft ² |
| Media Depth | 6.5 ft |
| Filter Loading Rate | 3.05 gpm/ft ¹ at 1100 gpm 1.53 gpm/ft ² at 550 gpm |
| Filter Media | Granular Activated Carbon 31 tons of 8 x 20 mesh (Effective Size of 0.8-1.0 mm) |
| Air Scour Rate | 720 scfm |
| Backwash Rate | 12 gpm/ft ² (2160 gpm) |

2.2.3 Existing Advanced Water Purification Facility

The existing AWP Facility has been described in detail in previous documents that are available on the City of San Diego's website. The first process is membrane filtration and this is performed by a Pall microfiltration system and a

Toray/H2O Innovation ultrafiltration system in parallel with each system treating approximately 50% of the total flow. The next process is the reverse osmosis (RO) process with two different train designs, one a 3-stage design and the other 2-stage. The 2-stage RO currently utilizes Hydranautics ESPA 2 membranes while the 3-stage RO currently operates with Toray membranes. Typical RO membrane warranty is for 3 years and the membranes at the AWP Facility have been in service for 42 months and thus are no longer considered "new". The RO membranes show signs of irreversible fouling and some loss in salt rejection. The last treatment process in the AWP facility is an advanced oxidation process with ultraviolet light (UV/AOP) that utilizes the Trojan UVPhox and hydrogen peroxide addition.

2.2.4 Description of Online Meters

New on-line meters were installed to monitor and establish the effect of operating conditions on treated water quality for the ozone and BAC system. Figure 2-4 shows the process flow diagram and on-line meter locations. Installed meters and their specifications are shown in Table 2-4.



Figure 2-4 On-line Meter Locations

Table 2-4 Summary of On-line Meters

| Treatment Process Location | Type of Meter | Manufacturer | Model |
|-----------------------------------|-------------------------|----------------------|----------------------------|
| Tertiary Effluent | UVT | Hach | UVA sc |
| | ТОС | GE Sievers | M5310C |
| Ozone Effluent | | Rosemount Analytical | 0Z499 |
| | | Hach | 9185 sc |
| | DO3 | Kuntze | Neon DES |
| | UVT | Hach | UVA sc |
| | Turbidity | Hach | 1720E |
| BAC Filter Effluent | UVT | Hach | UVA sc |
| | ТОС | GE Sievers | M5310C |
| | Turbidity | Hach | 1720E |
| | | | pHD Digital |
| | pH | Hach | Differential Sensor |
| | | | 1720E and |
| MF/UF Filtrate | Turbidity | Hach | FilterTrak 660 |
| | | | pHD Digital |
| | ORP | Hach | Differential Sensor |
| | Conductivity | Signet | 2842 |
| | Temperature | Signet | 3-2350-3 |
| | Total Chlorine Analyzer | Hach | CL17 |
| | Free Chlorine Analyzer | Hach | CL17 |
| Combined RO Permeate | Conductivity | Signet | 2841 |
| | ТОС | GE Sievers | M5310C |
| | UVT | Trojan UV | OptiView |

3 MATERIALS AND METHODS

3.1 SAMPLING LOCATIONS AND GENERAL METHOD

The process flow diagram and all sampling points are presented below in Figure 3-1 and Table 3-1.



Figure 3-1 AWP Facility Process Flow Diagram and Sampling Locations

| Sample Point | Description |
|--------------|----------------------------|
| ET-1 | Secondary effluent |
| ET-2 | Tertiary effluent |
| ET-3 | Ozone effluent |
| ET-4 | BAC effluent |
| ET-5 | MF Feed |
| ET-6 | UF Feed |
| ET-7 | MF Filtrate |
| ET-8 | UF Filtrate |
| ET-9 | MF/UF Filtrate |
| ET-10 | RO train A Feed |
| ET-11 | RO Train B Feed |
| ET-12 | RO Train A Permeate |
| ET-13 | RO Train B Permeate |
| ET-14 | UV/AOP Feed (RO effluent)* |
| ET-15 | UV/AOP Effluent |
| ET-16 | RO Concentrate |

Table 3-1 Sampling Location Descriptions

*After hydrogen peroxide addition point

Sampling methods followed protocols from the laboratory for the specific analyte. Biological samples were collected separately into sterile bottles. All sampling lines were fully flushed (~ 3 minutes) prior to sample collection as part of standard procedure for all sampling types. Field reagent blanks and duplicate at select sampling points were collected as part of quality control for the different sampling groups. Samples were packaged with in insulating coolers with ice packs and sent to the respective labs.

3.2 BIOLOGICAL SAMPLING METHODS

Biological samples included total and fecal coliforms, and coliphage sampling. Samples were collected in bottles provided by the City of San Diego and Biovir. A field blank and a duplicate samples were collected as quality control. Pathogen indicator testing was performed weekly and twice a week for sample locations described in Table 3-2.

| Sample Point: | Description: |
|---------------|--------------------|
| ET-1 | Secondary effluent |
| ET-2 | Tertiary effluent |
| ET-3 | Ozone effluent |
| ET-4 | BAC effluent |
| ET-7 | MF filtrate |
| ET-8 | UF filtrate |

Table 3-2 Sampling Locations for Pathogen Indicators

3.2.1 Total and Fecal Coliforms

Total coliform, fecal coliform analyses were performed by the City of San Diego Water Quality Laboratory located at the Alvarado Water Treatment Plant. Samples were collected by process order. A field blank and duplicate sample were also taken as quality control. The City of San Diego provided 120 mL sterile bottles containing sodium thiosulfate for quenching residual chlorine. A 100 mL sample was collected for all sampling points with the exception of the MF and UF effluent, and field blank. Additional volume, while still preserving headspace, was collected up to the neck of the sampling bottle (approximately 20 mL) for these samples to decrease the method detection limit. Samples were collected at different ozone doses to characterize the effect of ozone dose on coliform disinfection. Samples were packed in insulated travel coolers with ice packs for transport to City laboratory facilities. Samples were transferred to the City laboratory staff within a few hours after sampling. Samples were collected weekly and bi-weekly to generate a total of 352 measurements of total and fecal coliforms.

3.2.2 Somatic and Male Specific Bacteriophage

Native coliphage samples were analyzed by BioVir Laboratories, Inc. (Benicia, CA). Two types of coliphages were sampled for, male specific (MS-2) and somatic. A 250 mL sample with 5 mL 2% sodium thiosulfate sample vessels were collected and shipped to Biovir laboratories. Sampling points were flushed thoroughly and vessels were filled to the bottom of the neck to provide ample headspace. A field blank and duplicate sample was also taken as quality control. Samples were packed with ice packs in insulated coolers and delivered to Biovir Laboratories within 24 hours of sampling. Lab methods for total and fecal coliforms and coliphage analyses are presented below in Table 3-3. Samples were collected weekly to generate a total of 264 measurements of MS-2 and somatic bacteriophage.

| Analyzer | Analyte | Protocol | Units | MRL |
|------------|-----------------|----------|-------------|------------|
| | Total and Fecal | | | |
| City of SD | Coliforms | SM9221B | MPN/100 mL | 1.1 or 1.8 |
| BioVir | Coliphage | EPA 1602 | pfu/ 100 mL | 1 |

Table 3-3 Summary of Biological Analysis Methods

3.3 ORGANIC CONSTITUENTS

Samples were collected starting at the treatment feed water to the end of the train in process order. Samples were collected in bottles provided by Eurofins, City of San Diego, and Trussell Technologies Labs. A field blank and duplicate sample was also taken as quality control. Sampling for compounds of emerging concern, disinfection byproducts, and oxidation products are shown in Table 3-4.

| Sample Point: | Description: |
|---------------|-------------------------|
| ET-2 | Tertiary effluent |
| ET-3 | Ozone effluent |
| ET-4 | BAC effluent |
| ET-9 | MF/UF Filtrate |
| ET-14 | RO Effluent/UV/AOP Feed |
| ET-15 | UV/AOP Effluent |
| ET-16 | RO Concentrate |

| | Table 3-4 Sampl | ing Locations | for CECs, DBF | s, and Oxidation | Products |
|--|-----------------|---------------|---------------|------------------|----------|
|--|-----------------|---------------|---------------|------------------|----------|

3.3.1 Compounds of Emerging Concern

Samples were collected weekly for a total of 8 rounds, with at least 5 points per location, which generated over 6,200 data points. Compounds of emerging concern were analyzed by Eurofins Eaton Analytical (Monrovia, CA). Samples were collected in 40 mL amber glass vials with 80 μ L of 32 g/L NaOmadine and 5 mg/L of ascorbic acid. Samples were picked up by Eaton Analytical and analyzed within the 28 days hold time.

An integrated on-line Solid phase extraction-High Performance Liquid Chromatography-tandem Mass Spectrometer system was used for analysis of 95 compounds of emerging concern. Samples were extracted using Oasis HLB Solid Phase Extraction column and analyzed by LC-MS/MS in positive and negative electrospray ionization mode. Isotopically labeled internal standards were used to correct for solid phase extraction recoveries and matrix effects on electrospray ionization source to the MS/MS. A complete list of CECs analyzed by Eurofins and method reporting limits (MRL) for each analyte is presented in Table 3-5.

Table 3-5 Method Reporting Limits for Compounds of Emerging Concern

| Analyte | Me <u>thod</u> | MRL | Units |
|-----------------------------------|----------------|-----|---------|
| 2,4-D | LC-MS-MS | 5 | ng/L |
| 4-nonylphenol - semi quantitative | LC-MS-MS | 100 | ng/L |
| 4-tert-octylphenol | LC-MS-MS | 50 | ng/L |
| Acesulfame-K | LC-MS-MS | 20 | ng/L |
| Bendroflumethiazide | LC-MS-MS | 5 | ng/L |
| BPA | LC-MS-MS | 10 | ng/L |
| Butalbital | LC-MS-MS | 5 | ng/L |
| Butylparben | LC-MS-MS | 5 | ng/L |
| Chloramphenicol | LC-MS-MS | 10 | ng/L |
| Clofibric Acid | LC-MS-MS | 5 | ng/L |
| Diclofenac | LC-MS-MS | 5 | ng/L |
| Estradiol | LC-MS-MS | 5 | ng/L |
| Estrone | LC-MS-MS | 5 | ng/L |
| Ethinyl Estradiol - 17 alpha | LC-MS-MS | 5 | ng/L |
| Ethylparaben | LC-MS-MS | 20 | ng/L |
| Gemfibrozil | LC-MS-MS | 5 | ng/L |
| Ibuprofen | LC-MS-MS | 10 | ng/L |
| Iohexal | LC-MS-MS | 10 | ng/L |
| Iopromide | LC-MS-MS | 5 | ng/L |
| Isobutylparaben | LC-MS-MS | 5 | ng/L |
| Methylparaben | LC-MS-MS | 20 | ng/L |
| Naproxen | LC-MS-MS | 10 | ng/L |
| Propylparaben | LC-MS-MS | 5 | ng/L |
| Sucralose | LC-MS-MS | 100 | ng/L |
| Triclocarban | LC-MS-MS | 5 | ng/L |
| Triclosan | LC-MS-MS | 10 | ng/L |
| Warfarin | LC-MS-MS | 5 | ng/L |
| 1.7-Dimethylxanthine | LC-MS-MS | 10 | ng/L |
| Acetaminophen | LC-MS-MS | 5 | ng/L |
| Albuterol | LC-MS-MS | 5 | ng/L |
| Amoxicillin (semi-quantitative) | LC-MS-MS | 20 | ng/L |
| Andorostenedione | LC-MS-MS | 5 | ng/L |
| Atenolol | LC-MS-MS | 5 | ng/L |
| Atrazine | LC-MS-MS | 5 | ng/L |
| Azithromycin | LC-MS-MS | 20 | ng/L |
| Bezafibrate | LC-MS-MS | 5 | ng/L |
| Bromacil | LC-MS-MS | 5 | ng/L |
| Caffeine | LC-MS-MS | 5 | ng/L |
| Carbadox | LC-MS-MS | 5 | ng/L |
| Carbamazenine | LC-MS-MS | 5 | ng/L |
| Carisoprodol | LC-MS-MS | 5 | ng/I. |
| Chloridazon | LC-MS-MS | 5 | ng/I. |
| Chlorotoluron | LC-MS-MS | 5 | ng/I. |
| Cimetidine | | 5 | ···6/ L |
| Ginictiunit | | 5 | ng/l. |

| Analvte | Method | MRL | Units |
|-----------------------|----------|-----|-------|
| Cvanazine | LC-MS-MS | 5 | ng/L |
| DACT | LC-MS-MS | 5 | ng/L |
| DEA | LC-MS-MS | 5 | ng/L |
| DEET | LC-MS-MS | 10 | ng/L |
| Dehydronifedipine | LC-MS-MS | 5 | ng/L |
| DIA | LC-MS-MS | 5 | ng/L |
| Diazepam | LC-MS-MS | 5 | ng/L |
| Dilantin | LC-MS-MS | 20 | ng/L |
| Diltiazem | LC-MS-MS | 5 | ng/L |
| Diuron | LC-MS-MS | 5 | ng/L |
| Erythromycin | LC-MS-MS | 10 | ng/L |
| Flumegine | LC-MS-MS | 10 | ng/L |
| Fluoxetine | LC-MS-MS | 10 | ng/L |
| Isoproturon | LC-MS-MS | 100 | ng/L |
| Ketoprofen | LC-MS-MS | 5 | ng/L |
| Ketorolac | LC-MS-MS | 5 | ng/L |
| Lidocaine | LC-MS-MS | 5 | ng/L |
| Lincomycin | LC-MS-MS | 10 | ng/L |
| Linuron | LC-MS-MS | 5 | ng/L |
| Lopressor | LC-MS-MS | 20 | ng/L |
| Meclofenamic Acid | LC-MS-MS | 5 | ng/L |
| Meprobamate | LC-MS-MS | 5 | ng/L |
| Metazachlor | LC-MS-MS | 5 | ng/L |
| Metolachlor | LC-MS-MS | 5 | ng/L |
| Nifedipine | LC-MS-MS | 20 | ng/L |
| Norethisterone | LC-MS-MS | 5 | ng/L |
| Oxolinic acid | LC-MS-MS | 10 | ng/L |
| Pentoxifylline | LC-MS-MS | 5 | ng/L |
| Phenazone | LC-MS-MS | 5 | ng/L |
| Primidone | LC-MS-MS | 5 | ng/L |
| Progesterone | LC-MS-MS | 5 | ng/L |
| Propazine | LC-MS-MS | 5 | ng/L |
| Quinoline | LC-MS-MS | 5 | ng/L |
| Simazine | LC-MS-MS | 5 | ng/L |
| Sulfachloropyridazine | LC-MS-MS | 5 | ng/L |
| Sulfadiazine | LC-MS-MS | 5 | ng/L |
| Sulfadimethoxine | LC-MS-MS | 5 | ng/L |
| Sulfamerazine | LC-MS-MS | 5 | ng/L |
| Sulfamethazine | LC-MS-MS | 5 | ng/L |
| Sulfamethizole | LC-MS-MS | 5 | ng/L |
| Sulfamethoxazole | LC-MS-MS | 5 | ng/L |
| Sulfathiazole | LC-MS-MS | 5 | ng/L |
| TCEP | LC-MS-MS | 10 | ng/L |
| ТСРР | LC-MS-MS | 100 | ng/L |
| TDCPP | LC-MS-MS | 100 | ng/L |
| Testosterone | LC-MS-MS | 5 | ng/L |

Table 3.5 Method Reporting Limits for Compounds of Emerging Concern(continued)

| Analyte | Method | MRL | Units |
|---------------|----------|-----|-------|
| Theobromine | LC-MS-MS | 10 | ng/L |
| Theophylline | LC-MS-MS | 20 | ng/L |
| Thiabendazole | LC-MS-MS | 5 | ng/L |
| Trimethoprim | LC-MS-MS | 5 | ng/L |

Table 3.5 Method Reporting Limits for Compounds of Emerging Concern (continued)

3.3.2 Disinfection and Oxidation Byproducts

Samples were collected weekly for a total of 8 rounds per location, which generated over 850 data points. Disinfection and oxidation byproducts were analyzed by City of San Diego Water Quality Lab and Eurofins Eaton Analytical. Samples were collected in vessels provided by the City of San Diego and Eurofins. A summary of the constituents analyzed is presented below in Table 3-6.

| Analyte | Method | MRL/MDL | Units | Lab |
|-------------------------|-----------|---------|-------|-------------------|
| Acetaldehyde | EPA 556 | 1 | ug/L | Eurofins |
| Acetate-Glycolate | IC300 | 5 | ug/L | Eurofins |
| Bromate | EPA300.1 | 5 | ug/L | City of San Diego |
| Formaldehyde | EPA 556 | 5 | ug/L | Eurofins |
| Formate-Isobutyrate | IC300 | 5 | ug/L | Eurofins |
| Glyoxal | EPA 556 | 10 | ug/L | Eurofins |
| Methyl Glyoxal | EPA 556 | 10 | ug/L | Eurofins |
| NDMA | EPA 521 | 2 | ng/L | Eurofins |
| Oxalate | IC300 | 5 | ug/L | Eurofins |
| Pyruvate | L240 | 5 | ug/L | Eurofins |
| Total Trihalomethanes | EPA 551.1 | 0.5 | ug/L | Eurofins |
| Haloacetic Acids (HAA5) | SM 6251B | 2 | ug/L | Eurofins |

Table 3-6 Summary of Disinfection and Oxidation Byproduct Analyses

City of San Diego reports MDL and Eurofins reports MRL

For non-EPA analytical methods, a brief method summary of IC300 and L240 methods provided. IC300 is a direct injection ion chromatography/conductivity detector test with a holding time of 14 days. 40 mL samples are collected in amber glass VOA vials and preserved with mercury chloride up on receipt. Due to the chromatographic co-elution, acetic acid-Glycolic acid and formic acid-isobutyric acid have to be analyzed as pairs. L240 is a direct injection LC/ESI/MS/MS test with a holding time of 14 days for analysis of pyruvate. Samples were collected in 40 mL amber glass VOA vials and preserved with mercury chloride upon receipt.

3.3.3 Bulk Organic Parameters

Table 3-7 shows sampling locations for BAC sampling that was performed twice a week. Table 3-8 shows sampling locations for organics testing that coincided with CECs, DBPs, and oxidation products sampling events.

Table 3-7 Sample Locations for BAC organics testing

| Sample Point: | Description: |
|---------------|-------------------|
| ET-2 | Tertiary effluent |
| ET-3 | Ozone effluent |
| ET-4 | BAC effluent |

Table 3-8 Sample Locations for organics sampling coinciding with CEC,DBP and oxidation products sampling events

| Sample Point: | Description: |
|---------------|-------------------------|
| ET-2 | Tertiary effluent |
| ET-3 | Ozone effluent |
| ET-4 | BAC effluent |
| ET-9 | MF/UF Filtrate |
| ET-14 | RO Effluent/UV/AOP Feed |
| ET-15 | UV/AOP Effluent |
| ET-16 | RO Concentrate |

Samples were collected weekly for a total of 8 rounds per location, which generated over 510 data points, which included analyses for TOC, fluorescence, and UVT. TOC samples were analyzed by City of San Diego Water Quality Lab and Trussell Tech Lab (Pasadena, CA). The City's lab followed Standard Methods 5310B, and Trussell Tech Lab followed Standard Method 5310C. TOC samples were collected for each pretreatment unit process weekly for one month for both the City of San Diego Water Quality Lab and Trussell Tech Lab to verify TOC results. These TOC results were also used to evaluate performance of the on-line TOC meters analyzing the TOC concentration in the tertiary and BAC effluent. After one month of concurrent TOC testing, Trussell Tech Lab analyzed RO effluent and UV/AOP effluent TOC samples due to the samples' low TOC concentration. TOC samples were collected onsite starting at the treatment train feed to the end of the train in process order. The City of San Diego Water Quality Lab provided TOC sample vials for their samples, and TOC samples sent to Trussell Tech Lab were sampled using Qorpak (Bridgeville, PA) Low Level TOC vials. Sample locations were flushed thoroughly prior to collection. City of San Diego samples were transferred to the city at the AWP Facility.

3.3.3.1 Fluorescence Excitation Emission Matrix Spectroscopy

Samples were collected in clear 40 mL glass vials, brought to Trussell Technologies lab, and stored at 4°C. Excitation-emission matrices (EEM) were collected in a 3 mL square quartz cuvette cell (light path 10 mm × 10 mm, using an Aqualog benchtop fluorometer (Horiba Jobin Yvon) and plotted with MATLAB (MathWorksTM, Natick, MA).

EEMs qualitatively and quantitatively characterize changes in fluorescence intensity. In order to develop an EEM, the organic matter in a water sample is excited by light of various wavelengths (e.g., 240-470 nm), and the corresponding fluorescent emissions are recorded over a similar range of wavelengths (e.g., 280-580 nm). These wavelength ranges are selected due to their applicability to environmental matrices in addition to instrument limitations. After collecting the excitation-emission intensities, the raw data set is then processed with mathematical software to account for blank response, correct for instrument- and matrix-specific effects, and plot the final image. The final image includes the following regions of specific organic fractions summarized in Table 3-5. An example of a typical secondary effluent excitation-emission matrix is presented below in Figure 3-2.

Natural waters typically contain fulvic and humic acids, where are wastewaters will also contain soluble microbial products, signatures of proteins and biopolymers (amino acids such as tyrosine, tryptophan, phenylalanine) (McKnight, et al, 2001; Chen, et al, 2003; Her, et al, 2003). Changes in fluorescence of organic matter due to a treatment process, can be used to quantify the relative distribution of the fractions and overall changes in organics that have wastewater or natural origins.

| | | | gth Range |
|--------|--|--------------------|------------------|
| Region | Organic Fraction | Excitation (nm) | Emission (nm) |
| 1 | Aromatic proteins and soluble microbial products (SMPs) | 240 - 300 | 280 - 380 |
| 2 | Fulvic-like substances | 240 - 300 | 380 - 580 |
| 3 | Humic-like substances | 300 - 480 | 300 - 580 |

Table 3-9 Fluorescence Regional Integration Boundaries

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Figure 3-2 Excitation emission matrix for secondary effluent.

(Region I represents aromatic proteins and soluble products, region II represents fulvic-like substances and region III represents humic-like substances.)

3.3.3.2 Ultraviolet Transmittance

UVT (Ultraviolet Transmittance) samples were collected simultaneously with TOC samples to evaluate UVT as a surrogate for TOC removal. Samples were collected in glass beakers and analyzed onsite using a Hach DR4000 spectrophotometer. These samples were also used to confirm on-line UVT meter readings, which are described in the next section.

3.4 INORGANIC CONTITUENTS

Samples were collected weekly and monthly, generating over 7,600 water quality measurements. Table 3-10 provides sampling locations for monthly RO sampling. Table 3-11 shows sampling locations for supporting inorganic water quality analyses that coincided with CECs, DBPs, and oxidation products sampling. Inorganic constituents were sampled and delivered to City of San Diego, and on occasion Eurofins Laboratories. Samples were collected as part of monthly RO water quality sampling and as part of water quality measurements in addition to trace organic constituents and oxidation byproduct sampling. Inorganic constituents were collected in sample vessels provided by the City of San Diego or Eurofins Laboratories. The analysis methods for each lab are provided in Table 3-12 and Table 3-13.

| Sample Point: | Description: |
|------------------------|---------------------------------|
| AWPD_A1_PERM/ NCWRP | RO Train A, Stage 1 Permeate |
| AWPD_A2_PERM/ NCWRP | RO Train A, Stage 2 Permeate |
| AWPD_ACOMB_PERM/ NCWRP | RO Train A, Combined Permeate |
| AWPD_A1_FEED/ NCWRP | RO Train A Feed |
| AWPD_A1_CONC/ NCWRP | RO Train A, Stage 1 Concentrate |
| AWPD_A2_CONC/ NCWRP | RO Train A, Stage 2 Concentrate |
| AWPD_B1_PERM/ NCWRP | RO Train B, Stage 1 Permeate |
| AWPD_B2_PERM/ NCWRP | RO Train B, Stage 2 Permeate |
| AWPD_B1_FEED/ NCWRP | Ro Train B Feed |
| AWPD_B1_CONC/ NCWRP | RO Train B, Stage 1 Concentrate |
| AWPD_B2_CONC/ NCWRP | RO Train B, Stage 2 Concentrate |
| AWPD_B3_PERM/ NCWRP | RO Train B, Stage 3 Permeate |
| AWPD_BCOMB_PERM/ NCWRP | RO Train B, Combined Permeate |
| AWPD_B3_CONC/ NCWRP | RO Train B, Stage 3 Concentrate |
| AWPD_UV1/ NCWRP | UV Influent |

Table 3-10 Sample Locations for monthly RO sampling events

| Table 3-11 Sample I | Locations for in | organics s | sampling | coinciding | with CEC, |
|---------------------|------------------|-------------|----------|------------|-----------|
| DBP and oxidation | products samp | ling events | S | | |

| Sample Point: | Description: |
|---------------|-------------------------|
| ET-2 | Tertiary effluent |
| ET-3 | Ozone effluent |
| ET-4 | BAC effluent |
| ET-9 | MF/UF Filtrate |
| ET-14 | RO Effluent/UV/AOP Feed |
| ET-15 | UV/AOP Effluent |
| ET-16 | RO Concentrate |

| ANALYTE | PROTOCOL | MDL | UNITS |
|---------------------|-----------------|--------|-----------|
| Partial Alkalinity | SM2320_2340C | 0 | MG/L |
| Total Alkalinity | SM2320_2340C | 10 | MG/L |
| Aluminum | EPA200.7 | 0.846 | UG/L |
| Ammonia as N | SM4500_NO2_B | 0.031 | MG/L |
| Barium | EPA200.7 | 1.07 | UG/L |
| Boron | EPA200.7 | 2.25 | UG/L |
| Bromide | EPA300A | 0.1 | MG/L |
| Calcium | SM3111B | 5 | MG/L |
| Chlorate | EPA300.1 | 20 | UG/L |
| Chloride | EPA300A | 0.5 | MG/L |
| Conductivity | SM2320_2340C | NA | UMHO/CM |
| Fluoride | EPA300A | 0.02 | MG/L |
| Calcium Hardness | SM2540C | 10 | MG/L |
| Total Hardness | SM2540C | 10 | MG/L |
| Iron | SM3111B | 50 | UG/L |
| Magnesium | SM3111B | 3 | MG/L |
| Manganese | EPA200.7 | 0.04 | UG/L |
| Nitrate | SM4500_NO2_B | CALC | MG/L |
| Nitrate and Nitrite | SM4500_NO2_B | CALC | MG/L |
| Nitrite | SM4500_NO2_B | 0.0049 | MG/L |
| Total Nitrogen | SK475424X/50350 | 0.156 | MG/L |
| Perchlorate | EPA314 | 4 | UG/L |
| рН | SM4500_PH | NA | PH |
| Ortho Phosphate | EPA300A | 0.2 | MG/L |
| Total Phosphorus | SK475424X/50350 | 0.078 | MG/L |
| Potassium | SM3111B | 0.5 | MG/L |
| Silica | SM4500SI | 0.625 | MG/L |
| Sodium | SM3111B | 5 | MG/L |
| Strontium | EPA200.7 | 0.443 | , UG/L |
| Sulfate | EPA300A | 0.5 | MG/L |
| TDS | SM2540C | 28 | , MG/L |

Table 3-12 Summary of Inorganic Constituents Analyses Performed by theCity of San Diego

| ANALYTE | PROTOCOL | MRL | UNITS |
|--------------------------------|-------------|------|-------|
| Total Aluminum | EPA 200.8 | 20 | ug/L |
| Total Antimony | EPA 200.8 | 1 | ug/L |
| Total Arsenic | EPA 200.8 | 1 | ug/L |
| Total Barium | EPA 200.8 | 2 | ug/L |
| Total Beryllium | EPA 200.8 | 1 | ug/L |
| Total Boron | EPA 200.7 | 0.05 | mg/L |
| Total Cadmium | EPA 200.8 | 0.5 | ug/L |
| Total Calcium | EPA 200.7 | 1 | mg/L |
| Total Chromium | EPA 200.8 | 1 | ug/L |
| Total Cobalt | EPA 200.8 | 2 | ug/L |
| Total Copper | EPA 200.8 | 2 | ug/L |
| Hexavalent Chromium | EPA 218.7 | 0.03 | ug/L |
| Total Iron | EPA 200.7 | 0.02 | mg/L |
| Total Lead | EPA 200.8 | 0.5 | ug/L |
| Total Magnesium | EPA 200.7 | 0.1 | mg/L |
| Total Manganese | EPA 200.8 | 2 | ug/L |
| Total Molybdenum | EPA 200.8 | 2 | ug/L |
| Total Nickel | EPA 200.8 | 5 | ug/L |
| Nitrate as Nitrogen by IC | EPA 300.0 | 0.1 | mg/L |
| Nitrate as NO3 | EPA 300.0 | 0.44 | mg/L |
| Nitrite Nitrogen by IC | EPA 300.0 | 0.05 | mg/L |
| Total Nitrate, Nitrite-N, CALC | EPA 300.0 | 0.1 | mg/L |
| Total Nitrogen Calc | EPA 353-351 | 0.2 | mg/L |
| Ortho Phosphate as P | SM 4500P E | 0.01 | mg/L |
| Total Potassium | EPA 200.7 | 1 | mg/L |
| Total Selenium | EPA 200.8 | 5 | ug/L |
| Total Silver | EPA 200.8 | 0.5 | ug/L |
| Total Sodium | EPA 200.7 | 1 | mg/L |
| Total Thallium | EPA 200.8 | 1 | ug/L |
| Total Vanadium | EPA 200.8 | 3 | ug/L |
| Total Zinc | EPA 200.8 | 20 | ug/L |

Table 3-13 Summary of Inorganic Constituents Analyses Performed by Eurofins Laboratories

3.5 ONSITE ANALYSIS

Water samples were also collected and analyzed onsite. Total coliform and *E. coli*, and adenosine triphosphate (ATP), UVT, and ozone residuals were analyzed to confirm and support offsite laboratory testing to quantify disinfection through ozone.

3.5.1 Modified Indigotrisulfonate Ozone Residual Test

The first method used was a modified Indigotrisulfonate (ITS) ozone residual test (Rakness et al., 2010) to measure the ozone residual. A description of the method is as follows. A 1 L stock solution was prepared consisting of 770 mg potassium indigotrisulfonate, 29.75 mL of 20% phosphoric acid, and 10 g of sodium dihydrogen phosphate. A blank solution with 10 mL prepared stock solution and 90 mL of DI water was prepared. The total blank solution volume was recorded. For sample collection, an arbitrary amount (dependent on strength of ozone residual) of prepared stock solution was added to an open-mouth 125mL Erlenmeyer flask. Sample was added to the sample flask until the sampler noticed a change in color intensity of the indigotrisulfonate solution. The volume of the sample collected was recorded. The volume of the blank and sample was measured by subtracting the total weight of the blank/sample plus flask minus the flask tare weight. The absorbance at 600 nm was then measured using the Hach DR4000 spectrophotomer for both the blank and sample solution. The concentration of ozone residual at the sampling point was evaluated using the equation shown below.

$$0zone \ Residual\left(\frac{mg}{L}\right) = \frac{\left[(ABS_{blank} \times TV_{blank}) \times \left(\frac{IV_{sample}}{10}\right)\right] - (Abs_{sample} \times TV_{sample})}{f \times SV \times b}$$

where:

ABS_{blank} = Measured absorbance of the blank (cm⁻¹)

 TV_{blank} = Total volume of blank solution (10 mL Indigo solution plus DI water volume) (mL)

IV_{sample} = Volume of stock solution added to sample flask

 $ABS_{sample} = Measured absorbance of reacted sample (cm⁻¹)$

TV_{sample} = Total volume of reacted sample (IV_{sample} + sample water volume) (mL)

f = sensitivity coefficient = 0.42 L mg⁻¹ cm⁻¹

SV = Reacted sample volume ($TV_{sample} - IV_{sample}$) (mL)

b = Path length of spectrophotometer's chamber, cm⁻¹

3.5.2 Onsite Biological Analyses

Adenosine triphosphate (ATP) analyses were conducted onsite. Samples were collected for the secondary effluent, tertiary effluent, ozone effluent. BAC effluent. MF filtrate, and UF filtrate. Approximately 100 mL was collected at each sample point.

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Analyses were performed onsite using a LUMINULTRA (Canada) Quench-Gone[™] Aqueous test kit to measure total microbiological concentration. Results were calculated using the LumiCalc[™] software. ATP is used as an indicator for total living biomass. Luciferase, an enzyme found in the tails of fireflies, reacts with the ATP and the light emitted in the reaction is measured by the luminometer as Relative Light Units (RLU). The relevant reaction is shown below:

$$ATP + O_2 + luciferin \xrightarrow{luciferase} AMP + PPi + oxyluciferin + light$$

The QuenchGone aqueous (QGA) kit was designed to measure samples with low- solids. The test kit is capable of measuring down to 0.1 pg ATP/mL using the standard procedures provided with the test kit. Contents of the Quench-Gone[™] Aqueous and LuminUltra test kit include the following:

- 1) PhotonMaster[™] Luminometer and Equipment Set
 - a. Carry Case
 - b. Micropipettors
 - c. PhotonMaster Luminometer
 - d. Test Tube Racks
- 2) Quench-Gone Aqueous Kit Contents
 - a. Luminase[™] Enzyme & Buffer Vials b. UltraCheck[™] 1 Dropper Bottle c. UltraLyse[™] 7 Bottle

 - d. UltraLute[™] (Dilution) Tube, 9 mL
 - e. Quench-Gone Syringe Filters
 - f. 60 mL Syringe
 - q. 100 to 1000 μL Pipet Tips
 - h. 10 to 200 µL Pipet Tips
 - 12x55 mm Test Tubes i.

The method for measuring ATP using the Quench-Gone Aqueous kit is as follows. A calibration was performed for each sample set. Luminase was first allowed to reach ambient temperature prior to use. 2 drops of UltraCheck 1 and 100 µL of Luminase was added to a 12x55 mm test tube, swirled five times, and inserted into the PhotonMaster luminometer and measured using the LumiCalc software. This calibration was recorded as RLU_{ATP1} and accepted if RLU_{ATP1} \leq 5,000. 100 mL of sample was filtered through the 60 mL syringe and filter. 1 mL of UltraLyse 7 was then added to the syringe barrel after the filter was reattached to the syringe. UltraLyse 7 was then filtered slowly to dryness, collected in a 9 mL UltraLute (Dilution) Tube, and capped and inverted 3 times. 100 µL of the solution in the UltraLute (Dilution) Tube and 100 µL of Luminase were transferred to a 12x55 mm test tube. The mixture was gently mixed and immediately inserted into the luminometer for measurement using LumiCalc. This value was recorded
as RLU_{cATP}. Conversion of the measured values to cellular ATP, an indicator of total living biomass, is shown in the equation below.

$$cATP\left(\frac{pg\ ATP}{mL}\right) = \frac{RLU_{cATP}}{RLU_{ATP1}} \times \frac{10,000\ (pg\ ATP)}{V_{Sample}\ (mL)}$$

where

cATP = Cellular ATP

RLU_{cATP} = Calibration Relative Light Units

RLU_{ATP1} = Measured Sample Relative Light Units

V_{Sample} = Volume of the Sample Filtered

3.5.3 Ultraviolet Transmittance

UVT measurements were measured by a Hach DR/4000 spectrophotometer. The instrument was zeroed using DI water was the blank. Sample was transferred to a 10 mm UV quartz cell and absorbance was measured and recorded at 254 nm wavelength. This procedure was repeated for each sample. The measured absorbance was converted to an equivalent transmittance (%) using the equation shown below.

Transmittance (%) = $10^{-Absorbance} \times 100$

3.6 ON-LINE METERS

3.6.1 Ultraviolet Transmittance

The Hach UVA sc uses a Hach sc200 controller with data-logging capabilities. Organic compounds dissolved in water absorb UV light. The UVA sc measures absorption at 254 nm, which can be used as a correlation for TOC. The UVA sc bypass model with 50 mm pathlength and measuring absorbance range of 0.01- 60 m^{-1} was used. The Trajon UV OptiView follows the same measurement principle.

3.6.2 Turbidity

The Hach 1720E Low Range Turbidimeter consists of a turbidimeter body, a submerged photocell, the sensor head, and lamp. Collimated light from the sensor head assembly is directed downwards into the sample in the turbidimeter body. Particles dissolved in water will scatter the light and the light scattered

perpendicular to the center line of the incident light is detected by the submerged photocell. The amount of light scattered is proportional to the turbidity of the meter. The 1720E turbidimeter has a measuring range of 0-100 nephelometric turbidity units (NTU).

The Hach FilterTrak 660 sc nephelometer uses nephelometric detection of light scattered by particles in a sample. A laser diode with a 660 nm wavelength is collimated into a narrow beam to create high beam power intensity. This allows for high scattered intensity from smaller particles. The portion of the light that is not scattered by particles is absorbed by a light trap at the bottom of the nephelometer. The detector is fixed at 90 degrees incident to the centerline.

3.6.3 Total Organic Carbon

The Sievers M5310 C TOC Analyzer has dual-stream capabilities with an analysis time of 2 minutes. The analyzer measures the oxidation of organic compounds that form carbon dioxide (CO₂) under the presence of UV radiation and ammonium persulfate. Carbon dioxide is measuring using a membrane-based conductometric detection technique described in Godec et al. (R. Godec et al., "Method and Apparatus for the Determination of Dissolved Carbon in Water," U.S. Patent No. 5,132,094). Inorganic carbon species (CO₂, HCO₃⁻, and CO₂²⁻⁾ are first measured. Afterwards, the analyzer oxidizes the organic compounds and total carbon is measured. TOC is calculated using the difference between the concentrations of total carbon and inorganic carbon. The M5310 C analyzer has a measurement range from 4 ppb to 50 ppm.

3.6.4 Dissolved Ozone

The Rosemount 499AOZ consists of a membrane-covered amperometric sensor, gold cathode, silver anode, and electrolyte solution. The gas-permeable membrane is stretched across the gold cathode and allows ozone in the sample to diffuse through the membrane. Inside the sensor, the ozone reacts with the electrolyte solution to form an intermediate compound. A voltage is applied to the cathode to reduce the intermediate compound, which produces a current that the analyzer measures. The current measured is proportional to the rate of ozone diffusion across the membrane, which is proportional to the dissolved ozone concentration in the sample. A Pt 100 RTD in the sensor performs a temperature correction since the rate of ozone diffusion through the membrane is dependent on temperature. The sensor has a measurement range from 0 to 3 ppm as O_3 . The Hach 9185sc Ozone analyzer is also a membrane based amperometric sensor. The 9185sc has a measuring range from 0 to 2 ppm as O_3 .

The Kuntze Krypton DES potentiostatic sensor consists of a gold ring electrode. A defined potential is applied to the electrode, which results in an electrical charge. During the oxidation-reduction potential reaction, ozone molecules are removed, which creates an electrical charge. The electrical charge created is directly proportional to the concentration of dissolved ozone in the sample flow. The Krypton DES sensor has a measuring range from 0 to 10 ppm as O_3 .

3.6.5 Oxidation Reduction Potential and pH

The Hach pH/ORP Differential sc sensors are comprised of three electrodes. A process and reference electrode measures the pH or ORP differentially with respect to a third ground electrode. The pH sensor has a measuring range from - 2 to 14 pH and the ORP sensor has a measuring range from -1500 to 1500 mV.

3.6.6 Conductivity and Temperature

The Signet 2850 Conductivity/Resistivity Sensor is a submersible sensor that is ideal for applications with conductivities ranging from 0.055 to 400,000 μ S. The Signet 2350 temperature transmitter is also a submersible sensor housed in a PVDF body that is ideal for high purity water quality applications.

3.6.7 Total Chlorine

The Hach CL17 analyzer utilizes a buffer solution and DPD indicator for measurement. Both total and free chlorine measurements require DPD indicator, but different buffer solutions. Free available chlorine (hypochlorous acid and hypochlorite ions) in the sample oxidizes the DPD indicator reagent at a pH range between 6.3 and 6.6. The oxidation reaction result in a magenta-colored compound and the measured intensity of the resultant color is proportional to the concentration of chlorine in the sample. The buffer solution is used to maintain the proper pH range for this reaction. Total available chlorine (free available chlorine and combined chloramines) measurement requires the addition of potassium iodide to the reaction. Chloramines in the sample oxidize iodide to iodine. lodine and any free available chlorine oxidize the DPD indicator, resulting in the magenta color at a pH of 5.1. A buffer solution containing potassium iodide, different from the solution used in the free chlorine measurement, maintains the pH range necessary for the reaction. Absorbance measurements at 510 nm taken after the reaction are compared to the absorbance measurement taken prior to reagent addition. The difference between these measurements is used to calculate the free/total chorine concentration in the sample.

3.7 MEMBRANE AUTOPSY METHODS

Various characterization methods were used for analysis of the fuolant/sclant materials. These included scanning electron microscopy (SEM) technique, which provides direct observation of a sample, including membrane morphology and fouling layer. The SEM in combination with an energy-dispersive X-ray spectroscope (EDS) enables analysis of elemental composition of a grain, a spot, or a whole area, being imaged by the SEM. It provides detailed information on the size, shape, structure, and chemical composition of membrane material and foulants. SEM-EDS may also be used to characterize very thin fouling layer, such

as microbiological fouling, membrane scaling, or membrane degradation and defects.

Chromatic Elemental Imaging (CEI) is a proprietary analytical technique used to resolve the spatial distribution of elements in a foulant sample. In this technique, a beam of focused electrons is accelerated across the surface of a foulant sample and interacts with the sample's inorganic elements by causing the elements to emit electrons. Since each element has its own unique atomic shell, a particular element's electron emission from its atomic shell generates a characteristic X-ray spectrum that allows for its identification. CEI assigns each element a color and provides a high-resolution image of their exact location in a sample. An element's color intensity in a Chromatic Elemental Image is largely influenced by its concentration in the foulant sample; elements present in a higher percentage will be displayed with greater intensity in the image. CEI can uniquely identify the distinct elements in a mixed foulant sample containing a number of inorganic deposits. This technique also reveals the location and concentration of different elements relative to each other in a sample.

3.8 QUALITY ASSURANCE AND QUALITY CONTROL

Field blank samples were collected during every sampling event for all parameters. This was done by pouring reagent water into individual sample container in the field during collection of grab samples. This was done to verify the sampling techniques did not introduce any contamination by the samplers. In addition, selected samples were collected in duplicate, to verify laboratory method precision.

The data from existing and new on-line meters were monitored and compared with routine laboratory and onsite sampling to provide a basis for meter calibration. Relevant meter readings were recorded during water quality sampling to verify meter readings and to assess the reliability and accuracy of the meters.

UVT and dissolved ozone meters were verified using the onsite methods described in the previous section. TOC meters were verified by collecting grab samples and analyzed by an offsite lab.

4 OZONE/BAC TREATMENT PERFORMANCE

The ozone disinfection system and granular activated carbon filters were commissioned in June, 2014. The BAC filters were operated continuously to produce approximately 1080 gpm of filtrate with moderate headloss accumulation, allowing for a backwashing frequency of once (1) per week. Due to test site foot print constraints, it was not possible to install a large enough clearwell tank to perform filter backwashing with the filtrate water. So, instead the feed water (tertiary effluent) was used for backwashing. The filter recovery was determined to be 99.8% with limited water loss associated with the BAC filtration process. The recovery was determined based on actual filtrate and backwash supply flow meter totalizers.

During initial start-up the head loss were found to be caused by air binding, as ozonated feed water is saturated with dissolved oxygen. To achieve the weekly backwash interval, air binding was addressed by short periodic pauses in filter production. This was achieved by closing the effluent valve. Logic was added to filters' controller, so that filter 1 and 2 were programmed to rotate every hour. This allows each filter to rest every two hours briefly. A short rest period of 90 seconds, allowed trapped gas to evolute, while also keeping production with the spare filter. Figure 4-1 presents the headloss accumulation in the BAC filter over the one-week operating period with and without the "filter rest intervals", illustrating that less than 40 inches of water headloss accumulates over a week of operation.



Figure 4-1 Typical Headloss Accumulation Through the BAC Filters

4.1 BULK ORGANICS REMOVAL

For the duration of this study, the total organic carbon (TOC) concentrations were guantified in the tertiary effluent, after ozonation, and after filtration through the activated carbon. Initial TOC removal was greatest due to adsorption on the activated carbon, resulting in an initial product TOC of 3 mg/L (Figure 4-2). However, the activated carbon becomes exhausted and a biological population is established as disinfected recycled water continues to pass through the filtration system. With time, the granular activated carbon (GAC) becomes exhausted and the biology is driving TOC removal which transitions the GAC process into a biological activated carbon (BAC) filtration process. The BAC filter provides majority of the TOC removal through biodegradation, but studies have shown that filter media is an important factor in overall TOC removal and activated carbon performs better than anthracite or sand filter media for the same hydraulic retention time (Gerringer, et. al. 2015; Reaumea, et. al. 2015). It is believed that although the activated carbon is exhausted, the carbon must continue to facilitate partial adsorption as biodegradation frees up old adsorption sites through biodegradation. Figure 5.1 presents the TOC data from on-line meters and laboratory results through the BAC filters. It is important to note that the influent on-line meter was experiencing problems with low sample flow around 140 MG filtered that was resolved at ~180 MG.



Figure 4-2 Total Organic Carbon (TOC) Concentrations in BAC Influent and Effluent

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It can be observed from the data set that the laboratory measurements generally confirmed the on-line data generated in the field. In particular, the BAC product water TOC agreed extremely well. It is believed that the issues with sample flow rate may have also impacted the lab samples for the influent water during the period identified. Figure 4.3 presents the same TOC data as a percent removal. It can be observed that the BAC filter stabilized to a TOC removal of 40% around August, 2014 and remained at this average percent removal throughout the duration of the study. The three-month duration to exhaustion is typical for establishing a BAC process.



Figure 4-3 TOC Removal through the BAC filtration process

The TOC removal presented in Figure 4-3 is not possible without the ozone disinfection process ahead of the BAC filter. It is the ozone process that preferentially oxidizes the more complex organic molecules, breaking down the aromatic structure into smaller carbon molecules that are more readily metabolized through biodegradation. This oxidation of organic molecules is accomplished by direct reaction with the ozone molecule, but also with the hydroxyl radical generated through reaction of ozone with the organics as shown in the following equations:

$$O_3 + Organic Matter \rightarrow HO^\circ + byproducts$$
 5-1

$HO^{\circ} + Organic Matter \rightarrow by products$ 5-2

Ozone disinfection breaks down organic matter through direct reaction and through production of hydroxyl radicals, making it a powerful advanced oxidation process (AOP) in addition to disinfection process. The byproducts from this powerful AOP have been evaluated in this project and their removal through BAC will be presented in Section 6.



Figure 4-4 Removal of UVT by Ozone & BAC

The fluorescence excitation emission matrices (EEM) can further illustrate the removal of bulk organic matter by the Ozone/BAC pretreatment. Figure 4-5 shows EEM of tertiary effluent, RO feed, permeate, and concentrate with and without ozone/BAC pretreatment. These results are consistent with TOC data that shows that because the additional pretreatment impact the organics in the RO feed it also does so for the RO concentrate. Figure 4-5 shows that the fluorescence intensity of organics in RO concentrate are much lower than the tertiary effluent, when ozone/BAC pretreatment is used.



Figure 4-5 Fluorescene EEM of AWPF Membranes feed water, product, and reject (a) without ozone/BAC pretreatment and (b) with ozone/BAC pretreatment. (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

4.2 COMPOUNDS OF EMERGING CONCERN

Compounds of emerging concern (CECs), also known as trace organic contaminants (TOrC), were quantified through out the treatment train with and without ozone/BAC pretreatment in operation to contrast performance. This section presents the results of ozone disinfection as an AOP for removal of the detected CECs.

A total of 95 CECs were analyzed for in the tertiary effluent and only 30 compounds were detected in the tertiary effluent. The median values for the quantified CECs are presented in Table 4-1 for the tertiary and ozonated effluents to observe the removal through the ozone disinfection process. The majority of the detected compounds in the tertiary effluent were reduced to concentrations below the laboratory detection limit. There were only five (5) compounds that were measurable after the ozone disinfection process and they were TCEP, TCPP, TDCPP, lohexal, and Sucralose. These compounds are all known to be extremely resistant to oxidation with TCEP being a fire retardant, TCPP and TDCPP are degradation products of TCEP, iohexal is a contrast agent

and sucralose is a commonly used artificial sweetener commercially known as Splenda[®].

| Table 4-1 Removal of | of Trace | Organic C | Constituen | ts through | Ozone (n=5) |
|----------------------|----------|-----------|------------|------------|--------------------|
| | | Tertiary | Ozone | % | Log |
| Analyte | Units | Effluent | Effluent | Removal | Removal |
| Albuterol | ng/L | 7.4 | <5 | >32.4% | >0.2 |
| Amoxicillin | ng/L | 3300 | <20 | >99.4% | >2.2 |
| Atenolol | ng/L | 59 | <5 | >91.5% | >1.1 |
| Carbamazepine | ng/L | 71 | <5 | >93.0% | >1.2 |
| Carisoprodol | ng/L | 42 | <5 | >88.1% | >0.9 |
| Cimetidine | ng/L | 22 | <5 | >77.3% | >0.6 |
| Cotinine | ng/L | 13 | <10 | >23.1% | >0.1 |
| DEET | ng/L | 19 | <10 | >47.4% | >0.3 |
| Dilantin | ng/L | 35 | <20 | >42.9% | >0.2 |
| Diltiazem | ng/L | 42 | <5 | >88.1% | >0.9 |
| Diuron | ng/L | 12 | <5 | >58.3% | >0.4 |
| Erythromycin | ng/L | 35 | <10 | >71.4% | >0.5 |
| Lidocaine | ng/L | 140 | <5 | >96.4% | >1.4 |
| Lopressor | ng/L | 99 | <20 | >79.8% | >0.7 |
| Meprobamate | ng/L | 30 | <5 | >83.3% | >0.8 |
| Sulfamethoxazole | ng/L | 18 | <5 | >72.2% | >0.6 |
| TCEP | ng/L | 170 | 170 | 0.00% | 0.00 |
| ТСРР | ng/L | 1100 | 800 | 27.3% | 0.14 |
| TDCPP | ng/L | 310 | 280 | 9.7% | 0.04 |
| Thiabendazole | ng/L | 6.35 | <5 | >21.3% | >0.1 |
| Trimethoprim | ng/L | 16 | <5 | >68.8% | >0.5 |
| 2,4-D | ng/L | 34 | <5 | >85.3% | >0.8 |
| 4-nonylphenol | ng/L | 750 | <100 | >86.7% | >0.8 |
| 4-tert-Octylphenol | ng/L | 470 | <50 | >89.4% | >0.9 |
| Acesulfame-K | ng/L | 340 | <20 | >94.1% | >1.2 |
| Butalbital | ng/L | 5.9 | <5 | >15.3% | >0.1 |
| Diclofenac | ng/L | 110 | <5 | >95.5% | >1.3 |
| Gemfibrozil | ng/L | 19 | <5 | >73.7% | >0.6 |
| Iohexal | ng/L | 3300 | 760 | 76.9% | 0.64 |
| Sucralose | ng/L | 16000 | 5800 | 63.8% | 0.44 |
| Triclosan | ng/L | 14 | <10 | 28.6% | 0.15 |

The CECs detected in the ozonated effluent were further reduced through the BAC process as presented in Table 4-2. It is believed that these compounds are removed through a combination of adsorption and biological degradation processes. The most recalcitrant compound was sucralose with 4 μ g/L detected in the BAC effluent. The degradation products of TCEP were removed to below

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detection and TCEP approached the existing method detection limit. The combined removal of the ozone and BAC filtration pretreatment process was 75% for even the most recalcitrant compound, sucralose, which was present at high enough concentrations to be quantified.

| Analyta | Unite | Ozone | BAC | % | Log |
|-----------|-------|----------|----------|---------|---------|
| Analyte | Units | Effluent | Effluent | Removal | Removal |
| TCEP | ng/L | 170 | 15 | 91.2% | 1.05 |
| TCPP | ng/L | 800 | <100 | >87.5% | >0.90 |
| TDCPP | ng/L | 280 | <100 | >64.3% | >0.45 |
| Iohexal | ng/L | 760 | 480 | 36.8% | 0.20 |
| Sucralose | ng/L | 5800 | 4000 | 31.0% | 0.16 |

Table 4-2 Removal of Trace Organic Constituents through BAC (n=5)

The Division of Drinking Water (DDW) has defined an acceptable advanced oxidation process (AOP) for groundwater replenishment reuse as a process that removes 0.5-log of 1,4 Dioxane or organics removal from various indicator compounds as shown in Table 4-3. Since 1,4 Dioxane is not currently present in the tertiary effluent at the North City Water Reclamation Plant, the indicator/surrogate approach was evaluated for the results of the ozone disinfection process to see if it met the DDW criteria.

Table 4-3 DDW Surrogates/Indicators Approach

| Organio | Organics: Surrogates/Indicators Approach | | | | |
|--|--|--|--|--|--|
| | (A) Hydroxy aromatic | | | | |
| | (B) Amino/Acylamino Aromatic | | | | |
| must show | (C) Nonaromatic with carbon double bonds | | | | |
| 0.5-log | (D) Deprotonated Amine | | | | |
| removal | (E) Alkoxy Polyaromatic | | | | |
| | (F) Alkoxy Aromatic | | | | |
| | (G) Alkyl Aromatic | | | | |
| must show | (H) Saturated Aliphatic | | | | |
| 0.3-log removal | (I) Nitro Aromatic | | | | |
| Must establish at least one surrogate or operational parameter that reflects the removal of at least five of the nine indicator compounds | | | | | |

The measured CECs presented in Table 4-1 and Table 4-2 have been categorized based on their structure and the observed removal through the ozone/BAC process is presented in Table 4-4. The removal for all the identified contaminants exceeded the log removals required by DDW. In fact, nearly all the

log removals were "greater than" as the pretreatment process reduced these contaminants to concentrations that were below the method detection limit. The only exception was TCEP with a 1.1-log removal.

| | With Ozor | ne/BAC Pretreatme | nt | | |
|--------------------|---|------------------------|----------------|-----------------|-------------------------|
| Constituent | Tertiary Effluent (ng/L) | BAC Effluent (ng/L) | Log Removal | DDW Grouping | Removal Requirements |
| 4-tert-Octylphenol | 470 | <50 | >1.0 | ^ | |
| 4-Nonylphenol | 750 | <100 | >0.9 | A | |
| Sulfamethoxazole | 18 | <5 | >0.6 | В | |
| Carbamazepine | 71 | <5 | >1.1 | С | >05 |
| Trimethoprim | 16 | <5 | >0.5 | D | -0.5 |
| Atenolol | 59 | <5 | >1.1 | D | |
| Gemfibrozil | 19 | <5 | >0.6 | F | |
| DEET | With Ozone/BAC PretituentTertiary Effluent (ng/L)BAC Effl (ng/I)tylphenol470<50 | <10 | >0.3 | G | |
| Meprobamate | 30 | <5 | >0.8 | и | >0.2 |
| TCEP | 170 | 15 | 1.1 | | ~0.5 |

Table 4-4 Ozone/BAC Pretreatment Satisfies DDW Requirements for an Advanced Oxidation Process

4.3 BIOLOGICAL SURROGATE INACTIVATION WITH OZONE DISINFECTION

Biological surrogates commonly used in water reclamation were monitored to quantify removals through the ozone disinfection process. Total coliform, fecal coliform and somatic as well as male specific coliphage were monitored at sample locations through out the treatment train. Figure 4-5 presents the dependence of the applied ozone dose on the effluent total coliform concentrations from the ozone contactor. Although the general trend observed is that more effective total coliform activation occurs with increased ozone dose, it was common to have detections in the ozone effluent. Table 4.5 presents the total coliform concentrations through the entire pretreatment process, including membrane filtration. The total coliform concentration is reduced by 37% through the full-scale tertiary filters, but was significantly reduced (99.6%) through the ozone disinfection process. This translates to 2.5 log removal of total coliform on average through the ozone process. The total coliform increased 14 times through the BAC filter, which demonstrates the biological activity occurring the in the filter bed. Both membrane filtrates, MF and UF, produced effluents that were consistently non-detect for total coliform.

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Figure 4-6 Effect of Ozone Dose on Total Coliform Concentrations (n=24)

| | Median | Minimum | Maximum |
|--------------------|--------------|--------------|--------------|
| Sample | (MPN/100 mL) | (MPN/100 mL) | (MPN/100 mL) |
| Blank | <1 | <1 | <2 |
| Secondary Effluent | 12500 | 3300 | 49000 |
| Tertiary Effluent | 7900 | 2300 | 33000 |
| Ozone Effluent | 25 | <2 | 1600 |
| BAC Effluent | 350 | 46 | 920 |
| MF Filtrate | <1 | <1 | 2 |
| UF Filtrate | <1 | <1 | <2 |

| Table 4-5 Total Coliform Concentrations in the Treatment Train | (n=24) |) |
|--|--------|---|
| | | , |

Fecal coliform results are presented in Figure 4-6 and Table 4-6. The results indicate a similar trend to that observed for the total coliform with fewer coliform at the higher ozone dose. Fecal coliform was 67% through the tertiary filters and 99.9% removal through the ozone disinfection process, which translates to 3-log removal on average. Fecal coliform concentrations increased 7 times through the BAC, but it is unclear how much weekly BAC backwashes with non-disinfected

tertiary filtrate contributed to these fecal coliform numbers. Full-scale fecal coliform numbers are anticipated to be lower and possibly non-detect when backwashed with disinfected BAC filtrate.



Figure 4-7 Effect of Ozone Dose on Fecal Coliform (n=24)

| Table 4-0 Summary | | \mathbf{S} Results (II=24) | |
|--------------------|--------------|------------------------------|--------------|
| | Median | Minimum | Maximum |
| Sample | (MPN/100 mL) | (MPN/100 mL) | (MPN/100 mL) |
| Blank | <1 | <1 | <2 |
| Secondary Effluent | 7000 | 1100 | 49000 |
| Tertiary Effluent | 2750 | 49 | 11000 |
| Ozone Effluent | 3 | <2 | 1600 |
| BAC Effluent | 23 | 4 | 350 |
| MF Filtrate | <1 | <1 | <2 |
| UF Filtrate | <1 | <1 | <2 |

| Table 4-6 Summa | y of Fecal Coliforms | Results (| n=24) |
|-----------------|----------------------|------------------|-------|
|-----------------|----------------------|------------------|-------|

As surrogate for pathogenic virus, both somatic and male specific coliphage were quantified and the inactivations of both types are presented in Figure 4-7 and

Figure 4-8. Median, minimum, and maximums for both types of bacteriophage are presented in Table 4-7 and Table 4-8. The inactivation of indigenous coliphage was non-detect or at the detection limit following the ozone disinfection process. Somatic coliphage were more abundant than the male specific and 3-log removal was demonstrated on average with the peak inactivation of 3.2-log.



Figure 4-8 Effect of Ozone Dose on Somatic Coliphage (n=17)

| Sample Location | Median | Minimum | Maximum |
|--------------------|--------|---------|---------|
| Blank | <1 | <1 | 2 |
| Secondary Effluent | 1200 | 800 | 1900 |
| Tertiary Effluent | 830 | 450 | 1500 |
| Ozone Effluent | <1 | <1 | 9 |
| BAC Effluent | <1 | <1 | 2 |
| MF Filtrate | <1 | <1 | <1 |
| UF Filtrate | <1 | <1 | <1 |

| Table 4-7 Su | mmary of S | Somatic (| Coliphage | (pfu/100 ml |) | (n=17 | (|
|-----------------|------------|-----------|-----------|-------------|-------|----------|---|
| I a D C T I O U | | Junialic | | | - / ' | (11 - 1) | 1 |



| i igule 4-3 Ellect di Ozone Dose di male opecific odipitage (II-17 | Figure | 4-9 Effect | of Ozone | Dose of | n Male 3 | Specific | Coliphage | (n=17 |
|--|--------|------------|----------|---------|----------|----------|-----------|-------|
|--|--------|------------|----------|---------|----------|----------|-----------|-------|

| | n maie opee | | <u>je (pru/ 100 i</u> | |
|--------------------|-------------|---------|-----------------------|--|
| Sample Location | Median | Minimum | Maximum | |
| Blank | <1 | <1 | <1 | |
| Secondary Effluent | 6 | <1 | 18 | |
| Tertiary Effluent | 4 | <1 | 10 | |
| Ozone Effluent | <1 | <1 | <1 | |
| BAC Effluent | <1 | <1 | 21 | |
| MF Filtrate | <1 | <1 | <1 | |
| UF Filtrate | <1 | <1 | <1 | |

| Table 4-8 Summary of Male Specific Coliphage (pfu/100 mL) (n=1 | 17) |
|--|-----|
|--|-----|

As a measure of general biological activity in the water, adenosine triphosphate (ATP) was quantified at the various sample points throughout the treatment train and is shown in Table 4-9. ATP is present in the cytoplasm and nucleoplasm of every cell and essentially all the physiological mechanisms that require energy for operation obtain it directly from the stored ATP. The ATP assay used in this project allowed quantitation of total ATP, which includes ATP from both intact and dead cells. The ATP results from monitoring illustrate that the highest concentrations were measured in the secondary effluent and both the tertiary and BAC effluent were similar in activity. Total and fecal coliforms were more than a 100 times higher in tertiary effluent, than BAC effluent, so the levels of ATP detected in BAC effluent confirms biological activity, that it's not directly associated with presence of harmful bacteria.

Ozone disinfection reduced the activity significantly, as shown in Table 4-9, but not to the same degree that membrane filtration did. These results illustrate the effectiveness of ozone disinfection and more importantly, highlight the ability of MF/UF filters to physically remove microbiological contaminants from the water.

| | C | .) | |
|--------------------|--------|---------|---------|
| Sample | Median | Minimum | Maximum |
| Secondary Effluent | 564 | 298 | 985 |
| Tertiary Effluent | 88.5 | 70.2 | 185 |
| Ozone Effluent | 11.4 | 3.94 | 17.8 |
| BAC Effluent | 59.9 | 46.6 | 112 |
| MF Filtrate | 0.52 | 0.28 | 110 |
| UF Filtrate | 1.85 | 0.09 | 3.87 |

Table 4-9 Adenosine Triphosphate (ATP) Monitoring Results

5 TREATMENT TRAIN PERFORMANCE FOR CONTAMINANT REMOVAL WITH AND WITHOUT OZONE-BAC

Ozone-BAC pretreatment proceeding the AWP Facility demonstrated significant improvements to downstream AWP Facility effluent water quality and this was documented in Chapter 4 for many of the bulk organic parameters. This chapter presents the effects of O_3 -BAC pretreatment on the samples collected throughout the entire treatment train. Sampling was performed with the pretreatment processes in service and samples were also collected without the pretreatment barrier. Sampling was performed for disinfection byproducts, known oxidation byproducts, contaminants of emerging concern, as well as total organic carbon. Grab samples were collected starting at the head of the process. Due to a large number of surveyed analytes, the total time to collect all samples exceeded the hydraulic residence of the treatment process.

5.1 DISINFECTION BYPRODUCTS AND OXIDATION BYPRODUCTS IN THE TREATMENT TRAIN

Figure 5-1 presents the profile of the median total trihalomethanes (TTHMs) concentrations from various sampling locations in the treatment train. The TTHM concentrations are consistently well below the drinking water maximum contaminant level (MCL) of 80 μ g/L. Although the highest median concentration was observed in the MF/UF filtrate with the pretreatment process, this is not consistent with the lowest TTHM values being observed for both the RO permeate and UV-AOP product water with pretreatment in operation. The conclusion from these data is that the TTHM concentrations will remain unaffected by the pretreatment process and are well below human health concern.

Figure 5-2 presents the total of five (5) haloacetic acids (HAA5s) that, similar to TTHMs, must be monitored as a disinfection byproduct associated with the chlorination or chloramination process. Figure 5-2 illustrates that the HAA5s are well below the MCL of 60 μ g/L at all sampling locations and HAA5s were non-detect in the RO and UV product water. In more recent work, it was determined that periodically it was possible to draw chlorinated water from the reclamation plant's chlorine contactor to the feed of the demonstration facility during ramp downs of the reclaimed water flows. It is suspected that this may contribute to some of the HAA5 spikes prior to chlorine addition, which occurs downstream of the BAC in front of the MF/UF systems.



Figure 5-1 Effect of Ozone/BAC Pretreatment on Total Trihalomethanes (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)





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A modern disinfection byproduct that can be formed through reactions with chloramines and ozone is N-nitrosodimethylamine (NDMA). Although there is no federal regulation for NDMA, California Division of Drinking Water (DDW) has a public notification limit of 10 ng/L. Figure 5-3 presents the median concentrations from the treatment train profile sampling that was performed. Although NDMA is formed through the ozonation process, it is well removed by the BAC process and restored the NDMA concentrations to non-detect concentrations.



Figure 5-3 Effect of Ozone-BAC Pretreatment on NDMA in Treatment Train (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

Bromate is a regulated disinfection byproduct of ozone disinfection with a federal MCL of 10 μ g/L. At the concentrations of ozone being transferred in the extended testing project, a significant amount of bromate was formed. However, bromate is well removed by the RO membrane and bromate was consistently found to be below the detection limit in the RO permeate.

 Table 5-1 Effect of Ozone/BAC Pretreatment on Bromate (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

| | Wit | h Pretreatm | ient | Without Pretreatment | | |
|----------------|--------|-------------|---------|----------------------|---------|---------|
| | Median | Minimum | Maximum | Median | Minimum | Maximum |
| Sample | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| Tertiary | | | | | | |
| Effluent | <5 | <5 | <5 | <5 | <5 | <5 |
| Ozone Effluent | 134 | 5 | 165 | NA | NA | NA |
| RO Permeate | <5 | <5 | <5 | <5 | <5 | <5 |

Chlorate is an unregulated disinfection byproduct that is being monitored by the USEPA on the candidate contaminant list (CCL3). Table 5-2 presents the results from chlorate monitoring, which indicate that median chlorate concentrations were non-detect in the RO permeate with and without pretreatment. It is believed that the spikes in chlorate observed with pretreatment are artifacts of chlorinated water from the full-scale plant making its way back to the AWPF feed. Although it is possible to form some chlorate with ozone, the concentrations observed here are beyond those that could be explained by ozone addition.

 Table 5-2 Effect of Ozone/BAC Pretreatment on Chlorate (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

| | Wit | h Pretreatm | ient | Without Pretreatment | | |
|----------------|--------|------------------------|--------|----------------------|---------|---------|
| | Median | Median Minimum Maximum | | | Minimum | Maximum |
| Sample | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| Tertiary | | | | | | |
| Effluent | 30.65 | < 20 | 805 | < 20 | < 20 | < 20 |
| Ozone Effluent | 45.5 | < 20 | 808 | NA | NA | NA |
| RO Permeate | < 20 | < 20 | 24.1 | < 20 | < 20 | < 20 |

Another compound that is currently unregulated by the USEPA, but is regulated by DDW to 6 μ g/L in California is perchlorate. Since it is possible to form some perchlorate through ozone oxidation, samples were collected and the results were consistently non-detect for the RO permeate. It is unclear whether perchlorate detections can be attributed to ozone addition or chlorine contamination.

 Table 5-3 Effect of Ozone/BAC Pretreatment on Perchlorate (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

| | Wit | h Pretreatm | ient | Without Pretreatment | | |
|-------------------|--------|-------------|---------|----------------------|---------|---------|
| | Median | Minimum | Maximum | Median | Minimum | Maximum |
| Sample | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| Tertiary Effluent | <4 | <4 | 8.43 | < 4 | < 4 | < 4 |
| Ozone Effluent | <4 | <4 | 8.99 | NA | NA | NA |
| RO Permeate | <4 | <4 | <4 | < 4 | < 4 | < 4 |

Chromium is a naturally occurring element that is commonly found in groundwater and is relatively harmless in a reduced state, chromium (III). DDW has an MCL for total chromium of 50 μ g/L. However, the oxidized form of hexavalent chromium VI (Cr VI) is a known carcinogen and DDW recently promulgated a more restrictive MCL of 10 μ g/L for this form of chromium. Total chromium could be oxidized to the more restrictive form, Cr VI, through ozone addition. Figure 5-4 presents the results from the sampling events. Although the ozone process did form Cr VI, the concentrations are more than 50 times below the MCL and the RO process is very effective at removing Cr VI.



Figure 5-4 Effect of Ozone/BAC Pretreatment on Hexavalent Chromium (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

5.2 TOC CONCENTRATION PROFILE AND OXIDATION BYPRODUCTS

The bulk organic matter in the tertiary effluent is transformed by oxidation in the ozone contactor through a direct reaction with ozone and also by the formation of hydroxyl •OH radicals, which are formed as ozone reacts with organics and alkalinity in the water. The oxidation of organics preferentially attacks the more complex bonds associated with aromatic ring structures, cleaving these bonds and transforming the organics into more simple carbon molecules. The following

section presents the results of analysis that were performed to quantify the formation and removal of these oxidation byproducts through the treatment train.

Figure 5-5 presents the TOC concentrations through the treatment train. The TOC concentration is relatively unchanged following the ozonation process, but the organics have been transformed such that they are more readily removed biologically. On average, we observed 40% TOC removal through the BAC filtration process, which can be observed on Figure 5-5. The TOC of the MF/UF filtrate is relatively unchanged in contrast to the feedwater, but the RO permeate is significantly lower for both treatment trains. The RO permeate was reduced to 0.06 mg/L on average while the RO permeate with pretreatment was reduced to 0.04 mg/L. The UV effluent produced a similar number to the RO permeate because the AOP is not being operated at levels that would drive mineralization.



with O3-BAC without O3-BAC

Figure 5-5 Effect of Ozone-BAC Pretreatment on TOC in Treatment Train (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

Tables 5-4, 5-5, 5-6, and 5-7 present concentrations of compounds identified in the literature as potential products from the oxidation of natural occurring organic matter. These compounds are small organic compounds that are formed through the oxidation of larger complex organics and the relatively simple molecular structures of these low molecular weight compounds are presented in Figure 5-6.

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Figure 5-6 Molecular Structure of (a) Formaldehyde (b) Acetaldehyde (c) Glyoxal and (d) Methyl Glyoxal

These tables present a similar trend that these compounds are present both with and without pretreatment. The tables also illustrate that while these simple organics may be forming as a byproduct of ozone oxidation, they are also being readily removed through the BAC filtration process. There is not a significant difference between the concentrations measured in the final product with or without the pretreatment process. If these compounds were to show up in higher concentrations, it would increase the RO permeate TOC concentrations.

| | Wit | h Pretreatm | ent | Without Pretreatment | | |
|-------------------|--------|-------------|---------|----------------------|---------|---------|
| | Median | Minimum | Maximum | Median | Minimum | Maximum |
| Sample | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| Tertiary Effluent | 5.8 | 5.3 | 5.9 | 5.3 | 5.2 | 8.2 |
| Ozone Effluent | 100 | 6.6 | 110 | NA | NA | NA |
| BAC Effluent | 5.9 | 5.5 | 26 | NA | NA | NA |
| MF/UF Filtrate | 11 | 9.9 | 25 | 18.5 | 15.5 | 19 |
| RO Permeate | 27 | 7.8 | 47 | 64.5 | 64 | 73 |
| UV Effluent | 18 | 9.05 | 31 | 13 | 11 | 15 |

Table 5-4 Effect of Ozone/BAC Pretreatment on Formaldehyde (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

Table 5-5 Effect of Ozone/BAC Pretreatment on Acetaldehyde (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

| | Wit | h Pretreatm | ient | Without Pretreatment | | |
|-------------------|--------|-------------|---------|----------------------|---------|---------|
| | Median | Minimum | Maximum | Median | Minimum | Maximum |
| Sample | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| Tertiary Effluent | 3 | 2.6 | 3.2 | 2.5 | 2.5 | 2.7 |
| Ozone Effluent | 25 | 2.8 | 26.5 | NA | NA | NA |
| BAC Effluent | 2.7 | 2.4 | 3 | NA | NA | NA |
| MF/UF Filtrate | 3.2 | 2.4 | 3.6 | 5.75 | 5.6 | 6.05 |
| RO Permeate | 1 | 1 | 1.6 | 1 | 1 | 1.25 |
| UV Effluent | 1 | 1 | 1 | 1.4 | 1.1 | 1.7 |

| | Wit | h Pretreatm | ent | Without Pretreatment | | |
|-------------------|--------|-------------|---------|----------------------|---------|---------|
| | Median | Minimum | Maximum | Median | Minimum | Maximum |
| Sample | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| Tertiary Effluent | <10 | <10 | 5.9 | <10 | <10 | NA |
| Ozone Effluent | 59 | <10 | 110 | NA | NA | NA |
| BAC Effluent | <10 | <10 | 26 | NA | NA | NA |
| MF/UF Filtrate | <10 | <10 | 25 | <10 | <10 | <10 |
| RO Permeate | <10 | <10 | 47 | <10 | <10 | <10 |
| UV Effluent | <10 | <10 | 31 | <10 | <10 | <10 |

 Table 5-6 Effect of Ozone/BAC Pretreatment on Glyoxal (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

Table 5-7 Effect of Ozone/BAC Pretreatment on Methyl Glyoxal (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

| | Wit | h Pretreatm | ient | Without Pretreatment | | |
|-------------------|------------------|-------------------|-------------------|----------------------|-------------------|-------------------|
| Sample | Median (µg/L) | Minimum (µg/L) | Maximum (μg/L) | Median (µg/L) | Minimum (µg/L) | Maximum (µg/L) |
| Tertiary Effluent | <10 | <10 | <10 | <10 | <10 | <10 |
| Ozone Effluent | 26.5 | <10 | 32 | NA | NA | NA |
| BAC Effluent | <10 | <10 | <10 | NA | NA | NA |
| MF/UF Filtrate | <10 | <10 | <10 | <10 | <10 | <10 |
| RO Permeate | <10 | <10 | <10 | <10 | <10 | <10 |
| UV Effluent | <10 | <10 | <10 | <10 | <10 | <10 |

Acetone has been identified as causing a notable increase in the final product TOC concentrations at the Orange County Water District's Groundwater Replenishment System (GWRS). Acetone is has a similar structure to formaldehyde, but instead of two hydrogens, it has two methyl groups (see Figure 5-7). Acetone has also been observed as an oxidation byproduct.

 H_2

Figure 5-7 Molecular Structure of Acetone

Figure 5-8 presents the acetone concentrations throughout the treatment train. Although acetone was formed, it was effectively removed by the biological activity in the BAC process. The majority of sampling locations were non-detect for acetone.



Figure 5-8 Effect of Ozone/BAC Pretreatment on Acetone (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

Tables 5-8 through 5-11 present the results of oxidation byproducts through out the treatment train. A consistent theme is that oxidation byproducts do appear to be formed through the ozone oxidation process and the BAC filter is effective at removing these byproducts through biological oxidation.

| | Wi | th Pretreatm | ent | Without Pretreatment | | |
|-------------------|--------|--------------|---------|----------------------|---------|---------|
| | Median | Minimum | Maximum | Median | Minimum | Maximum |
| Sample | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| Tertiary Effluent | <5 | <5 | 5 | <5 | <5 | <5 |
| Ozone Effluent | 220 | <5 | 310 | NA | NA | NA |
| BAC Effluent | <5 | <5 | 5 | NA | NA | NA |
| MF/UF Filtrate | <5 | <5 | 5 | <5 | <5 | <5 |
| RO Permeate | <5 | <5 | 9.3 | <5 | <5 | 5.1 |
| UV Effluent | <5 | <5 | 5 | <5 | <5 | <5 |

 Table 5-8 Effect of Ozone/BAC Pretreatment on Acetate-Glycolate (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

| | Wit | h Pretreatm | ent | Without Pretreatment | | |
|-------------------|--------|-------------|---------|----------------------|---------|---------|
| | Median | Minimum | Maximum | Median | Minimum | Maximum |
| Sample | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| Tertiary Effluent | <5 | <5 | <5 | <5 | <5 | <5 |
| Ozone Effluent | 200 | 110 | 620 | NA | NA | NA |
| BAC Effluent | <5 | <5 | <5 | NA | NA | NA |
| MF/UF Filtrate | 78 | 62 | 94 | <5 | <5 | 57 |
| RO Permeate | 14 | 9.4 | 31 | 12 | 8.7 | 19 |
| UV Effluent | 5.4 | <5 | 6 | 7.9 | <5 | 17 |

Table 5-9 Effect of Ozone/BAC Pretreatment on Formate-Isobutyrate (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

Table 5-10 Effect of Ozone/BAC Pretreatment on Oxalate (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

| | Wit | h Pretreatm | ent | Without Pretreatment | | | |
|-------------------|---------|-------------|---------|----------------------|---------|---------|--|
| Sample | Median | Minimum | Maximum | Median | Minimum | Maximum | |
| Sample | (µ6/ IJ | (µ5/ Ľ) | (µ6/Ľ) | (µ6/ IJ | (µ5/ IJ | (µ5/ IJ | |
| Tertiary Effluent | <5 | <5 | <5 | <5 | <5 | <5 | |
| Ozone Effluent | <5 | <5 | <5 | NA | NA | NA | |
| BAC Effluent | <5 | <5 | <5 | NA | NA | NA | |
| MF/UF Filtrate | <5 | <5 | <5 | <5 | <5 | <5 | |
| RO Permeate | <5 | <5 | <5 | <5 | <5 | 5.5 | |
| UV Effluent | <5 | <5 | <5 | <5 | <5 | <5 | |

Table 5-11 Effect of Ozone/BAC Pretreatment on Pyruvate (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

| | With Pretreatment | | | Without Pretreatment | | |
|-------------------|-------------------|---------|---------|----------------------|---------|---------|
| Sample | Median | Minimum | Maximum | Median | Minimum | Maximum |
| Sample | (µg/ IJ | (µg/ IJ | (µg/ĽJ | (µg/ ĽJ | (µg/ IJ | (µg/ ĽJ |
| Tertiary Effluent | <5 | <5 | <5 | <5 | <5 | <5 |
| Ozone Effluent | <5 | <5 | <5 | NA | NA | NA |
| BAC Effluent | <5 | <5 | <5 | NA | NA | NA |
| MF/UF Filtrate | <5 | <5 | <5 | <5 | <5 | <5 |
| RO Permeate | <5 | <5 | <5 | <5 | <5 | 5.5 |
| UV Effluent | <5 | <5 | <5 | <5 | <5 | <5 |

5.3 CONSTITUENTS OF EMERGING CONCERN

As the population continues to expand and the number of chemicals we use in our modern lives continuous to grow, the number of constituents of emerging concern (CECs) will also continue to grow as will our ability to detect them. Although many of these chemicals do not have any significant health effects at the concentrations typically observed in a municipal wastewater, the general public would prefer water that does not contain these contaminants. The environmental community would also prefer to minimize the degree to which these CECs, some which may be endocrine disrupting compounds, are discharged to the environment. This section presents the results from water quality analyses that were performed on CECs to quantify the concentrations with the treatment train profile.

5.3.1 Non-Biodegradable Sweeteners

Figure 5-9 presents the concentration profile for sucralose, which is a commonly used artificial sweetener marketed as SplendaTM. This figure shows that the concentration was reduced through the ozone/BAC pretreatment process. So, while the RO feedwater was 18,000 ng/L without pretreatment, it was a little less than 4,000 ng/L with pretreatment. Regardless of the pretreatment process, the RO removed the sucralose very effectively and produced non-detect sucralose concentrations.



Figure 5-9 Effect of Ozone/BAC Pretreatment on Sucralose (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

Figure 5-10 presents the concentration profile for another common sweetener, Acesulfame potassium. The results for this sweetener were similar with the concentration being substantially reduced through the ozone/BAC pretreatment process. So, while the RO feedwater was 420 ng/L without pretreatment, it was a little more than 50 ng/L with pretreatment. Regardless of the pretreatment

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process, the RO removed the Acesulfame-K very effectively and produced nondetect concentrations.



Figure 5-10 Effect of Ozone/BAC Pretreatment on Acesulfame-K in Treatment Train (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

5.3.2 Household Compounds

Figure 5-11 presents the concentration profile for 4-nonylphenol, which is a breakdown product of non-ionic detergents. This compound persists in the environment and there is significant concern on the estrogenic effects of this compound on fish. The data collected for this project demonstrates that the concentration is frequently below the MRL at all sampling locations after the MF/UF process and the ozone process effectively removed this compound and the concentrations observed. Figure 5-12 presents the results from 4-tert-Octylphenol which is another breakdown product of non-ionic detergents. These data show that the RO process removes this compound to below the MRL without pretreatment, but the ozone process effectively removes it when the pretreatment as well.



Figure 5-11 Effect of Ozone/BAC Pretreatment on 4-Nonylphenol (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)



Figure 5-12 Effect of Ozone/BAC Pretreatment on 4-tert-Octylphenol (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

Figure 5-13 presents the concentrations of triclosan, a common antibacterial addition to household soaps. The triclosan was observed at low levels and ozone pretreatment as well as the RO membrane effectively removed this compound.



Figure 5-13 Effect of Ozone/BAC Pretreatment on Triclosan (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

Figure 5-14 presents the concentrations of Diethyl-M-Toluamide (DEET), a commonly applied mosquito repellent. These data show that the ozone and RO processes were effective at removing this compound at the concentrations observed. As a result, the RO feedwater had non-detect DEET when ozone/BAC pretreatment was in place. However, the RO and UV samples were below the MRL of 10 ng/L regardless of whether the pretreatment was in service or not.



Figure 5-14 Effect of Ozone/BAC Pretreatment on DEET (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

5.3.3 Pharmaceuticals and Hospital Compounds

Figures 5-15 through 5-21 present the concentration profiles for commonly detected pharmaceuticals in wastewater effluents. These compounds are atenolol (a beta blocker), carbamazepine (anti-seizure), diclofenac (anti-inflammatory), gemfibrozil (lipid regulator), meprobamate (anti-anxiety), sulfamethoxazole (antibiotic), and trimethoprim (antibiotic). All of these compounds were detected in the tertiary effluent and were oxidized to below the detection limit through the ozonation process and remained non-detect at the downstream locations. Without the pretreatment process, the MF/UF filtrate had quantifiable concentrations and the RO process successfully removed these compounds to below the MRL.



Figure 5-15 Effect of Ozone/BAC Pretreatment on Atenolol (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)



Figure 5-16 Effect of Ozone/BAC Pretreatment on Carbamazepine (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)



Figure 5-17 Effect of Ozone/BAC Pretreatment on Diclofenac (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)



Figure 5-18 Effect of Ozone/BAC Pretreatment on Gemfibrozil (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)



Figure 5-19 Effect of Ozone/BAC Pretreatment on Meprobamate (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)



Figure 5-20 Effect of Ozone/BAC Pretreatment on Sulfamethoxazole (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)





Figure 5-22 presents the concentration profile for iohexal, a commonly used Xray contrast agent in the medical field. The results indicate that the pretreatment process was effective at reducing the observed concentration by 75% and was primarily driven by ozone oxidation. The RO process reduced the concentration to below the MRL regardless of whether the pretreatment was in service or not.


Figure 5-22 Effect of Ozone/BAC Pretreatment on Iohexal (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

5.3.4 Flame Retardant

Figures 5-23, 5-24, and 5-25 present the concentration profiles for the flame retardant, TCEP, along with its metabolites. By design, this family of compounds is extremely resistant to oxidation and demonstrated little transformation through the ozonation process. However, the BAC filters significantly reduced the concentrations and this is believed to have occurred through adsorption. Similar to most of the CECs, the RO product was non-detect regardless of the pretreatment process.



Figure 5-23 Effect of Ozone/BAC Pretreatment on TCEP (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)



Figure 5-24 Effect of Ozone/BAC Pretreatment on TCPP (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

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Figure 5-25 Effect of Ozone/BAC Pretreatment on TDCPP (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

5.3.5 CEC Summary

Table 5-12 presents a summary of all the CEC compounds that were quantified through this project. The table highlights that the ozone and BAC filtration process was extremely effective at removing most of these compounds ahead of the RO process. For example, out of 33 detected CEC compounds in tertiary effluent, only 3 were detected in MF/UF filtrate. The RO process then effectively removes all of these organics to below the detection limits of today's modern analytical equipment.

Table 5-13 illustrates the impact of this enhanced water quality on the contaminants in the RO concentrate that will ultimately be disposed of to the environment. The CECs are reduced to significantly in concentration, frequently to non-detect levels. The reduction of many contaminants is between 80 and 90%, preventing these compounds from being concentrated and discharged to the environment.

| | Median Concentration (ng/L) | | | | |
|-------------------|-----------------------------|----------------|-------------|--|--|
| CEC: | Tertiary Effluent | MF/UF Filtrate | UV Effluent | | |
| 4-Nonylphenol | 750 | <100 | <100 | | |
| 4-tert-Ocylphenol | 470 | <50 | <50 | | |
| Estrone | 5.2 | <5 | <5 | | |
| Triclosan | 14 | <10 | <10 | | |
| 2,4-D | 34 | <5 | <5 | | |
| Albuterol | 7.4 | <5 | <5 | | |
| Amoxicillin | 3300 | <20 | <20 | | |
| Butalbital | 5.9 | <5 | <5 | | |
| Diuron | 12 | <5 | <5 | | |
| Sulfamethoxazole | 18 | <5 | <5 | | |
| Carbamazepine | 71 | <5 | <5 | | |
| Cotinine | 13 | <10 | <10 | | |
| Atenolol | 59 | <5 | <5 | | |
| Cimetidine | 22 | <5 | <5 | | |
| Diclofenac | 110 | <5 | <5 | | |
| Lidocaine | 140 | <5 | <5 | | |
| Lopressor | 99 | <20 | <20 | | |
| Thiabendazole | 6.35 | <5 | <5 | | |
| Trimethoprim | 16 | <5 | <5 | | |
| Acesulfame-K | 340 | 57 | <20 | | |
| Diltiazem | 42 | <5 | <5 | | |
| Gemfibrozil | 19 | <5 | <5 | | |
| DEET | 19 | <10 | <10 | | |
| Dilantin | 35 | <20 | <20 | | |
| Carisoprodol | 42 | <5 | <5 | | |
| Erythromycin | 35 | <10 | <10 | | |
| Iohexal | 3300 | 470 | <10 | | |
| Meprobamate | 30 | <5 | <5 | | |
| Sucralose | 16000 | 4000 | <100 | | |
| TCEP | 170 | 15 | <10 | | |
| ТСРР | 1100 | <100 | <100 | | |
| TDCPP | 310 | <100 | <100 | | |

Table 5-12 Summary of CEC Removal with Pretreatment (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

| | RO Concentrate Medi | an Concentration | |
|-------------------|----------------------|-------------------|-----------|
| | (ng/l | L) | % |
| CEC: | Without Pretreatment | With Pretreatment | Reduction |
| 2,4-D | 24 | <5 | >79% |
| 4-Nonylphenol | 780 | <100 | >87% |
| 4-tert-Ocylphenol | 1800 | <50 | >97% |
| Acesulfame-K | 2000 | 290 | 86% |
| Albuterol | 11 | <5 | >55% |
| Amoxicillin | 3100 | <20 | >99% |
| Atenolol | 200 | <5 | >98% |
| Butalbital | 12 | <5 | >58% |
| Caffeine | 6.7 | <5 | >25% |
| Carbamazepine | 620 | <5 | >99% |
| Carisoprodol | 120 | 8 | 93% |
| Cotinine | 64 | 26 | 59% |
| DEET | 150 | <10 | >93% |
| Dehydronifedipine | 16 | <5 | >69% |
| Dilantin | 130 | <20 | >85% |
| Diltiazem | 73 | <5 | >93% |
| Diuron | 83 | <5 | >94% |
| Erythromycin | 48 | <10 | >79% |
| Estrone | 7.5 | <5 | >33% |
| Gemfibrozil | 56 | <5 | >91% |
| Ibuprofen | 26 | <10 | >62% |
| Iohexal | 11000 | 1400 | 87% |
| Lidocaine | 570 | <5 | >99% |
| Lopressor | 480 | <20 | >96% |
| Meprobamate | 260 | 25 | 90% |
| Naproxen | 17 | <10 | >41% |
| Nifedipine | 41 | <20 | >51% |
| Simazine | 6.9 | <5 | >28% |
| Sucralose | 47000 | 13000 | 72% |
| TCEP | 430 | 66 | 85% |
| ТСРР | 4200 | 380 | 91% |
| TDCPP | 750 | <100 | >87% |
| Thiabendazole | 6.35 | <5 | >21% |
| Trimethoprim | 16 | <5 | >69% |

Table 5-13 Effect of Ozone/BAC Pretreatment on Trace Organic Constituents in RO Concentrate (n=3 for sampling without ozone/BAC, n=5 for sampling with ozone/BAC)

6 UV/AOP PERFORMANCE WITH SODIUM HYPOCHLORITE AND HYDROGEN PEROXIDE ADDITION

A number of recent studies describe the use of free chlorine combined with ultraviolet light (UV/HOCI) as a new approach to producing an Advanced Oxidation Process (Feng, et al. 2007; Watts and Linden 2007; Watts, et al. 2007; Sichel, et al. 2011; Chan, et al. 2012; Wang, et al. 2012; Watts, et al. 2012; Pisarenko, et al. 2013; Rosenfeldt, et al. 2013; Fang, et al. 2014; Shu, et al. 2014). In comparison to the combination of hydrogen peroxide and ultraviolet light (UV/H₂O₂), which is currently the most commonly deployed AOP in potable reuse projects implementing groundwater recharge in California, the UV/HOCI can be expected to provide some benefits to a water treatment system operator, potentially offering similar performance for removal of organic contaminants (such as 1,4-dioxane) and lower power and chemical cost. The objective of this testing was evaluate the performance of UV/H_2O_2 and UV/HOCI for the destruction of 1,4-dixone.

6.1 TEST CONDITIONS

Previous testing by the City of San Diego evaluated destruction of 1,4-dioxane by the UV/H_2O_2 at various hydrogen peroxide dose conditions (City of San Diego 2013). The previous project showed electrical energy dose (EED in kWh per kgal of treated water) of 0.30 and hydrogen peroxide dose of 2.6 mg/L was needed to achieve greater than 0.5-log removal target goal of 1,4-dioxane, as shown in Figure 6-1. An EED of 0.225 kWh/kgal, which is used at Orange County GWRS, was insufficient to achieve target log removal at the tested conditions. Both are shown in Figure 6-1.

For the experiments performed in this project, the electrical energy dosing of 0.3 kWh/kgal was used for comparison of UV/H_2O_2 and UV/HOCI. Table 6-1 provides a summary of the test conditions, such as power and water flow, and target chemical dosing for this evaluation.

A batch aqueous solution was prepared on-site by carefully mixing neat 1,4dioxane into potable water in a 30 gallon tank. A peristaltic pump was used to continuously dose the solution for the duration of the test. During this testing the product water was diverted to drain. Grab samples were collected before and after various UV and/or oxidant dosing. Sodium hypochlorite feed was diverted to RO permeate line close to the addition point of hydrogen peroxide. This temporarily disabled feeding of ammonium hydroxide and sodium hypochlorite at the MF/UF feed line and thus chloramines residual was not present in combined RO permeate during this evaluation.



Figure 6-1 Removal of 1,4-dioxane by UV/H_2O_2 during previous testing. Specifically, Red = OC GWRS operating conditions; Blue = San Diego Demonstration plant first year AOP calibration.

| Power | Water | EED | H_2O_2 Dose | HOCI Dose |
|---------|-----------|------------|---------------|----------------------------|
| Setting | Flow (gm) | (kWh/kgal) | (mg/L) | (mg/L as Cl ₂) |
| 65% | 670 | 0.300 | 1.50 | 1.00 |
| 65% | 670 | 0.300 | 2.25 | 2.00 |
| 65% | 670 | 0.300 | 3.00 | 3.00 |
| 65% | 670 | 0.300 | 4.00 | 4.00 |

Table 6-1 Test Conditions Summary

A practice run was performed dosing each chemical to determine the correct dosing rate prior to 1,4-dioxane spiking. Figure 6-2 shows a plot of feed rates for both hydrogen peroxide and sodium hypochlorite chemical pumps in gallons per hour (GPH) vs. obtained residual in the combined RO permeate at a flow of 670 gallons per minute. The difference between the feed rates of two separate pumps amounts to the difference in the concentration and specific gravity of the hydrogen peroxide and sodium hypochlorite solutions and pump head. The dosing rates were used to dial in appropriate chemical dose and verified by test kits in the field prior to sample collection.



Figure 6-2 Feed rates for H₂O₂ and NaOCI chemical pumps

6.2 REMOVAL OF 1,4-DIOXANE

The results from laboratory and field analysis for grab samples of the feed (before UV) water are shown by Table 6-2. Based on observed levels of the total nitrogen, the RO permeate water quality was consistent during the duration of the test. Changes in TOC of RO permeate are shown in Figure 6-3. During 1,4-dioxane dosing, TOC increased to approximately 170 μ g/L.

| Analyte | Units | HOCI Dose (mg/L as Cl ₂) | | | ŀ | H_2O_2 Dos | se (mg/L | _) | |
|----------------------------|-------|--------------------------------------|--------|-------|--------|--------------|----------|--------|--------|
| | mg/L | 1.1 | 2.1 | 3.3 | 3.9 | 1.6 | 2.2 | 3.0 | 4.0 |
| Alkalinity | mg/L | 5.2 | 6.7 | 7.2 | 9.0 | 4.1 | 4.3 | 4.2 | 4.4 |
| рН | | 5.81 | 5.80 | 6.05 | 6.09 | 6.36 | 5.64 | 5.65 | 5.74 |
| Temperature | °C | 23.3 | 23.5 | 23.3 | 23.5 | 22.6 | 23.2 | 23.1 | 23.4 |
| Conductivity | μS/cm | 46.2 | 48.7 | 48.4 | 53.8 | 40.2 | 39 | 39.3 | 39.44 |
| Nitrate-N | mg/L | 0.93 | 0.94 | 0.96 | 0.98 | 0.98 | 0.94 | 0.93 | 0.94 |
| Nitrate as NO ₃ | mg/L | 4.1 | 4.2 | 4.2 | 4.3 | 4.3 | 4.1 | 4.1 | 4.1 |
| Total Nitrogen | mg/L | 0.93 | 0.94 | 0.96 | 0.98 | 0.98 | 0.94 | 0.93 | 0.93 |
| Ammonia-N | mg/L | <0.05 | <0.05 | <0.05 | <0.05 | < 0.05 | <0.05 | <0.05 | <0.05 |
| Nitrite-N | mg/L | <0.05 | < 0.05 | <0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |

Table 6-2 Water quality results during 1,4-dioxane removal



Figure 6-3 RO Permeate TOC (µg/L) during 1,4-Dioxane Spike Experiment

The removal of 1,4-dioxane by UV/H_2O_2 and UV/HOCI are presented by Figure 6-4. Error bars shown in the figure are based on duplicate samples. In both cases, higher than target 0.5 log removals were observed, than during previous testing conducted by the City. The primary reason for this—absence of chloramines residual that decreases UV transmittance and scavenges available hydroxyl radicals.

Chemical concentration is shown in units of molarity (mili mol/L) and removal of 1,4-dioxane in log_{10} of C/Co. Showing the concentration of hydrogen peroxide and hypochlorous acid in mmol/L (10^{-3} mol/L) rather than mg/L, allows more direct comparison between the two chemicals on the extent of hydroxyl radical yield and advanced oxidation process effectiveness as shown by the extent of 1,4-dioxane removal. The results shown in Figure 6-4, indicate that even at lower concentration, UV/HOCI can provide comparable removal of 1,4-dioxane to that of UV/H₂O₂ process. This confirms that UV/HOCI has the potential to be equally effective at removal of 1,4-dioxane as UV/H₂O₂.

Further analysis of the data reveals that the dosing of HOCI at lower concentration of 0.03 mmol/L (2.1 mg/L as CI_2), provided nearly the same log removal of 1,4-dioxane as at concentration of 0.05 mmol/L (3.5 mg/L as CI_2). When dosing above 0.05 mmol/L (3.5 mg/L as CI_2) the efficiency of removing 1,4-dioxane dropped off slightly. This may be explained by the effect of additional scavenging due to change in alkalinity as well as a slight rise in the pH, which in

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turn increases the fraction of hypochlorite ion (OCI⁻). This trend is shown by Figure 6-5. Thus, the applied chemical dosing of UV/HOCI may need to be optimized to minimize an increase in alkalinity and/or pH, while providing the same level removal of the 1,4-dioxane.



Figure 6-4 Removal of 1,4-dioxane by UV/H₂O₂ and UV/HOCI



Figure 6-5 Changes in alkalinity and OCI⁻ fraction during addition of HOCI

For chemical cost comparison, chemical pricing for hydrogen peroxide and sodium hypochlorite were obtained from Orange County Water District. The cost for 12.5% wt sodium hypochlorite was \$0.58/gal and \$2.81/gal for 50% wt hydrogen peroxide. Calculated cost for the dosing used in this study are presented in Table 6-3. To achieve 1.7 log removal of 1,4-dioxane, an HOCI dose of 2.1 mg/L or H₂O₂ dose of 1.6 mg/L is needed. At these near equivalent conditions, chemical costs are quite similar at \$8.08 for HOCI and \$7.50 for H₂O₂ per 1 million gallons. The costs provided in Table 6-3 do not account for breakpoint chlorination to remove chloramines. Quenching of chloramines maybe required downstream of the UV/AOP before blending with receiving, thus it is subjective on how to compare the costs more accurately. In terms of AOP effectiveness, both UV/HOCI and UV/H₂O₂ provide similar results. This was the primary objective of the current work to establish the feasibility of using UV/HOCI and to determine, if it is at all possible to achieve appreciable removal of 1,4dioxane at exact same UV conditions, that were used during UV/H₂O₂ testing performed side by side.

| HOCI | Log | Cost | H2O2 | Log | Cost |
|--------|---------|---------|--------|---------|---------|
| (mg/L) | Removal | (\$/MG) | (mg/L) | Removal | (\$/MG) |
| 1.1 | 1.275 | \$4.23 | 1.6 | 1.778 | \$7.50 |
| 2.1 | 1.682 | \$8.08 | 2.2 | 1.957 | \$10.31 |
| 3.3 | 1.718 | \$12.70 | 3.0 | 2.018 | \$14.06 |
| 3.9 | 1.541 | \$15.01 | 4.0 | 2.338 | \$18.75 |

| Table 6-3 Chemica | I cost compariso | on for HOCI and H ₂ O ₂ |
|--------------------------|------------------|---|
|--------------------------|------------------|---|

6.3 SUMMARY OF UV/AOP PERFORMANCE TESTING

The results shown in this section show that both UV/H₂O₂ and UV/HOCI were similarly effective to provide removal of 1,4-dioxane at tested conditions. The optimal dose of HOCL appears to be approximatly 2.1 mg/l as Cl2, because larger doses are counter-balanced by increasing alkalinity and pH. Dosing of HOCI at 0.03 mmol/L (2.1 mg/L as Cl₂), provided nearly the same log removal of 1,4-dioxane as at concentration of 0.05 mmol/L (3.5 mg/L as Cl₂). Evaluation of the chemical costs also shows that the cost of using sodium hypochlorite in liu of hydrogen peroxide is comparable up to HOCI residual of 2.1 mg/L, in the absence of chloramines. At higher HOCI/H₂O₂ residuals, the UV/HOCI was slightly less effective than UV/H₂O₂, but less costly. Breakpoint chlorination to remove chloramines would increase the chemical costs of sodium hypochlorite, however, it can also provide an ancillary benefit of decreasing total nitrogen concentration in the purified water. The additional benefits of using sodium hypochlorite are that it is a more common chemical for the treatment plants and it

may not require quenching, as any left over residual would provide disinfection for conveyance pipeline.

It's also noteworthy to point out that in the absence of the chloramines residual, the observed log removals of 1,4-dioxane were significantly higher at the same test condition as previous work that evaluated indirect potable reuse, published in 2013. Current work showed greater than 1 log removal at same EED and hydrogen peroxide dose conditions, which indicates that presence of chloramines and/or associated water quality parameters, exhibits significant scavenging of hydroxyl radicals during UV/H_2O_2 process and increases both power and chemical costs.

7 Membrane Performance Evaluation

While the primary purposes of adding ozonation and biological filtration to the Advanced Water Purification (AWP) facility are to provide additional barriers for pathogens and chemicals, there are other potential benefits that may be realized by using these technologies in potable reuse applications.

Membrane fouling is a critical parameter to be considered in membrane process design (Mulder, van Voorthuizen et al. 2005). Natural organic matter (NOM) and effluent organic matter (EfOM) have been shown to be the predominant cause of physically irreversible fouling of membranes (Kimura, et al. 2004; Yamamura, et al. 2007; Yamamura, et al. 2007). Most organic foulants are hydrophobic and carry a surface charge that can interact with the surface of the membrane in a manner that can either facilitate or deter accumulation. Wastewater EfOM tends to have different properties than surface water NOM and thus can lead to different fouling behavior from organic matter in water reclamation applications than in drinking water applications. Polysaccharides and proteins are the main components of EfOM, which can result in a much more hydrophilic character than observed in surface water NOM (Zhao, et al. 2010; Tang, et al. 2011).

Ozone pretreatment has been shown to reduce the fouling associated with organic matter in membrane bioreactors (Williams and Pirbazari 2007), microfiltration membranes (Serna, et al. 2013), reverse osmosis membranes (Stanford, et al. 2011; Stanford, et al. 2013), and its application as a control option for NOM/EfOM fouling in multiple membrane systems and configurations has been extensively reviewed elsewhere (van Geluwe, et al. 2011). Biological activated carbon filtration provides an additional barrier for CECs and achieves significant reduction in total organic carbon (TOC) concentrations (30-40%) as demonstrated in this project and other past studies (Macova, et al. 2010; Farré, et al. 2011; Gerrity, et al. 2011). A lower level of TOC in the feed water to the membrane systems should reduce associated organic fouling. This chapter focuses on the effects of ozone and biological filtration pretreatment to microfiltration, ultrafiltration, and reverse osmosis membranes at AWP Facility.

7.1 EFFECTS OF OZONE/BAC PRETREATMENT ON WATER QUALITY

The effects of ozone and BAC pretreatment are perhaps best highlighted by the apparent changes in the properties and concentration of the dissolved organic matter. Ozone is known for removal of color or light absorbance as well as fluorescence of the organics. Figure 7-1 shows fluorescence excitation-emission matrices of the tertiary effluent and ozone/BAC effluent. Table 7-1 provides a summary of water quality paramters for the membranes feed water, that of tertiary effluent with no ozone/BAC and that of with ozone/BAC pretreatment.



Figure 7-1 Fluorescence EEM of (a) tertiary and (b) ozone/BAC effluents

Figure 7-1 shows very apparent changes in the total fluorescence of the ozone/BAC effluent to that of the tertiary effluent. Results presented in Table 7-1 show that ozone/BAC on average removed 88.5% of fluorescence and 71% of UV absorbance at 254. These changes were accompanied with 42.7% removal of TOC by the BAC process. These results confirm that ozone/BAC pretreatment is highly effective at transforming and achieving partial removal of dissolved organic

| | | No | With | % |
|------------------------|---------|---------------------|---------------------|---------|
| Analyte | Units | O ₃ /BAC | O ₃ /BAC | Removal |
| Total Alkalinity | mg/L | 126 | 121 | |
| Conductivity | uMHO/cm | 1667 | 1750 | |
| Nitrate as N | mg/L | 12.2 | 13.2 | |
| Ammonia-N | mg/L | 1.34 | 1.35 | |
| Nitrite as N | mg/L | 0.02 | <0.005 | |
| Total Organic Carbon | mg/L | 7.2 | 4.1 | 42.7 |
| UV Absorbance | a.u. | 0.155 | 0.045 | 71.0 |
| Total Fluorescence | a.u. | 45657 | 5260 | 88.5 |
| Aluminum | ug/L | 4.8 | 5.0 | |
| Iron | ug/L | 49.5 | 29.9 | 39.6 |
| Manganese | ug/L | 47.5 | 1.7 | 96.5 |
| Total Dissolved Solids | mg/L | 1064 | 1079 | |

Table 7-1 Water Quality of Membrane Feed Water with and without ozone/BAC pretreatment

In addition to removal of the dissolved organic matter, the ozone/BAC pretreatment provided significant removal of manganese at 96.5% and iron

removal at 39.6%, as shown in Table 7-1. Both iron and manganese are known scalants for MF and UF membranes.

Separately from analysis of tertiary feed water and after ozone and BAC, grab samples of BAC backwash water were sent for metal analysis. These data are shown in Table 7-2. Unfiltered BAC backwash water contained a variety of metals bound to suspended solids that were being removed by the BAC. The results from analysis of the filtered sample indicate the soluble fraction of the metals. These results confirm removal of manganese and iron as well as aluminum, which is a known RO membrane scalant. Removal of these scalants should play a beneficial role on downstream membrane processes.

| Parameter | MRL (μg/L) | Unfiltered | Filtered |
|------------|------------|------------|----------|
| Aluminum | 24 | 3290 | <24 |
| Antimony | 2.4 | 5.88 | <2.4 |
| Barium | 0.7 | 400 | 27 |
| Beryllium | 0.05 | 0.62 | <0.05 |
| Boron | 1.4 | 343 | 306 |
| Cadmium | 0.3 | 0.29 | <0.3 |
| Chromium | 0.5 | 12.9 | 1.1 |
| Cobalt | 0.2 | 63.4 | 0.4 |
| Copper | 2.2 | 109 | 3.1 |
| Iron | 16 | 10700 | <16 |
| Lead | 1.7 | 12 | <1.7 |
| Manganese | 0.8 | 29200 | 2.4 |
| Molybdenum | 0.3 | 13.9 | 5.8 |
| Nickel | 0.6 | 262 | 6.3 |
| Silver | 0.8 | 2.52 | <0.8 |
| Thallium | 3.1 | 26.8 | <3.1 |
| Vanadium | 0.5 | 18.1 | 2.3 |
| Zinc | 4.2 | 1600 | 27 |

Table 7-2 Water Quality of BAC Backwash water

7.2 UF SYSTEM

Prior to ozone and BAC and up until mid June 2013, the UF system was operated at the design flux of 30 gfd (gallons/ft²/day) and 95-96% recovery. Changes in specific flux for this operational period are shown in Figure 7-2. At the flux of 30 gfd, chemical clean in-place (CIP) was performed approximately every 6 months of continuous run time. The CIP was performed following manufacturer's guidelines using sodium hypochlorite and citric acid. No other additional chemical cleanings was needed. To investigate the effects of

ozone/BAC on the performance of the UF system, a baseline run at higher fluxes was also performed.



Figure 7-2 Historic changes in specific flux of UF system at 30 gfd

By isolating some of the modules, while maintaining the same flow rate, the operating flux was increased to 35 gfd, then to 41 gfd, and 50 gfd. This was performed by closing manual ball valves on the inlet and outlet of the UF modules. Changes in specific flux during this period are shown in Figure 7-3. Air scour flow rate during backwashes was lowered accordingly to account for isolated modules. At operating flux of 35 gfd for the first test run, a CIP was needed after 4.1 months. A second run at this flux, resulted in CIP interval of 3.2 months. Since, the first increase to 35 gfd was initiated without the CIP, the second run is more representative of the CIP interval. Following testing at 35 gfd, the flux was increased to 41 gfd at approximately 16,500 run hours. At this flux, CIP was performed after one month of continuous run time. Testing at 41 gfd was repeated a second time and demonstrated similar CIP interval, indicating the system can be expected to run stably. CIP cleans continued to return the temperature corrected specific flux back to the 8 to 9 gfd/psi range, which is close to the original permeability of 9.0 gfd/psi after the very first CIP performed in September of 2011.

Figure 7-4 shows test runs at 41 gfd before and after ozone and BAC became operational that were repeated twice to provide a baseline performance. At a flux rate of 41 gfd, a CIP was performed after one month of continuous run time. Testing at 41 gfd was repeated a second time and demonstrated similar CIP interval, indicating the system can be expected to run stably.



Figure 7-3 Performance of UF system at higher fluxes



Figure 7-4 Effects of ozone/BAC on performance of UF system at 41 gfd

Ozone and BAC became operational at approximately 19,000 run hours. This test spanned to a total of 2700 run hours, without needing a CIP. This result confirms that ozone and BAC had a beneficial effect on the performance of UF membranes and extended the CIP interval to 112 days (3.7 months), which comparable to the test run conditions of 35 gfd, without pretreatment. Recently the system was tested at even higher flux of 50 gfd and accumulated over 800 run hours (1.1 months) without needing a CIP. Table 7-3 provides a summary of CIP intervals during this testing. The addition of ozone/BAC pretreatment had a significant impact on extending the CIP interval of the UF system even at higher fluxes. This would potentially provide significant capital and O&M cost reductions in future installations employing this kind of membrane pretreatment.

| Operating | UF CIP Interval | | | | |
|-----------|-----------------|--------------|--|--|--|
| Flux | No ozone/BAC | W/ ozone/BAC | | | |
| 30 GFD | 6 mo | N/A | | | |
| 35 GFD | 3.2 mo | N/A | | | |
| 41 GFD | 1 mo | 3.7 mo | | | |
| 50 GFD | <1 mo | >1.1 mo | | | |

Table 7-3 UF CIP Summary

7.3 MF SYSTEM

Similar to the UF, the MF system has been operated at a flux of 29 gfd. The specific flux observed during this operational period is shown in Figure 7-5. At flux rate of 29 gfd, the system needed a CIP after approximately 9 months of continuous operation. Ozone and BAC systems became operational at approximately 20,500 run hours. Almost immediately, the trans membrane pressure (TMP) dropped, which is indicated by a slight increase in specific flux shown in Figure 7-6.

Currently the system is undergoing testing at higher operating fluxes of 40 gfd and 57 gfd. The system accumulated over 24 days of continuous operation at these conditions, with stable TMP. Though, it was too early to tell the full effects of pretreatment on CIP frequency, it is evident that the ozone/BAC pretreatment was also beneficial for operation of the MF system.



Figure 7-5 Historic changes in specific flux of MF system at 29 gfd



Figure 7-6 Effects of ozone/BAC on performance of MF system

7.4 RO SYSTEMS

Both RO trains have been operating for several years. Initial operating conditions targeted flux of 12 gfd and 80% water recovery. Figure 7-7 shows historic changes in specific flux for RO Train A (2-stage system).



Figure 7-7 Performance of RO Train A

Similarly, RO Train B (3-stage system) performance data is shown in Figure 7-8. In 2013, further analysis of the operating conditions and water quality revealed that the water recovery was overestimated by using flow meter data. After meter recalibration, both systems were readied for testing of 85% recovery. While Train B operated at 12 gfd, Train A flux was increased to 14 gfd.



Figure 7-8 Performance of RO Train B

7.4.1 RO Train A Performance

Operation of Train A at higher flux of 14 gfd and recovery of 85% and 80% occurred between 12,600 and 17,800 run hours. Change in specific flux during these conditions is shown in Figure 7-9. Operating at water recovery of 85% resulted in rapid decline of specific flux, which occurred at 14,500-15,500 run hours during summer of 2013. Several CIPs were required to restore the specific flux to previous levels prior to testing at higher recoveries and flux. Due to higher recycled water demand in the summer months, CIP was performed only on stage 2. At the same time, the water recovery was reduced to 80% in order to control rapid decline in specific flux and rise in operating pressures. A full CIP was performed at approximately 17,700 hours, which recovered some of the lost performance at higher flux and recovery. After the CIP, the system was restarted to operate at 80% recovery. The specific flux continued to decline at this recovery until the system was cleaned again at approximately 18,600 hours. After the CIP, the recovery and flux were lowered to 12 gfd and 75% recovery. Performance at this flux and recovery was much more stable and based on previous run data, CIP was expected after 8-9 months of run time. With the addition of ozone and BAC pretreatment RO train A has accumulated more than 9.4 months of continuous run time. Further testing is needed in order to observe the full change in CIP frequency.



Figure 7-9 Performance of RO Train A at higher recovery and flux

7.4.2 RO Train B Performance

Operation of Train B at higher flux of 12 gfd and recovery of 85% and 80% occurred between 6,200 and 14,900 run hours for Train B. Changes in specific flux during testing of these conditions is shown in Figure 7-10. Operating at higher recovery of 85% resulted in rapid decline of specific flux, which occurred at approximately 11,000 run hours. Based on operational data it was determined that Stage 3 was severely scaled by operating at this recovery. Due to higher recycled water demand in the summer months, CIP was performed only on stage 3 at approximately 11,750 run hours. After the CIP, the water recovery was reduced to 80% in order to control rapid decline in specific flux and rise in operating pressures. A full system CIP was performed at approximately 14,760 hours, which recovered some of the lost performance at higher flux and recovery. After the CIP, the recovery was lowered to 75%. Similar to Train A, performance at this flux and recovery was much more stable and based on previous run data, CIP was expected after 8-9 months of run time. With the addition of ozone and BAC pretreatment at approximately 16,700 run hours, RO train B has

accumulated more than 8.7 months of continuous run time. Further testing is needed in order to observe the full change in CIP frequency.



Figure 7-10 Performance of RO Train B at higher recovery

7.4.3 RO CIP Summary

Based on testing performed to date at different operating conditions, such as flux and water recovery, the Table 7-4 provides historic run hours, operating conditions, and time intervals between CIPs conducted for RO Trains A and B. Both Train A and B were operated under variable recovery and Train A also at different flux rates. Some CIP events were only on last stage and often the recovery and flux conditions were adjusted throughout the operating period, based on the available flow (limited by the MF/UF feed pump) or to minimize the chance of rapid fouling/scaling. Also, there have been no adjustments to the pH to control scaling since operations began in June 2011. The average RO feed water pH has been 7.2 over the past several years or operation.

| | | | Initial-Final | | |
|------------------|---------------------|------|---------------|-------|--------|
| RO System | Time Interval | Flux | Recovery (%) | Hours | Months |
| | Jun 2011 - Oct 2011 | 12 | 75-80% | 2245 | 3.1 |
| | Oct 2011 - Apr 2012 | 12 | 75-80% | 4020 | 5.5 |
| | Apr 2012 - Feb 2013 | 12 | 80-75% | 6304 | 8.6 |
| Train A | Feb 2013 - Aug 2013 | 14 | 85-80% | 3120 | 4.3 |
| | Aug 2013 - Nov 2013 | 14 | 80% | 2002 | 2.7 |
| | Nov 2013 - Jan 2014 | 12 | 80-75% | 945 | 1.3 |
| | Jan 2014 - Mar 2015 | 12 | 75% | 6946 | 9.5 |
| | Jun 2011 - Oct 2011 | 12 | 75-80% | 2027 | 2.8 |
| | Oct 2011 - Apr 2012 | 12 | 75-80% | 4270 | 5.8 |
| | Apr 2012 - Jun 2012 | 12 | 80-87% | 1032 | 1.4 |
| Train B | Jun 2012- Jan 2013 | 12 | 77-82% | 2425 | 3.3 |
| | Jan 2013 - Jul 2014 | 12 | 85-77% | 2003 | 2.7 |
| | Jul 2013 - Jan 2014 | 12 | 80-75% | 3038 | 4.2 |
| | Jan 2014 - Mar 2015 | 12 | 75% | 6497 | 8.9 |

Table 7-4 RO Operation and CIP Summary

Based on the analysis of data collected to date, approximate CIP intervals at different recovery conditions were determined and are presented in Table 7-5. The outlined CIP interval estimates assume operation at close to 12 gfd, with no pH adjustments of the feed water. As can be seen from Table 7-5, operating at recovery higher than 80%, may significantly reduce the CIP intervals, while operation at below 80% significantly extends the run time. Operating at a recovery of 75% extends the CIP interval to every 6-9 months. With the addition of ozone/BAC pretreatment, that provides removal of organics, manganese, iron, and possibly aluminum, the CIP intervals demonstrated in this project were longer than 9 months of continuous operation. The addition of sulfuric acid to control scaling could potentially extend the CIP interval, when operating at higher recovery.

Table 7-5 RO CIP Intervals

| | 85% | 1-2 months |
|-------------------|-----|------------|
| Tertiary-MF/UF-RO | 80% | 2-3 months |
| | 75% | 6-9 months |
| With O3/BAC | 75% | >9 months |
| | | |

7.5 RO MEMBRANE AUTOPSY

As discussed in previous section, the RO elements in both Train A and Train B have been in use since June 2011 and have been subjected to operation under various recoveries and have had 6 CIP events. Testing at higher recoveries has resulted in significant flux loss, which could not be recovered by cleaning with standard chemicals such as pH 10 solution of sodium hydroxide (NaOH) and 2% citric acid solution. Following manufacturer's guidelines, more aggressive chemical cleans with longer soak periods were performed during the last CIP event on each train. However, since full recovery of specific flux was not observed, then some irreversible foulant/scalant still remained on the membranes. To investigate the nature of the foulant/scalant material, lead membranes from first stage and last element from last stage were harvested from both RO trains for an autopsy in October 2014.

7.5.1 Wet Testing of RO Membranes

To identify which elements showed greatest loss in permeability, all 7 elements in first and last vessel of Train A and one vessel from each stage of Train B were extracted and wet tested at Avista Technologies laboratory to determine membrane permeability and salt rejection. Table 7-6 and Table 7-7 show results of the wet testing of RO elements from each train. Serial numbers shown in bold were selected for membrane autopsy and foulant/scalant characterization described in the following sections.

| Train A | Serial Number | Factory (GPD) | Oct. 2014 (GPD) | % Change in Permeability | Factory Salt Rejection (%) | Oct. 2014 Salt Rejection (%) | % Change in Rejection |
|-------------|------------------|------------------|--------------------|-----------------------------|-------------------------------|---------------------------------|--------------------------|
| | SOY35615 | 10351 | 6034 | -41.7% | 99.6 | 99.2 | 0.4 |
| STACE 1 | SOY35025 | 9827 | 5242 | -46.7% | 99.6 | 99.2 | 0.4 |
| | SOY34195 | 9426 | 5443 | -42.3% | 99.6 | 99.2 | 0.4 |
| Vossol #1 | SOY34875 | 10430 | 5760 | -44.8% | 99.6 | 99.2 | 0.4 |
| vessei#1 | SOY35325 | 9674 | 5645 | -41.6% | 99.6 | 99.2 | 0.4 |
| | SOY33555 | 10427 | 3730 | -64.2% | 99.6 | 99.2 | 0.4 |
| | SOY34325 | 9482 | 4507 | -52.5% | 99.5 | 99.2 | 0.3 |
| | SOY32235 | 10262 | 5270 | -48.6% | 99.5 | 99.2 | 0.3 |
| | SOY35145 | 9827 | 5918 | -39.8% | 99.6 | 99.2 | 0.4 |
| STACE 2 | SOY32245 | 10844 | 5890 | -45.7% | 99.6 | 99.2 | 0.4 |
| STAGE 2, | SOY34545 | 9656 | 5846 | -39.5% | 99.5 | 99.2 | 0.3 |
| vessei # 14 | SOY34085 | 9488 | 6077 | -36.0% | 99.6 | 99.1 | 0.5 |
| | SOY34435 | 9827 | 5443 | -44.6% | 99.5 | 98.7 | 0.8 |
| | S0735015 | 9858 | 3283 | -66.7% | 99.6 | 98.0 | 1.6 |

 Table 7-6 Train A Permeability and Salt Rejection of Lead and Tail Vessels

The results from the October 2014 testing were compared to results of new membranes tested at the factory. The results are shown in Table 7-6 indicate that RO elements in Stage 1 and Stage 2 of RO Train A have moderate loss of permeability as well as decrease in salt rejection. Both trends are not uncommon

for older membranes, however, what is particularly interesting is that the loss in permeability on average is very similar between both Stage 1 and Stage 2. This would suggest that both fouling of the lead stage and scaling of the last stage have occurred.

Similarly, RO membranes were pulled from each stage on Train B to perform wet testing. Table 7-7 shows the results from permeability and salt rejection testing. In contrast to the 2-stage Train A, Sage 1 and 2 show moderate loss in permeability and stage 3 showing significant loss in permeability. These would indicate that scaling material has accumulated on 3rd Stage, which may require more frequent cleaning. In addition, higher loss in salt rejection was also observed on the last elements of Stage 3.

| Train B | Serial Number | Factory (GPD) | Oct. 2014 (GPD) | % Change in Permeability | Factory Salt Rejection (%) | Oct. 2014 Salt Rejection (%) | Change in Rejection |
|------------|------------------|------------------|--------------------|-----------------------------|-------------------------------|---------------------------------|------------------------|
| | 101122325 | 11969 | 8352 | -30.2% | 99.8 | 99.3 | 0.5 |
| | 101122328 | 11981 | 9979 | -16.7% | 99.8 | 99.3 | 0.5 |
| STAGE 1, | 101122317 | 11493 | 9994 | -13.0% | 99.7 | 99.1 | 0.6 |
| Vessel #1 | 101122327 | 12094 | 10080 | -16.7% | 99.8 | 99.3 | 0.5 |
| | 101122315 | 11106 | 10368 | -6.6% | 99.8 | 99.5 | 0.3 |
| | 101122335 | 12165 | 10181 | -16.3% | 99.8 | 99.4 | 0.4 |
| | 101122347 | 11988 | 10123 | -15.6% | 99.8 | 99.4 | 0.4 |
| | 101122353 | 11961 | 10555 | -11.8% | 99.8 | 99.3 | 0.5 |
| STAGE 2, | 101122346 | 13345 | 10224 | -23.4% | 99.8 | 99.3 | 0.5 |
| Vessel #12 | 101122331 | 12816 | 10253 | -20.0% | 99.8 | 99.3 | 0.5 |
| | 101022404 | 15094 | 10267 | -32.0% | 99.7 | 99.3 | 0.4 |
| | 101130093 | 12777 | 11606 | -9.2% | 99.8 | 99.3 | 0.5 |
| | 100930289 | 12698 | 10584 | -16.6% | 99.8 | 99.4 | 0.4 |
| | 100930301 | 13340 | 10109 | -24.2% | 99.8 | 99.4 | 0.4 |
| STAGE 3, | 100930302 | 13189 | 4133 | -68.7% | 99.8 | 98.5 | 1.3 |
| Vessel #20 | 100930419 | 13138 | 2304 | -82.5% | 99.7 | 97.7 | 2.0 |
| | 100930385 | 10993 | 1253 | -88.6% | 99.8 | 96.5 | 3.3 |
| | 100930418 | 13089 | <720 | >94.5% | 99.7 | N/A | N/A |

Table 7-7 Train B Permeability and Salt Rejection of Lead and Tail Vessels

Membranes from both RO Trains A and B showed significant loss in permeability, however, Train A on average had higher percent change from factory testing. This may be due to a longer cumulative operating period and due to operation at more aggressive flux of 14 gfd. At the time of the harvesting, Train A had accumulated 23,302 run hours, while B had 18,825 run hours. Thus, Train A had run for 6 months longer.

7.5.2 Fujiwara Test

Fujiwara test was conducted to determine if the membrane samples had been exposed to an oxidizing halogen, such as chlorine, bromine, or iodine. The test analyzes qualitatively whether halogens have become part of the polyamide polymer structure through oxidative attack. The test results were positive for all tested elements, indicating oxidative damage had occurred. This may explain observed loss in salt rejection discussed in section 7.5.1.

7.5.3 Dye Testing

After the Rhodamine B was applied to the active layer, the support layer was completely clean for all of the element samples, indicating that no leakage occurred. The results of dye testing showed that none of the membrane elements experienced mechanical damages.

7.5.4 Microscopy Analysis

The lead position element from the 1st stage of each train and the last position element of the last stage of each train were submitted for additional analysis of floulant/scalant materials on the membrane surfaces. These elements re highlighted in bold in Table 7-6 and Table 7-7. While Avista Technologies performed the primary analysis, additional analyses were performed at New Mexico State University. Copies of full reports from each laboratory are provided in Appendices. Discussion and highlights of these results are provided below.

A summary of the analyses by scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) are provided in Table 7-8. SEM analysis of the lead elements from both RO trains showed relatively clean surface with patches of some aluminum silicate particles. SEM analysis of the tail elements showed heterogeneous fouling layer and identified strong presence of calcium phosphate.

| S/N SOY35615 | S/N SOY35015 | S/N 101122325 | S/N 100930418 |
|---|---|---|---|
| Train A-Lead | Trains A-Tail | Train B-Lead | Train B-Tail |
| Membrane surface had a few small Al- silicate particles and a very thin layer of aluminum silicates. | Heavy presence of calcium phosphate deposition and presence of magnesium and aluminum. | Membrane surface had a few small Al- silicate particles. | Heavy presence of calcium phosphate deposition on membrane surface with small amount of magnesium. |

Table 7-8 Summary of SEM/EDS Analyses

Chromatic Elemental Imaging (CEI) identified isolated patches of organic foulants, presence of iron and aluminum hydroxide particles on both lead elements, as shown in Figure 7-11. For both tail membrane elements, CEI showed presence of calcium phosphate as primary scalant.



Figure 7-11 Chromatic Elemental Images of RO membranes

7.5.5 Membrane Foulant and Scalant Characterization

In addition to microscopy analyses, foulants were extracted from membrane surfaces to quantify the elements of the foulants and scalants on a larger area than SEM/EDS/CEI scanning. Deionized water, 0.8M HNO₃ solution, and 0.1 M NaOH solution were used as extractants. Membrane specimens (50 cm²) taken from the middle section of each membrane sample were cut into small pieces, soaked in 100 mL deionized water, 100 mL of 0.8 M HNO₃, and 100 mL of 0.1 M NaOH. These were then sonicated for 30 min in a typical laboratory sonication bath. Standard inorganic elements of the extracted solutions were analyzed using inductive coupled plasma (ICP) mass spectrometer (MS) and ion chromatography (IC). Total organic content of the solutions was analyzed using a total organic carbon (TOC) analyzer. Protein and humic or fulvic-like substances were analyzed using F-EEM spectroscopy.

The TOC and ICP-MS results of extracted foulant material showed that the lead membranes from Train A (SOY35615) and Train B (101122325) have much less organic fouling and inorganic scaling than the tail membranes (Train A Tail=SOY35015) and (Train B Tail=100930418). Membranes of the tail-end elements were mainly fouled by the precipitation of calcium phosphate with small

amount of magnesium and trace amount of Al, Sr, Ba. This is consistent with the SEM/EDS and CEI.

7.5.6 Cleaning Studies

Flat sheet membrane samples (harvested from the full element) were placed in a cell test apparatus and cleaned with various Avista chemicals to determine the most effective cleaner combinations and the amount of time required for an effective cleaning. In addition, a whole element, from each train was tested by King Lee Technologies (KLT), using specialty cleaning solutions. The full reports from both cleaning studies can be found in the Appendices.

Results from flat sheet cleaning study indicated that both specialty cleaning agents and generic ones effectively restored permeability of both lead and tail elements of Train B membranes. Specifically, cleaning with citric acid followed by sodium hydroxide solution performed similarly to Avista's P303 and P111 cleaners. In contrast to Train B, the specialty cleaners more effectively cleaned Train A membranes. In addition, higher increases in salt transport were observed in Train A membranes, than Train B after the cleaning. This maybe attributed to a combination of higher cumulative foulant material over longer service period and the relative extent of oxidation damage between the two RO trains.

Whole elements that were in vessel position next to the tail elements, were tested independently at KLT laboratory using 5 different cleaning agents. Specialty cleaner KL-1000 was found effective for restoring performance of tail element from Train B, which was heavily scaled by calcium phosphate. For Train A, a specialty cleaner DiamiteBFT, which targets a variety of organic and colloids was most effective. Similar to the flat sheet testing performed by Avista, more effective cleaning of Train A membrane resulted in marked increase of salt transport.

The results of these cleaning studies should be considered for future CIPs. The primary scalant in the form of calcium phosphate can be effectively cleaned with acid cleaners, including commonly used citric acid, especially for the third stage of Train B. For Train A, moderate cleaning procedures with shorter soak times should be attempted first, before performing more aggressive cleanings in order to minimize the increase in salt transport.

7.6 RO VESSEL CONDUCTIVITY MONITORING

RO vessel permeate conductivity was monitored monthly for both RO trains and is shown in Figure 7-12 and Figure 7-13. Historically conductivities of all vessels in both trains have been increasing over time, which is not uncommon and correlates to the overall salt rejection of the whole train. During membrane harvesting in October of 2014, significant wear was observed in the pressure vessel seals and permeate interconnector o-rings of both RO systems. Figure 7-14 shows a photo of an o-ring on the permeate interconnector as example.



Figure 7-12 Vessel Conductivity for RO Train A



Figure 7-13 Vessel Conductivity for RO Train B

The type of damage illustrated by Figure 7-14 is a result of long-term exposure to chloramines of lower grade of EPDM materials (such as sulfur-cured EPDM) commonly used by the industry. Several studies identified that peroxide-cured EPDM material offers significantly higher resistance to chloramines and is commercially available. After changing to new seals, a marked improvement in vessel conductivities was observed in both Trains as shown in Figure 7-12 and Figure 7-13.



Figure 7-14 Permeate Interconnector O-ring

7.7 SUMMARY

Ozone and BAC pretreatment resulted in significant total organic carbon, complex organics (i.e. UVT), and manganese removal. This allowed the UF membrane system to be operated at a higher flux without necessitating more frequent cleans. At operating flux of 41 gfd, ozone and BAC pretreatment extended the run time by at least 3.75 times. At 50 gfd, the UF system accumulated over 1.1 months, without change in TMP. The MF system has accumulated over a week of operation at 55 gfd, with minimal changed in TMP. These results indicate significant cost savings of reduced energy and chemical use as well as operator staff hours to carry out fewer CIPs can be realized from the ozone/BAC pretreatment. In addition, ozone and BAC pretreatment can reduce the capital cost of membranes by reducing the required membrane area for the design flow. Further testing of RO membranes is needed to determine if similar benefits can be observed.

After nearly 3 years of continuous operation, significant wear was observed in the pressure vessel seals and permeate interconnector o-rings of both RO systems. Seal degradation was a result of long-term exposure to chloramines of lower grade of EPDM materials (such as sulfur cured EPDM) commonly used by the industry. It is recommended to switch to peroxide cured EPDM material that offers higher resistance to chloramines and is commercially available.

The results of the membrane autopsy testing utilized a variety of analytical tools that independently confirmed strong presence of calcium phosphate and traces of aluminum hydroxide. This is not uncommon phenomenon that has been observed at other potable water reuse facilities. Operation at higher recovery can exacerbate scaling. Both RO trains have been subjected to testing at higher recovery without adjustment of feed water pH, resulting in more rapid scaling.

While the solubility of calcium phosphate can be addressed by lowering the pH of the feed water and/or by additional removal through the wastewater treatment, aluminum is not easily addressed by pH alone and would require alternative solutions, when operating at higher recovery rates (e.g. 85%). Control of these limiting scalants for achieving higher recovery rates should be tested further in order to determine optimal design conditions for the full-scale facilities.

8 Ozone and BAC Pretreatment Cost Impacts

The addition of ozone disinfection and BAC filters will add additional construction cost to a 30 MGD full-scale advanced water purification facility at the North City location. The following section presents an analysis of the additional treatment costs as well as potential offsets in the capital and O&M costs offered by the enhanced water quality produced with Ozone/BAC pretreatment.

8.1 CAPITAL COSTS

A finalized TM was provided to the City of San Diego on June 9th 2014 entitled, "Potential Treatment Additions for Direct Potable Reuse at the North City Water Reclamation Plant and Harbor Drive Facilities." This TM provides the cost basis that will be further developed in this extended testing report.

The flow rates and capital costs for this analysis were developed using the criteria provided in Table 8.1. This table assumes a recovery of 99.8% for the Ozone/BAC, 95% for membrane filtration (MF), and 85% for the RO process.

| Location | Flow, MGD |
|------------|-----------|
| Ozone/BAC | 37.2 |
| MF Feed | 37.2 |
| RO Feed | 35.3 |
| Pure Water | 30.0 |

Table 8-1 Assumed Design Flow Conditions

Based on the flow rates above, a Class 5 opinion of probable construction cost was prepared for each unit process as presented in Table 8.2. The membrane filtration system cost was reduced by 33% due to the enhanced performance discussed in Chapter 7. Although the improvements in membrane filtration performance did significantly reduce the construction cost of this step in the advanced treatment train, there is still a net additional cost associated with the ozone disinfection and biological filtration processes. A 30% contingency is recommended by the Association for the Advancement of Cost Engineering International for a Class 5 estimate. The AWPF costs for producing purified water is estimated at \$169.5M while the AWPF costs with ozone/BAC pretreatment are \$192.6M. With or without the ozone/BAC pretreatment, these AWPF cost estimates have been prepared with adequate unit process treatment capacity to maintain 30 MGD of production year round and do not include any necessary conveyance or treatment facilities beyond the AWPF.

| Linit Process | Canacity MGD | No Pretreatment | | O ₃ /BAC Pretreatment | | |
|--|--------------|------------------------|-------|----------------------------------|-------|--|
| | | Construction Cost, \$M | | | | |
| Ozone disinfection | 37.2 | | - | \$ | 11.1 | |
| Biological activated carbon filtration | 37.2 | | - | \$ | 23.4 | |
| Membrane filtration | 35.3 | \$ | 49.4 | \$ | 32.6 | |
| Reverse osmosis | 30.0 | \$ | 60.0 | \$ | 60.0 | |
| Ultraviolet with Advanced Oxidation | 30.0 | \$ | 10.5 | \$ | 10.5 | |
| Post-treatment | 30.0 | \$ | 10.5 | \$ | 10.5 | |
| Subtotal | - | \$ | 130.4 | \$ | 148.2 | |
| Contingency, 30% | | \$ | 39.1 | \$ | 44.4 | |
| Total | | \$ | 169.5 | \$ | 192.6 | |

Table 8-2 Capital Cost for the Advanced Water Purification Facility

Estimates of the operational and maintenance (O&M) costs were prepared based on the full-scale Orange County Water District's Groundwater Replenishment System (GWRS) and presented in Table 8-3. Although power data was collected from the Demonstration Facility and is presented in the **Section 8.2**, it was determined that there were significant inefficiencies with the Demonstration plant design that would not occur at a full-scale facility. In particular, the feed pumps to the AWPF require adequate pressure (>20 psi) to be maintained ahead of a pressure-reducing valve (PRV) to maintain the flow setpoint. Immediately downstream of this PRV, feed pumps then re-boost the feed pressure to the MF and UF membrane systems. The full-scale facility will not have multiple pumping locations with intentional reduction in pressure, such as through a pressure relief valve. There are other inefficiencies with the Demonstration Facility, such as onsite oxygen generation with a pressure swing adsorption system, that will not occur at the full-scale. As a result, the power estimates in Table 8-3 have been developed using data from full-scale facilities.

Observing Table 8-3, additional power and chemical will be required with ozone/BAC pretreatment. The power comes from the need to generate ozone, transfer it into solution, and provide additional pumping for BAC filtration. The additional chemical costs come from liquid oxygen (LOX) that must be delivered to maintain ozone production. Although the power and chemical costs are higher with ozone/BAC pretreatment, the replacement and repair costs were significantly reduced because there are fewer membrane modules to repair and replace every 10 years. Both facilities will be highly automated, but additional meters are required for the advanced treatment train without dilution water requirements and additional maintenance costs are assumed for this treatment train. Although operational cost savings may also be realized (i.e. reduced chemical and power costs), there was not enough data generated at the end of this extended testing project to estimate those savings. At this point, chemical consumption for the AWPF is assumed unchanged with the additional monies for oxygen for the ozone pretreatment. Additional months of operation at increased flux conditions are necessary to quantify the potential chemical savings.

| | No P | retreatment | O ₃ /B/ | AC Pretreatment | | |
|------------------------|-----------------|-------------|--------------------|-----------------|--|--|
| | Annual O&M, \$M | | | | | |
| Power cost | \$ | 7.0 | \$ | 7.1 | | |
| Chemical cost | \$ | 2.3 | \$ | 2.6 | | |
| Labor cost | \$ | 6.0 | \$ | 6.0 | | |
| Replacement and repair | \$ | 2.8 | \$ | 2.4 | | |
| Maintenance | \$ | 1.3 | \$ | 1.7 | | |
| Total | \$ | 19.4 | \$ | 19.7 | | |

Table 8-3 Annual O&M for the Advanced Water Purification Facility

*Assumed power cost \$0.13/kWh

8.2 DEMONSTRATION POWER MONITORING

The demonstration facility has power-monitoring devices to track the power consumption for most of the major process equipment items. Table 8-4 presents the average power as well as production for each unit process and reports the outcome from the extended testing period as kWh/MG. The results of the extended testing are also directly compared to the prior values reported in the Demonstration Project final report for the San Vicente Reservoir.

 Table 8-4 Summary of Power Usage in Treatment Train

| | Daily | Average | Power Use per Treated Flow (kWh/MG) | |
|---|--------------------------|-------------------------|--|---------------------------------|
| Treatment Process & Auxillary Equipment | Power Usage (kWh/day) | Treated Volume (MGD) | Extended Testing | IPR Demonstration Project |
| Ozone Feed Pump | 496 | 1.5 | 331 | - |
| Oxygen Generation and Cooling | 824 | 1.5 | 549 | - |
| Ozone Generator | 533 | 1.5 | 356 | - |
| BAC Valves & Control Panel | 9 | 1.5 | 6 | - |
| Filter Backwash & Air Scour | 0.2 | 0.065 | 2 | - |
| Pretreatment Total | 1,863 | 1.5 | 1,242 | - |
| MF/UF Feed Pump | 528 | 1.5 | 352 | 899* |
| MF Monitor | 62 | 0.75 | 83 | 171 |
| UF Monitor | 319 | 0.74 | 433 | 404 |
| Train A Power | 868 | 0.52 | 1,676 | 1600 |
| Train B Power | 734 | 0.49 | 1,508 | 1700 |
| UV power | 317 | 0.99 | 321 | 300 |
| AWPF without 03/BAC Pretreatment | 2,827 | 0.99 | 2,856 | 3200 |
| AWPF with O3/BAC Pretreatment | 4,690 | 0.99 | 4,737 | - |

*Average of estimated energy use for MF/UF pumping

Most of the major process units exhibit similar power draw through the extended period as observed in the previous project (see Table 8-4). The only discrepancy is between the MF/UF feed pump, which was previously a calculated value.
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Through the Extended Testing project, power meters were installed to monitor the transfer pump that delivered the ozone/BAC product water to the MF/UF system and reflects a more efficient condition. The ozone system power summary does an excellent job at documenting the Demonstration Facility's power conditions, but these data are not representative of full-scale conditions. Two major items will be different that impact the power draw significantly:

- 1) Pressure swing adsorption with an air compressor is used to generate oxygen gas where the full-scale facility will have liquid oxygen delivered
- 2) A sidestream induction of ozone gas will be used to transfer ozone into the water where the demonstration facility used "full flow" to reduce the complexity at this scale

9 Summary & Conclusions

A 1.5 MGD ozone and biological activated carbon (BAC) facility was designed, installed, and operated to evaluate the benefits in water quality and determine the impacts on the downstream full advanced treatment. The ozone/BAC pretreatment was selected to enhance redundancy and robustness to develop a treatment train with adequate reliability to eliminate the requirement for dilution water. Ozone is a powerful disinfectant and oxidant that is capable of inactivating microbes and providing destruction of many organic constituents. The performance of ozone/BAC pretreatment was quantified with more than 19,500 laboratory analyses were performed as part of this 22-month study.

Over 11,000 measurements were collected for presence of compounds of emerging concern, disinfection byproducts, and supporting water quality measurements. This study demonstrated that ozone/BAC process *met the requirements* established by DDW for an advanced oxidation process in the final 2014 Groundwater Replenishment Reuse regulations. This means that not only does the ozone process provide a redundant (i.e. additional) disinfection barrier to enhance reliability, but it also serves as a redundant barrier to prevent any unanticipated spikes in influent organic concentrations from being able to carry through and impact the RO permeate water quality. Ozone/BAC pretreatment also significantly reduced the TOC concentration in the RO permeate. In summary, the additional pretreatment enhanced reliability through treatment redundancy and robustness, meeting disinfection goals as well as contaminant removals, which potentially would allow implementation of future potable reuse projects without a dilution water requirement.

In addition to the significant improvements in water quality of the feed water to downstream membranes, the removal of trace organic constituents such as pharmaceuticals, endocrine disruptors, flame-retardants, and personal care compounds before the RO membranes, significantly minimizes concentrations of these constituents in the RO concentrate.

Ozone/BAC pretreatment enhanced the sustainable membrane flux for both: the microfiltration and ultrafiltration processes. The cleaning interval for the UF system was increased from 1 month to 4 months with the ozone/BAC pretreatment in service at a flux of 41 gfd. The enhanced membrane performance provides two significant cost savings for a future full-scale membrane filtration system:

- 1) A reduced capital cost with fewer membrane modules being required to maintain production capacity
- 2) A reduced O&M cost with fewer chemical cleanings and lower pressures being maintained.

For this project, a capital cost savings was estimated to be 33% for the membrane filtration system and no reduction in O&M costs were assumed. Even with the reduction in membrane filtration system costs, the AWPF with ozone/BAC pretreatment cost \$23.1 million in additional construction costs. Although O&M savings are anticipated, additional long-term data is needed to quantify any O&M savings and these data should be developed in future projects to support the full-scale cost estimates.

This project demonstrated the feasibility of using sodium hypochlorite in lieu of hydrogen peroxide to drive the AOP process with UV light and also evaluated the overall economics of the pretreatment process. The results indicated that UV/HOCI could provide similar log removals at approximately equivalent chemical cost, in the absence of chloramines. Breakpoint chlorination would increase the chemical costs of sodium hypochlorite, however, it can also provide an ancillary benefit of decreasing total nitrogen. Sodium hypochlorite is a less hazardous chemical than hydrogen peroxide and any left over residual after AOP would be in the form of HOCI, which would ensure disinfection for the pure water in the conveyance pipeline.

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11 Appendices

Appendix A: Membrane Autopsy Reports by Avista Technologies Appendix B: Membrane Autopsy Reports by NMSU Appendix C: RO Cleaning Study by King Lee Technologies



Appendix A: Membrane Autopsy Reports by Avista Technologies



Membrane Autopsy Report

Completed for:

Trussell Technologies North City Water Reclamation Serial Number SOY35615 Position A-1-1 - Lead Element Hydranautics ESPA2-LD

11/07/2014 WO#101614-2

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Executive Summary

Background

Trussell Technologies provided thirty-two reverse osmosis (RO) elements to Avista Technologies for wet testing with four of the elements designated for full membrane autopsy. Element Serial Number (SN#) SOY35615 was removed from position A-1-1 in the RO system and was a Hydranautics ESPA2-LD model.

Initial Element Testing

Element SN# SOY35615 produced lower than normal flow (71% of normal), lower than normal rejection (99.2%) and a delta pressure of 3 psi during baseline wet testing.

External Inspection

No damage to the external components including the fiberglass casing, anti-telescoping devices (ATDs), permeate tube and brine seal was detected during the external inspection. The element also passed integrity testing indicating that there was no damage to the internal mechanical components of the spiral-wound element.

Internal Inspection and Testing

Both scroll ends were discolored (brown). Large foulant debris (black shavings, white orange brown flakes, metal mesh) was visible on the feed scroll end (brine seal end), especially concentrated on the outer radius. The concentrate scroll end was virtually free of large. Slight telescoping (shifting of internal components) was also observed during the scroll end examination. The majority of the exposed membrane surfaces were lightly coated with brown foulant; black and orange particles which were observed near the feed end of the element. The feed spacers, glue lines and permeate spacers were in good condition; however, the element tested positive for the presence of halogens (e.g. chlorine) in the membrane structure.

Cell Testing Results

Flat sheet samples harvested from both the feed and concentrate ends of the element produced 73% of normal water passage and 125% of normal salt passage.



Foulant Analysis

The loss on ignition, foulant density measurement and zeta potential testing could not be performed due to the lack of removable foulant. Acid testing was negative, suggesting that any carbonates present were below the visual detection limit. Microscope analysis of foulant that could be scraped from the membrane surface identified a mixture of amorphous organic material, fungi, Gram negative bacteria, algae and Gram positive bacteria. Fourier Transform Infrared (FT-IR) spectrum of the membrane surfaces identified mainly bands associated with the membrane itself and with organic material (primarily carbohydrates).

The Energy Dispersive X-ray (EDX) analysis identified iron and trace aluminum on the feed end of the element. Only trace silicon and aluminum were detected on the concentrate end. The Scanning Electron Microscope (SEM) images showed isolated patches of smooth and granular material on both the feed and concentrate scroll ends. Particles were also randomly dispersed across both end of the membrane. Chromatic Elemental Imaging (CEI) confirmed that the patches were composed of organics by displaying a high concentration of carbon. The granular material and particles present on the feed end was composed of iron oxides and aluminum hydroxides. Some of the isolated patches on the concentrate end were composed of clay (aluminum silicates) and aluminum hydroxide.

Cleaning Study

Flat sheet samples harvested from the full element were cleaned using RoClean P303 followed by RoClean P111 (each cleaner at 2% by weight), hydrochloric acid (HCl pH 2.5) followed by sodium hydroxide (NaOH pH 11.5) and citric acid (pH 2.5) followed by sodium hydroxide (pH 11.5). All cleaning solutions were heated to approximately 35°C and allowed to circulate for two hours. The RoClean P303/RoClean P111 cleaners increased water passage within the manufacturers range. The HCl/NaOH cleans increased water passage to 92% of normal water passage and the citric acid/NaOH cleaners brought water passage up to 85% of normal.



Initial Element Test Results

Element Weight

Because element weight is often indicative of the degree of fouling, elements are weighed prior to the autopsy.

SN# SOY35615 weighed 32 pounds; new eight inch elements weigh approximately 30 to 35 pounds.

Wet Test

The element was wet tested on dechlorinated San Marcos, CA city water. Wet test results were normalized to the manufacturer's published test conditions.

| Hydranautics ESPA2-LD | Flow | Rejection | Pressure Drop |
|-------------------------------|--------------|--------------|---------------|
| | (gpm) | (%) | (psi) |
| SN# SOY35615 | 4.18 | 99.2 | 3 |
| Manufacturer's Specifications | 5.90 to 7.90 | 99.5 to 99.6 | ≤10 |



Element Wet Testing



Integrity Test

To determine if a membrane performance problem is possibly caused by mechanical damage, membranes are tested to check for vacuum decay that may indicate abnormal bypass.

In this test a vacuum of about 22 inches Mercury (in. Hg) is applied to the permeate side of the membrane for a duration of 120 seconds. If over 35% of the vacuum is lost within a 120 second period, then the membrane can be said to have severe physical damage.

SN# SOY35615 passed integrity testing.



Integrity Test Results for SN# SOY35615



External Inspection

The external inspection of a membrane element is an important step in the autopsy process. Physical damage to the exterior components can contribute to performance issues in the element or may yield clues as to the operating conditions of the membrane system that led to poor membrane performance. As most of the external components are damaged during the autopsy process, documenting any significant finds before further work is completed is essential.

This section covers the fiberglass casing, anti-telescoping devices (ATDs), permeate tube, and brine seal. In addition the scroll ends are also examined for any foulant/scale material that may be interfering with flow and for feed spacer extrusion also known as telescoping and gapping in the scroll end which may cause localized scaling (uneven hydraulics).

Spiral-Wound Membrane Element Construction







Fiberglass Casing

The fiberglass casing is an integral part of each element. The purpose of this wrap is to protect the element from external differential pressure, provide compressive strength to prevent telescoping and to ensure that the various membrane components are held in their correct position for optimum performance. Damage to the wrap can be an indication of rough handling or damage from excessive differential pressure across the membrane surface.

The fiberglass casing was in good condition although green foulant was visible on one portion of the casing.



Fiberglass Casing for SN# SOY35615

Brine Seal

The purpose of the brine seal is to seal against the inside diameter of the pressure vessels and the outside diameter of the membrane to ensure that all the feed water passes through the membrane element. Chevron type seals are used to aid in membrane loading and to seal to a variety of pressure vessel inside surfaces.

No damage to the brine seal was detected during the external inspection.

Permeate Tube

At the center of each membrane element is a round section of pipe that is called the permeate tube. Down the length of the tube, holes are drilled through the pipe wall to the tube center. This tube is bonded to the membrane leaves and permits water to flow from the leaves outward at each end of the full element and the through the holes for collection. To function properly, the permeate tube must be free from gouges or damage that can prevent proper o-ring sealing at each end. Poor sealing can result in bypass from the highpressure feed/concentrate flow into the permeate stream.

The permeate tube was free from damage which could allow for the bypass of feed water into the permeate stream.



Anti-Telescoping Device (ATD)

When assembled at the factory, membrane elements are commonly fitted with Anti-Telescoping Devices (ATDs) at each end of the element. These devices are designed to prevent telescoping of the membrane leaves under normal operating conditions that can cause membrane damage.

The feed and concentrate anti-telescoping devices (ATDs) were in good condition and free from physical damage.



Image of feed ATD (left) and concentrate ATD (right) for SN# SOY35615



Internal Inspection & Testing

Scroll End Examination

Once the anti-telescoping devices are removed, the scroll ends of the membrane leaves are examined for presence of colloidal particles, biofouling, feed spacer extrusion and membrane gapping. In addition, each scroll end is examined for the gradual axial shift of the element leaves from outer diameter of the element towards the permeate tube. This type of damage is termed "telescoping" and is caused by the development of high differential pressure (usually greater than 10 psi) across the element.

Large foulant debris (black shavings, white orange brown flakes, metal mesh) was visible on the feed scroll end, especially concentrated on the outer radius. The concentrate scroll end was virtually free of visible foulant. Slight telescoping was also observed during the scroll end examination.



Image of feed scroll end (left) and concentrate scroll end (right) for SN# SOY35615

Membrane Surface Visual Examination

When assembled, the surface of the membrane is a uniform, shiny surface with no visual contamination or impurities. Although the membrane surface contamination can be sometimes hard to detect visually many times contamination is very visible and easy to detect with the naked eye.

The majority of the membrane surfaces were lightly coated with a brown colored foulant material. The feed end contained large black and orange colored debris.





Exposed membrane surface for SN# SOY35615



Exposed membrane surface from feed end for SN# SOY35615





Close up image of black and orange particles observed near the feed end

Feed Spacer Visual Examination

The feed spacer is a plastic net material designed to separate membrane surfaces to form a flow path and to promote turbulence within feed water channel.

The feed spacers were free of foulant debris.



Glue Line Integrity Examination

Membrane leaves are glued on three sides to separate feed and permeate streams. Glue lines are inspected to ensure that there are no sections of unbounded material referred to as glue flaps that may block the feed channel into the element module. In some worst case situations, glue lines may fail at the feed end of the membrane permitting contamination. The glue lines are also inspected for pouching and delamination which often occur on the concentrate end of last stage elements. This type of physical damage may indicate permeate backpressure caused by positive pressure on the permeate side of the membrane.

The glue lines were in good condition and free of pouching, delamination and glue flaps.

Permeate Spacer Visual Examination

Permeate spacer provides a path for permeate flow to channel towards the central permeate tube which minimizes permeate-side pressure losses.

The permeate spacers were in good mechanical condition and free of visible foulant contamination.



Testing for the Presence of Oxidizing Halogens

The Fujiwara test is used to confirm that a polyamide (PA) thin-film membrane has been exposed to an oxidizing halogen, such as chlorine, bromine, or iodine. This test analyzes whether halogens have become part of the polymer structure through oxidative attack. Please note that the Fujiwara test is a qualitative test and that any color change indicates the presence of a halogen in the membrane structure. However the test does not quantify the amount of exposure or which exact halogen is attached.

Fujiwara testing was positive for the presence of halogens (e.g. chlorine) in the membrane structure.



Example of negative (left) and positive (right) Fujiwara color change



Cell Test for Permeate Flow & Salt Passage

To determine membrane performance characteristics membrane samples are tested in a cell test apparatus (CTA). The water passage constant is expressed as the "A" value, and the salt passage constant is expressed by a "B" value. Both constants are functions of the chemical-physical properties of the membrane plus any fouling layer present.

"A" and "B" value constants are also independent of operating parameters such as pressure, temperature, and salt content of the feed stream. "A" value units are cm/sec/atm. "B" value units are cm/sec. The table below shows baseline performance data before cleaning.

Comparing cell testing of the membrane material to the original specification for the full spiral membrane element is a useful comparison tool. This data is collected in order to factor out any additional mechanical aspects the element construction may have caused in the spiral configuration.

| SN# SOY35615 | Water Passage Constant "A" Value* | Salt Passage Constant "B" Value* |
|-------------------------------------|--------------------------------------|-------------------------------------|
| Flat Sheet Membrane-Feed End | 0.96E-04 | 8.54E-06 |
| | 71% of Normal | 121% of Normal |
| Flat Sheet Membrane-Concentrate End | 1.00E-04 | 9.11E-06 |
| | 74% of Normal | 129% of Normal |
| Manufacturer's Specifications | 1.35 to 1.83E-04 | 5.64 to 7.06E-06 |
| | Normal Range | Normal Range |

Note: Testing Conducted with dechlorinated city water from San Marcos, CA

*Averages value based on six flat sheet samples tested



Foulant Analysis

Organic Content Testing

Loss on ignition (LOI) testing gives an approximation of the organic content of the foulant. Values in excess of 35% typically represent the presence of organic content.

Due to the lack of removable foulant, the organic content could not be determined.

Foulant Density Measurement

Membrane foulant density is the weight of dry foulant per area of membrane surface. Foulant densities determined from past autopsies range from 0.02 to 1.84 mg/cm² and average 0.51 mg/cm².

As a sufficient amount of foulant could not be removed from the membrane surfaces to determine the foulant density measurement.

Testing for the Presence of Carbonates

Acid testing is used to determine the presence of carbonates on the membrane surface. In this test, several drops of dilute hydrochloric acid were placed on the foulant surfaces. Effervescing indicates a positive test result.

No effervescing was observed as acid was applied to the active membrane surfaces indicating any carbonates present were below the visual detected limit.



Testing for the Presence of Microbiological Organisms

Foulant samples were stained and examined with a light microscope at 1000x using an oil immersion lens. Gram positive bacteria are stained blue while Gram negative bacteria are stained red.

Foulant scraped from the membrane surface contained a mixture of amorphous material, fungi, Gram negative bacteria, algae and Gram positive bacteria.



Light microscope images (1000x) of foulant scraped from SN#SOY35615



Testing for the Presence of Coagulant

Zeta potential testing of the membrane surface foulant can determine the presence of excess coagulant by measuring the charge associated with the surface colloids. Most naturally occurring colloids are negatively charged and surrounded by a double layer of counter ions. Zeta potential is the charge that resides at the double layer boundary, which we can conveniently measure with a zeta potential meter.

Electrostatic repulsion becomes significant when two colloids approach each other and their charged double layers begin to interfere. Because of this mutual repulsion, coagulation and flocculation are difficult to accomplish and coagulants are often overfed into the RO system resulting in a positive zeta potential. Samples that show a near zero or neutral zeta potential represent the optimum coagulant dosage.

The zeta potential testing could not be performed based on the lack of removable foulant.





Fourier Transform Infrared Spectroscopy Analysis

Fourier Transform Infrared Spectroscopy (FT-IR) analysis identifies the functional groups of organic and inorganic foulant constituents. FT-IR is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation.

FT-IR spectrum of the membrane surface identified mainly bands associated with the membrane material itself along with organic content (primarily carbohydrates).



FT-IR spectral image of the membrane surface of SN#SOY35615

| Peaks | Yes | Weak |
|---------|-----|------|
| С-Н | | X |
| C-N | X | |
| N-H | | X |
| C-C | | X |
| C=C | | X |
| H-C-OH | X | |
| N-H-C=O | | |
| N-C=O | | X |
| C-O-C | X | |



Testing to Identify Inorganic Foulant Constituents

Energy Dispersive X-ray (EDX) analysis is conducted in conjunction with scanning electron microscopy (SEM) to identify inorganic foulant constituents. The electron beam in the microscope causes specimens to emit x-rays including those from the k, I and m atomic shells. Spectrometer counts of these x-rays, which are said to be "characteristic" of the elements present in the specimen, can be used to calculate composition for a full qualitative analysis.

| Elements | Feed End (150x) Average Weight Percent* | Concentrate End (150x) Average Weight Percent* |
|----------|--|---|
| Carbon | 79.13 | 79.46 |
| Oxygen | 12.86 | 15.33 |
| Sulfur | 5.49 | 4.96 |
| Aluminum | 0.13 | 0.15 |
| Silicon | ND** | 0.10 |
| Iron | 2.39 | ND |

Inorganic Foulant Constituents Test Results

* Weight percentages based on average of four areas at magnification 150x from either the feed or concentrate end of the element **ND-Below the detection limit





SEM image (500x) of the membrane surface on the feed end





Chromatic Elemental Imaging (CEI)

Chromatic Elemental Imaging (CEI) is an analytical technique used to resolve the spatial distribution of elements in a foulant sample. In this technique, a beam of focused electrons is accelerated across the surface of a foulant sample and interacts with the sample's inorganic elements by causing the elements to emit electrons. Since each element has its own unique atomic shell, a particular element's electron emission from its atomic shell generates a characteristic X-ray spectrum that allows for its identification. CEI assigns each element a color and provides a high resolution image of their exact location in a sample. An element's color intensity in a Chromatic Elemental Image is largely influenced by its concentration in the foulant sample; elements present in a higher percentage will be displayed with greater intensity in the image. CEI can uniquely identify the distinct elements in a mixed foulant sample containing a number of inorganic deposits. This technique also reveals the location and concentration of different elements relative to each other in a sample.



CEI image (1500x) of the feed end





| CEI image | (1500x) | of the | concentrate | end |
|-----------|---------|--------|-------------|-----|
|-----------|---------|--------|-------------|-----|



Testing Comments and Interpretation

The Energy Dispersive X-ray (EDX) analysis identified iron and trace aluminum on the feed end of the element. Only trace silicon and aluminum were detected on the concentrate end. The sulfur weight percentage is contributed by the membrane surface itself.

The Scanning Electron Microscope (SEM) images showed isolated patches of smooth and granular material on both the feed and concentrate scroll ends. Particles were also randomly dispersed across both end of the membrane.

Chromatic Elemental Imaging (CEI) confirmed that the patches were composed of organics by displaying a high concentration of carbon. The granular material and particles present on the feed end was composed of iron and aluminum hydroxides. Some of the isolated patches on the concentrate end were composed of clay (aluminum silicates) and excess aluminum hydroxide. The membrane surface itself, represented by sulfur, was visible in areas lacking foulant and where the foulant layer was relatively thin in both images.



Cell Test & Laboratory Clean-in-Place Study

Flat sheet membrane samples harvested from the full element are placed in a cell test apparatus and cleaned with various Avista chemicals to determine the most effective cleaner combinations and the amount of time required for an effective cleaning.

The table below shows performance data before and after cleaning. Flat sheet samples harvested from the full element were cleaned using RoClean P303 followed by RoClean P111 (each cleaner 2% by weight), hydrochloric acid (HCl pH 2.5) followed by sodium hydroxide (NaOH pH 11.5) and citric acid (pH 2.5) followed by sodium hydroxide (pH 11.5). All cleaning solutions were heated to approximately 35°C and allowed to circulate for two hours.

| | Water Passage Constant | Salt Passage Constant | |
|-------------------------------------|------------------------|-----------------------|--|
| SN# SOY35615 | "A" Value* | "B" Value* | |
| Pre Clean | 0.96E-04 | 8.61E-06 | |
| RoClean P303/RoClean P111 | 71% of Normal | 122% of Normal | |
| Post Clean | 1.60E-04 | 9.11E-06 | |
| RoClean P303/RoClean P111 | Normal | 129% of Normal | |
| Pre Clean | 0.97E-04 | 8.97E-06 | |
| HCl (pH 2.5)/NaOH (pH 11.5) | 72% of Normal | 127% of Normal | |
| Post Clean | 1.24E-04 | 9.11E-06 | |
| HCl (pH 2.5)/NaOH (pH 11.5) | 92% of Normal | 129% of Normal | |
| Pre Clean | 1.00E-04 | 8.83E-06 | |
| Citric Acid (pH 2.5)/NaOH (pH 11.5) | 74% of Normal | 125% of Normal | |
| Post Clean | 1.14E-04 | 21.5E-06 | |
| Citric Acid (pH 2.5)/NaOH (pH 11.5) | 85% of Normal | 134% of Normal | |
| Manufacturer's Specifications | 1.35 to 1.83E-04 | 5.64 to 7.06E-06 | |
| | Normal Range | Normal Range | |

Note: Testing Conducted with dechlorinated city water from San Marcos, CA *Pre and post clean data based on average of feed and concentrate samples



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Certification by Laboratory

| Report Number | Report Content | Element Serial Number | Report Date | |
|---------------|-------------------------|-----------------------|-------------------|--|
| WO#101614-2 | Standard Spiral Autopsy | 100930418 | | |
| | | SOY35615 | November 07, 2014 | |
| | | 101122325 | | |
| | | SOY35015 | | |

We the undersigned being the Technical Specialists in Membrane Autopsy and related testing procedures and protocol for Avista Technologies certify to the best of our knowledge and belief that the tests listed above have been conducted following Avista standard testing practices and that the results are accurate and complete.

By signing this certificate neither the laboratory employees nor their employer makes any warranty, expressed or implied, concerning the cleaning study results.

Date: 11/07/2014

Signed:

Sara Pietsch Laboratory Services Manager

Guill Robles

Erica Robles Laboratory Services Chemist




Membrane Autopsy Report

Completed for:

Trussell Technologies North City Water Reclamation Serial Number 101122325 Position B-1-2 (V1)- Lead Element Toray TML20-400

11/07/2014 WO#101614-2

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Executive Summary

Background

Trussell Technologies provided thirty-two reverse osmosis (RO) elements to Avista Technologies for wet testing with four of the elements designated for full membrane autopsy. Element Serial Number (SN#) 101122325 was removed from position B-1-2 in V1 and was a Toray TML20-400.

Initial Element Testing

Element SN# 101122325 produced normal flow (5.80 gpm), normal rejection (99.3%) and a delta pressure of 3 psi during baseline wet testing.

External Inspection

The fiberglass casing, anti-telescoping devices (ATDs) and permeate tube were in good mechanical condition. Multiple scratches were observed on the surfaces of the brine seal. The element passed integrity testing indicating that there was damage to the internal mechanical components of the spiral-wound element.

Internal Inspection and Testing

Both scroll ends were discolored (brown and black). Black, orange and white colored particles and flakes were observed on the feed scroll end (brine seal end), while the concentrate scroll end (opposite brine seal) was virtually free from debris. The exposed membrane surfaces were lightly coated with brown colored foulant material. Black and orange colored particles were observed on the feed end of the element. Inspection of the interior of the membrane leaf revealed no foulant on the permeate side (membrane backing, permeate spacer material) of the element, however black colored foulant was found inside the glue lines of every membrane leaf except two. The black colored glue line area was swabbed and tested for the presence of heterotrophic bacteria and yeast/mold. Bacteria and mold/yeast all showed growth within 120 hours. Osmotic bubbling was also observed on the concentrate end of the element but remained on the outer edge of the glue line. The element also tested positive for the presence of halogens (e.g. chlorine) in the membrane structure.

Cell Testing Results

Flat sheet samples harvested from the full element produced normal water passage and normal salt passage during baseline cell testing.



Foulant Analysis

The organic content (loss on ignition), foulant density and zeta potential could not be determined due to the lack of scrapable foulant material on the membrane surfaces. Acid testing was negative, suggesting that any carbonates present were below the visual detection limit. Microscope analysis of foulant scraped from the membrane surface identified primarily amorphous material. Gram negative bacteria, fungi, algae and Gram positive bacteria were also visible under the microscope. Fourier Transform Infrared (FT-IR) spectrum of the membrane surfaces identified bands contributed by the membrane surface itself with weaker bands associated with organic material (primarily carbohydrates).

The Energy Dispersive X-ray (EDX) analysis identified iron and lesser amounts of aluminum on the feed end and only trace amounts of aluminum on the concentrate end. The Scanning Electron Microscope (SEM) images showed isolated, smooth patches of foulant across the membrane surfaces. Particles were observed on both end of the membrane (feed and concentrate). Chromatic Elemental Imaging (CEI) identified the isolated patches as organic by showing a high carbon content in these areas. Iron and aluminum hydroxide particles on the feed end and aluminum hydroxide on the concentrate end.

Cleaning Study

Flat sheet samples harvested from the full element produced normal water and salt passage. Additionally were cleaned using RoClean P303 followed by RoClean P111 (each cleaner at 2% by weight), hydrochloric acid (HCl pH 2.5) followed by sodium hydroxide (NaOH pH 11.5) and citric acid (pH 2.5) followed by sodium hydroxide (pH 11.5). All cleans showed approximately a 5% increase in water passage.



Initial Element Test Results

Element Weight

Because element weight is often indicative of the degree of fouling, elements are weighed prior to the autopsy.

SN# 101122325 weighed 30 pounds; new eight inch elements weigh approximately 30 to 35 pounds.

Wet Test

The element was wet tested on dechlorinated San Marcos, CA city water. Wet test results were normalized to the manufacturer's published test conditions.

| Toray TML20-400 | Flow | Rejection | Pressure Drop |
|-------------------------------|--------------|--------------|---------------|
| | (gpm) | (%) | (psi) |
| SN# 101122325 | 5.80 | 99.3 | 3 |
| Manufacturer's Specifications | 5.60 to 7.00 | 99.0 to 99.7 | ≤20 |



Element Wet Testing



Integrity Test

To determine if a membrane performance problem is possibly caused by mechanical damage, membranes are tested to check for vacuum decay that may indicate abnormal bypass.

In this test a vacuum of about 22 inches Mercury (in. Hg) is applied to the permeate side of the membrane for a duration of 120 seconds. If over 35% of the vacuum is lost within a 120 second period, then the membrane can be said to have severe physical damage.

SN# 101122325 passed integrity testing.



Integrity Test Results for SN# 101122325



External Inspection

The external inspection of a membrane element is an important step in the autopsy process. Physical damage to the exterior components can contribute to performance issues in the element or may yield clues as to the operating conditions of the membrane system that led to poor membrane performance. As most of the external components are damaged during the autopsy process, documenting any significant finds before further work is completed is essential.

This section covers the fiberglass casing, anti-telescoping devices (ATDs), permeate tube, and brine seal. In addition the scroll ends are also examined for any foulant/scale material that may be interfering with flow and for feed spacer extrusion also known as telescoping and gapping in the scroll end which may cause localized scaling (uneven hydraulics).

Spiral-Wound Membrane Element Construction







Fiberglass Casing

The fiberglass casing is an integral part of each element. The purpose of this wrap is to protect the element from external differential pressure, provide compressive strength to prevent telescoping and to ensure that the various membrane components are held in their correct position for optimum performance. Damage to the wrap can be an indication of rough handling or damage from excessive differential pressure across the membrane surface.

The fiberglass casing of the element was in good mechanical condition.



Fiberglass Casing for SN# 101122325

Brine Seal

The purpose of the brine seal is to seal against the inside diameter of the pressure vessels and the outside diameter of the membrane to ensure that all the feed water passes through the membrane element. Chevron type seals are used to aid in membrane loading and to seal to a variety of pressure vessel inside surfaces.





Image of the brine seal



Permeate Tube

At the center of each membrane element is a round section of pipe that is called the permeate tube. Down the length of the tube, holes are drilled through the pipe wall to the tube center. This tube is bonded to the membrane leaves and permits water to flow from the leaves outward at each end of the full element and the through the holes for collection. To function properly, the permeate tube must be free from gouges or damage that can prevent proper o-ring sealing at each end. Poor sealing can result in bypass from the highpressure feed/concentrate flow into the permeate stream.

The permeate tube was free from damage which could allow for the bypass of feed water into the permeate stream.

Anti-Telescoping Device (ATD)

When assembled at the factory, membrane elements are commonly fitted with Anti-Telescoping Devices (ATDs) at each end of the element. These devices are designed to prevent telescoping of the membrane leaves under normal operating conditions that can cause membrane damage.

Physical damage was not observed on either anti-telescoping device (ATD).



Image of feed ATD (left) and concentrate ATD (right) for SN# 101122325



Internal Inspection & Testing

Scroll End Examination

Once the anti-telescoping devices are removed, the scroll ends of the membrane leaves are examined for presence of colloidal particles, biofouling, feed spacer extrusion and membrane gapping. In addition, each scroll end is examined for the gradual axial shift of the element leaves from outer diameter of the element towards the permeate tube. This type of damage is termed "telescoping" and is caused by the development of high differential pressure (usually greater than 10 psi) across the element.

Both scroll ends were discolored (brown and black). Black, orange and white colored particles and flakes were observed on the feed scroll end, while the concentrate scroll end was virtually free from debris.



Image of feed scroll end (left) and concentrate scroll end (right) for SN# 101122325

Membrane Surface Visual Examination

When assembled, the surface of the membrane is a uniform, shiny surface with no visual contamination or impurities. Although the membrane surface contamination can be sometimes hard to detect visually many times contamination is very visible and easy to detect with the naked eye.

The exposed membrane surfaces were lightly coated with brown colored foulant material. Black and orange colored particles were observed on the feed end of the element.





Exposed membrane surface for SN# 101122325



Exposed membrane surface from feed end for SN# 101122325





Image of particles observed on the feed end of the element

Feed Spacer Visual Examination

The feed spacer is a plastic net material designed to separate membrane surfaces to form a flow path and to promote turbulence within feed water channel.

The feed spacers of the element were virtually free of foulant material.



Image of feed spacer



Glue Line Integrity Examination

Membrane leaves are glued on three sides to separate feed and permeate streams. Glue lines are inspected to ensure that there are no sections of unbounded material referred to as glue flaps that may block the feed channel into the element module. In some worst case situations, glue lines may fail at the feed end of the membrane permitting contamination. The glue lines are also inspected for pouching and delamination which often occur on the concentrate end of last stage elements. This type of physical damage may indicate permeate backpressure caused by positive pressure on the permeate side of the membrane.

Black colored foulant was observed in the glue lines of all but two membrane leaves. The area was swabbed and the sample placed in a sterile buffer to test for heterotrophic bacteria and yeast/mold. The samples were incubated and growth observed every 24 hours. Bacteria and mold/yeast showed growth within 120 hours. Osmotic bubbling was also observed on the concentrate end of the element but remained on the outer edge of the glue line.



Image of black foulant observed within the glue lines (left) and image of foulant observed when glue lines were pulled apart (right)

Permeate Spacer Visual Examination

Permeate spacer provides a path for permeate flow to channel towards the central permeate tube which minimizes permeate-side pressure losses.

The permeate spacers were in good mechanical condition and free of visible foulant contamination.



Testing for the Presence of Oxidizing Halogens

The Fujiwara test is used to confirm that a polyamide (PA) thin-film membrane has been exposed to an oxidizing halogen, such as chlorine, bromine, or iodine. This test analyzes whether halogens have become part of the polymer structure through oxidative attack. Please note that the Fujiwara test is a qualitative test and that any color change indicates the presence of a halogen in the membrane structure. However the test does not quantify the amount of exposure or which exact halogen is attached.

Fujiwara testing was positive for the presence of halogens (e.g. chlorine) in the membrane structure.



Example of negative (left) and positive (right) Fujiwara color change



Cell Test for Permeate Flow & Salt Passage

To determine membrane performance characteristics membrane samples are tested in a cell test apparatus (CTA). The water passage constant is expressed as the "A" value, and the salt passage constant is expressed by a "B" value. Both constants are functions of the chemical-physical properties of the membrane plus any fouling layer present.

"A" and "B" value constants are also independent of operating parameters such as pressure, temperature, and salt content of the feed stream. "A" value units are cm/sec/atm. "B" value units are cm/sec. The table below shows baseline performance data before cleaning.

Comparing cell testing of the membrane material to the original specification for the full spiral membrane element is a useful comparison tool. This data is collected in order to factor out any additional mechanical aspects the element construction may have caused in the spiral configuration.

| SN# 101122325 | Water Passage Constant "A" Value* | Salt Passage Constant "B" Value* |
|-------------------------------------|--------------------------------------|-------------------------------------|
| Flat Sheet Membrane-Feed End | 0.93E-04 | 10.6E-06 |
| | Normal | Normal |
| Flat Sheet Membrane-Concentrate End | 1.04E-04 | 12.1E-06 |
| | Normal | Normal |
| Manufacturer's Specifications | 0.90 to 1.22E-04 | 4.31 to 14.5E-06 |
| | Normal Range | Normal Range |

Note: Testing Conducted with dechlorinated city water from San Marcos, CA

*Averages value based on six flat sheet samples tested



Foulant Analysis

Organic Content Testing

Loss on ignition (LOI) testing gives an approximation of the organic content of the foulant. Values in excess of 35% typically represent the presence of organic content.

The loss on ignition could not be determined due to the lack of scrapable foulant material.

Foulant Density Measurement

Membrane foulant density is the weight of dry foulant per area of membrane surface. Foulant densities determined from past autopsies range from 0.02 to 1.84 mg/cm² and average 0.51 mg/cm².

The foulant density measurement could not be determined based on the lack of removable foulant material.

Testing for the Presence of Carbonates

Acid testing is used to determine the presence of carbonates on the membrane surface. In this test, several drops of dilute hydrochloric acid were placed on the foulant surfaces. Effervescing indicates a positive test result.

No effervescing was observed as acid was applied to the active membrane surfaces, indicating that any carbonates present were below the visual detection limit.



Testing for the Presence of Microbiological Organisms

Foulant samples were stained and examined with a light microscope at 1000x using an oil immersion lens. Gram positive bacteria are stained blue while Gram negative bacteria are stained red.

Foulant scraped from the membrane surface contained primarily amorphous material. Gram negative bacteria, fungi, algae and Gram positive bacteria were also visible under the microscope.





Light microscope images (1000x) of foulant scraped from SN#101122325



Testing for the Presence of Coagulant

Zeta potential testing of the membrane surface foulant can determine the presence of excess coagulant by measuring the charge associated with the surface colloids. Most naturally occurring colloids are negatively charged and surrounded by a double layer of counter ions. Zeta potential is the charge that resides at the double layer boundary, which we can conveniently measure with a zeta potential meter.

Electrostatic repulsion becomes significant when two colloids approach each other and their charged double layers begin to interfere. Because of this mutual repulsion, coagulation and flocculation are difficult to accomplish and coagulants are often overfed into the RO system resulting in a positive zeta potential. Samples that show a near zero or neutral zeta potential represent the optimum coagulant dosage.

The zeta potential testing could not be performed based on the lack of removable foulant.



Image based on diagram from Particle Characterization Laboratories, Inc.



Fourier Transform Infrared Spectroscopy Analysis

Fourier Transform Infrared Spectroscopy (FT-IR) analysis identifies the functional groups of organic and inorganic foulant constituents. FT-IR is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation.

FT-IR spectrum of the membrane surfaces identified bands contributed by the membrane surface itself along with weak bands associated with organic material (mainly carbohydrates).



FT-IR spectral image of the membrane surface of SN#101122325

| Peaks | Yes | Weak |
|---------|-----|------|
| C-H | | X |
| C-N | X | |
| N-H | | X |
| C-C | | X |
| C=C | | X |
| Н-С-ОН | X | |
| N-H-C=O | | |
| N-C=O | | X |
| C-O-C | X | _ |



Testing to Identify Inorganic Foulant Constituents

Energy Dispersive X-ray (EDX) analysis is conducted in conjunction with scanning electron microscopy (SEM) to identify inorganic foulant constituents. The electron beam in the microscope causes specimens to emit x-rays including those from the k, I and m atomic shells. Spectrometer counts of these x-rays, which are said to be "characteristic" of the elements present in the specimen, can be used to calculate composition for a full qualitative analysis.

| Elements | Feed End (150x) Average Weight Percent* | Concentrate End (150x) Average Weight Percent* |
|----------|--|---|
| Carbon | 81.30 | 81.23 |
| Oxygen | 12.65 | 13.35 |
| Sulfur | 5.23 | 5.30 |
| Iron | 0.76 | ND** |
| Aluminum | 0.06 | 0.12 |

Inorganic Foulant Constituents Test Results

* Weight percentages based on average of four areas at magnification 150x from either the feed or concentrate end of the element **ND-Below the detection limit





SEM image (500x) of the membrane surface on the feed end



SEM image (500x) of the membrane surface on the concentrate end



Chromatic Elemental Imaging (CEI)

Chromatic Elemental Imaging (CEI) is an analytical technique used to resolve the spatial distribution of elements in a foulant sample. In this technique, a beam of focused electrons is accelerated across the surface of a foulant sample and interacts with the sample's inorganic elements by causing the elements to emit electrons. Since each element has its own unique atomic shell, a particular element's electron emission from its atomic shell generates a characteristic X-ray spectrum that allows for its identification. CEI assigns each element a color and provides a high resolution image of their exact location in a sample. An element's color intensity in a Chromatic Elemental Image is largely influenced by its concentration in the foulant sample; elements present in a higher percentage will be displayed with greater intensity in the image. CEI can uniquely identify the distinct elements in a mixed foulant sample containing a number of inorganic deposits. This technique also reveals the location and concentration of different elements relative to each other in a sample.







CEI image (1500x) of the membrane surface on the concentrate end



Testing Comments and Interpretation

The Energy Dispersive X-ray (EDX) analysis identified iron and lesser amounts of aluminum on the feed end and only trace amounts of aluminum on the concentrate end. The sulfur weight percentage represents the membrane material itself rather than the foulant layer.

The Scanning Electron Microscope (SEM) images showed isolated, smooth patches of foulant on both the feed and concentrate areas of the membrane. Particles were also observed across both ends of the membrane.

Chromatic Elemental Imaging (CEI) identified the isolated patches as organic by showing a high carbon content in these areas. Iron and aluminum hydroxide particles on the feed end and aluminum hydroxide on the concentrate end. The membrane surface itself (represented by sulfur) was visible in areas lacking foulant material and where the foulant was less thick.



Cell Test & Laboratory Clean-in-Place Study

Flat sheet membrane samples harvested from the full element are placed in a cell test apparatus and cleaned with various Avista chemicals to determine the most effective cleaner combinations and the amount of time required for an effective cleaning.

The table below shows performance data before and after cleaning. Flat sheet samples harvested from the full element were cleaned using RoClean P303 followed by RoClean P111 (each cleaner 2% by weight), hydrochloric acid (HCl pH 2.5) followed by sodium hydroxide (NaOH pH 11.5) and citric acid (pH 2.5) followed by sodium hydroxide (pH 11.5). All cleaning solutions were heated to approximately 35 °C and allowed to circulate for two hours.

| SN# 101122325 | Water Passage Constant | Salt Passage Constant | |
|-------------------------------------|------------------------|-----------------------|--|
| | "A" Value* | "B" Value* | |
| Pre Clean | 1.02E-04 | 11.9E-06 | |
| RoClean P303/RoClean P111 | Normal | Normal | |
| Post Clean | 1.28E-04 | 12.0E-06 | |
| RoClean P303/RoClean P111 | 105% of Normal | Normal | |
| Pre Clean | 1.01E-04 | 11.5E-06 | |
| HCl (pH 2.5)/NaOH (pH 11.5) | Normal | Normal | |
| Post Clean | 1.29E-04 | 12.1E-06 | |
| HCl (pH 2.5)/NaOH (pH 11.5) | 106% of Normal | Normal | |
| Pre Clean | 0.99E-04 | 10.6E-06 | |
| Citric Acid (pH 2.5)/NaOH (pH 11.5) | Normal | Normal | |
| Post Clean | 1.27E-04 | 12.7E-06 | |
| Citric Acid (pH 2.5)/NaOH (pH 11.5) | 104% of Normal | Normal | |
| Manufacturer's Specifications | 0.90 to 1.22E-04 | 4.31 to 14.5E-06 | |
| | Normal Range | Normal Range | |

Note: Testing Conducted with dechlorinated city water from San Marcos, CA

*Pre and post clean data based on average of feed and concentrate samples



Certification by Laboratory

| Report Number | Report Content | Element Serial Number | Report Date | |
|---------------|-------------------------|-----------------------|---------------------|--|
| WO#101614-4 | Standard Spiral Autopsy | 100930418 | | |
| | | 101122325 | November 07, 2014 | |
| | | SOY35615 | NOVEITIDEI 07, 2014 | |
| | | SOY35015 | | |

We the undersigned being the Technical Specialists in Membrane Autopsy and related testing procedures and protocol for Avista Technologies certify to the best of our knowledge and belief that the tests listed above have been conducted following Avista standard testing practices and that the results are accurate and complete.

By signing this certificate neither the laboratory employees nor their employer makes any warranty, expressed or implied, concerning the cleaning study results.

Date: 11/07/2014

Signed:

Sara Pietsch Laboratory Services Manager

Gull #

Erica Robles Laboratory Services Chemist





Membrane Autopsy Report

Completed for:

Trussell Technologies North City Water Reclamation Serial Number SOY35015 **Position A-2-7 - Tail Element Hydranautics ESPA2-LD**

11/07/2014

WO#101614-2

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Executive Summary

Background

Trussell Technologies provided thirty-two reverse osmosis (RO) elements to Avista Technologies for wet testing with four of the elements designated for a full membrane autopsy. Element Serial Number (SN#) SOY35015 was removed from position A-2-7 in the RO system and was a Hydranautics ESPA2-LD.

Initial Element Testing

Element SN# SOY35015 produced lower than normal flow (38% of normal), lower than normal rejection (98.0%) and a delta pressure of 3 psi during baseline wet testing.

External Inspection

The fiberglass casing, anti-telescoping devices (ATDs), permeate tube and brine seal were in good mechanical condition. The element also passed integrity testing indicating that there was no damage to the internal mechanical components of the spiral-wound element.

Internal Inspection and Testing

The scroll ends were discolored (brown) but free of large debris. The exposed membrane surfaces were evenly coated with a white colored foulant material. The foulant adhered tightly to the membrane surfaces. The feed spacers were free of visual foulant. The glue lines and permeate spacers were in good condition, however the flat sheet samples tested positive for the presence of halogens (e.g. chlorine) in the membrane structure.

Cell Testing Results

Flat sheet samples harvested from the full element produced 38% of normal water passage and 183% of normal salt passage during baseline cell testing.



Foulant Analysis

The foulant material adhered too tightly to the membrane surfaces to obtain a representative sample to determine the organic content (loss on ignition), foulant density or zeta potential. Acid testing was negative, suggesting that any carbonates present were below the visual detection limit. Microscope analysis of foulant scraped from the membrane surface identified primarily amorphous material. Gram negative bacteria, Gram positive bacteria and algae were also visible under the microscope. Fourier Transform Infrared (FT-IR) spectrum of the membrane surface identified bands contributed by the membrane material, bands matching the spectrum of calcium phosphate and weaker bands associated with organic material (primarily carbohydrates).

The Energy Dispersive X-ray (EDX) analysis identified calcium and phosphorus as the primary inorganic contributors to the surface foulant material on both the feed and concentrate end. Trace amounts of salts including sodium and magnesium were also detected. The Scanning Electron Microscope (SEM) images showed a granular foulant layer covering the majority of the membrane surfaces on both ends. Dispersed particles were also observed across the membrane. Close up SEM (5000x) imaging also detected microorganisms above the even foulant layer. Chromatic Elemental Imaging (CEI) identified the foulant on both ends of the element layer as calcium phosphate with isolated calcium carbonate crystals and random spherical particles composed primarily of carbon. Microorganisms were also coated with calcium phosphate.

Cleaning Study

Flat sheet samples harvested from the full element were cleaned using RoClean P303 (2% by weight), hydrochloric acid (HCl pH 2.5) and citric acid (pH 2.5) alone and the combinations of RoClean P303 followed by RoClean P111 (each cleaner at 2% by weight), hydrochloric acid (HCl pH 2.5) followed by sodium hydroxide (NaOH pH 11.5) and citric acid (pH 2.5) followed by sodium hydroxide (pH 11.5).. All cleaning solutions were heated to approximately 35°C and allowed to circulate for two hours. Cleaning results showed that the combination of both high and low pH were required to remove the bulk of the scale. The RoClean P303/RoClean P111 combination water passage to within the manufacturers specified range. The HCl/NaOH clean increased water passage to 89% of normal water passage. The citric acid/NaOH clean increased water passage to 85% of normal.



Initial Element Test Results

Element Weight

Because element weight is often indicative of the degree of fouling, elements are weighed prior to the autopsy.

SN# SOY35015 weighed 32 pounds; new eight inch elements weigh approximately 30 to 35 pounds.

Wet Test

The element was wet tested on dechlorinated San Marcos, CA city water. Wet test results were normalized to the manufacturer's published test conditions.

| Hydranautics ESPA2-LD | Flow | Rejection | Pressure Drop |
|-------------------------------|--------------|--------------|---------------|
| | (gpm) | (%) | (psi) |
| SN# SOY35015 | 2.28 | 98.0 | 3 |
| Manufacturer's Specifications | 5.90 to 7.90 | 99.5 to 99.6 | ≤10 |



Element Wet Testing



Integrity Test

To determine if a membrane performance problem is possibly caused by mechanical damage, membranes are tested to check for vacuum decay that may indicate abnormal bypass.

In this test a vacuum of about 22 inches Mercury (in. Hg) is applied to the permeate side of the membrane for a duration of 120 seconds. If over 35% of the vacuum is lost within a 120 second period, then the membrane can be said to have severe physical damage.

SN# SOY35015 passed integrity testing.



Integrity Test Results for SN# SOY35015



External Inspection

The external inspection of a membrane element is an important step in the autopsy process. Physical damage to the exterior components can contribute to performance issues in the element or may yield clues as to the operating conditions of the membrane system that led to poor membrane performance. As most of the external components are damaged during the autopsy process, documenting any significant finds before further work is completed is essential.

This section covers the fiberglass casing, anti-telescoping devices (ATDs), permeate tube, and brine seal. In addition the scroll ends are also examined for any foulant/scale material that may be interfering with flow and for feed spacer extrusion also known as telescoping and gapping in the scroll end which may cause localized scaling (uneven hydraulics).

Spiral-Wound Membrane Element Construction







Fiberglass Casing

The fiberglass casing is an integral part of each element. The purpose of this wrap is to protect the element from external differential pressure, provide compressive strength to prevent telescoping and to ensure that the various membrane components are held in their correct position for optimum performance. Damage to the wrap can be an indication of rough handling or damage from excessive differential pressure across the membrane surface.

The fiberglass casing of the element was in good mechanical condition, although brown foulant was observed on the casing.



Fiberglass Casing for SN# SOY35015

Brine Seal

The purpose of the brine seal is to seal against the inside diameter of the pressure vessels and the outside diameter of the membrane to ensure that all the feed water passes through the membrane element. Chevron type seals are used to aid in membrane loading and to seal to a variety of pressure vessel inside surfaces.

The brine seal was in good condition and no damage was noted during the external inspection.

Permeate Tube

At the center of each membrane element is a round section of pipe that is called the permeate tube. Down the length of the tube, holes are drilled through the pipe wall to the tube center. This tube is bonded to the membrane leaves and permits water to flow from the leaves outward at each end of the full element and the through the holes for collection. To function properly, the permeate tube must be free from gouges or damage that can prevent proper o-ring sealing at each end. Poor sealing can result in bypass from the highpressure feed/concentrate flow into the permeate stream.

The permeate tube was free from damage which could allow for the bypass of feed water into the permeate stream.


Anti-Telescoping Device (ATD)

When assembled at the factory, membrane elements are commonly fitted with Anti-Telescoping Devices (ATDs) at each end of the element. These devices are designed to prevent telescoping of the membrane leaves under normal operating conditions that can cause membrane damage.

Both anti-telescoping devices (ATDs) were in good condition.



Image of feed ATD (left) and concentrate ATD (right) for SN# SOY35015



Internal Inspection & Testing

Scroll End Examination

Once the anti-telescoping devices are removed, the scroll ends of the membrane leaves are examined for presence of colloidal particles, biofouling, feed spacer extrusion and membrane gapping. In addition, each scroll end is examined for the gradual axial shift of the element leaves from outer diameter of the element towards the permeate tube. This type of damage is termed "telescoping" and is caused by the development of high differential pressure (usually greater than 10 psi) across the element.

The scroll ends were discolored (brown) but free of large debris.



Image of feed scroll end (left) and concentrate scroll end (right) for SN# SOY35015

Membrane Surface Visual Examination

When assembled, the surface of the membrane is a uniform, shiny surface with no visual contamination or impurities. Although the membrane surface contamination can be sometimes hard to detect visually many times contamination is very visible and easy to detect with the naked eye.

Granular, white colored foulant material was observed evenly coating the exposed membrane surfaces of the element. The foulant adhered tightly to the membrane surface.





Exposed membrane surface for SN# SOY35015



Exposed membrane surface from feed end for SN# SOY35015



Feed Spacer Visual Examination

The feed spacer is a plastic net material designed to separate membrane surfaces to form a flow path and to promote turbulence within feed water channel.

The feed spacers in the element were virtually free of foulant material.



Image of feed spacer



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Glue Line Integrity Examination

Membrane leaves are glued on three sides to separate feed and permeate streams. Glue lines are inspected to ensure that there are no sections of unbounded material referred to as glue flaps that may block the feed channel into the element module. In some worst case situations, glue lines may fail at the feed end of the membrane permitting contamination. The glue lines are also inspected for pouching and delamination which often occur on the concentrate end of last stage elements. This type of physical damage may indicate permeate backpressure caused by positive pressure on the permeate side of the membrane.

The glue lines appeared to be in good condition, with no delamination, pouching or glue flaps, however osmotic bubbling was observed on the concentrate end of the element, but remained on the outer edge of the glue line.

Permeate Spacer Visual Examination

Permeate spacer provides a path for permeate flow to channel towards the central permeate tube which minimizes permeate-side pressure losses.

The permeate spacers were in good mechanical condition and free of visible foulant contamination.



Testing for the Presence of Oxidizing Halogens

The Fujiwara test is used to confirm that a polyamide (PA) thin-film membrane has been exposed to an oxidizing halogen, such as chlorine, bromine, or iodine. This test analyzes whether halogens have become part of the polymer structure through oxidative attack. Please note that the Fujiwara test is a qualitative test and that any color change indicates the presence of a halogen in the membrane structure. However the test does not quantify the amount of exposure or which exact halogen is attached.

Fujiwara testing was positive for the presence of halogens (e.g. chlorine) in the membrane structure.



Example of negative (left) and positive (right) Fujiwara color change



Cell Test for Permeate Flow & Salt Passage

To determine membrane performance characteristics membrane samples are tested in a cell test apparatus (CTA). The water passage constant is expressed as the "A" value, and the salt passage constant is expressed by a "B" value. Both constants are functions of the chemical-physical properties of the membrane plus any fouling layer present.

"A" and "B" value constants are also independent of operating parameters such as pressure, temperature, and salt content of the feed stream. "A" value units are cm/sec/atm. "B" value units are cm/sec. The table below shows baseline performance data before cleaning.

Comparing cell testing of the membrane material to the original specification for the full spiral membrane element is a useful comparison tool. This data is collected in order to factor out any additional mechanical aspects the element construction may have caused in the spiral configuration.

| SN# SOY35015 | Water Passage Constant | Salt Passage Constant | |
|--------------------------------------|------------------------|-----------------------|--|
| | A value | B value | |
| Flat Sheet Membrane-Feed End* | 0.51E-04 | 11.9E-06 | |
| | 38% of Normal | 169% of Normal | |
| Flat Sheet Membrane-Concentrate End* | 0.51E-04 | 13.8E-06 | |
| | 38% of Normal | 195% of Normal | |
| Manufacturer's Specifications | 1.35 to 1.83E-04 | 5.64 to 7.06E-06 | |
| | Normal Range | Normal Range | |

Note: Testing Conducted with dechlorinated city water from San Marcos, CA

*Average value based on six flat sheet samples tested



Foulant Analysis

Organic Content Testing

Loss on ignition (LOI) testing gives an approximation of the organic content of the foulant. Values in excess of 35% typically represent the presence of organic content.

The foulant adhered too tightly to the membrane surfaces to collect a representative sample for determining the organic content.

Foulant Density Measurement

Membrane foulant density is the weight of dry foulant per area of membrane surface. Foulant densities determined from past autopsies range from 0.02 to 1.84 mg/cm² and average 0.51 mg/cm².

The foulant density measurement could not be determined as the foulant material adhered tightly to the membrane surfaces.

Testing for the Presence of Carbonates

Acid testing is used to determine the presence of carbonates on the membrane surface. In this test, several drops of dilute hydrochloric acid were placed on the foulant surfaces. Effervescing indicates a positive test result.

No effervescing was observed as acid was applied to the active membrane surfaces, indicating that any carbonates present were below the visual detection limit.



Testing for the Presence of Microbiological Organisms

Foulant samples were stained and examined with a light microscope at 1000x using an oil immersion lens. Gram positive bacteria are stained blue while Gram negative bacteria are stained red.

Foulant scraped from the membrane surface contained primarily amorphous material. Gram negative bacteria, Gram positive bacteria and algae were also visible under the microscope.



Light microscope images (1000x) of foulant scraped from SN#SOY35015



Testing for the Presence of Coagulant

Zeta potential testing of the membrane surface foulant can determine the presence of excess coagulant by measuring the charge associated with the surface colloids. Most naturally occurring colloids are negatively charged and surrounded by a double layer of counter ions. Zeta potential is the charge that resides at the double layer boundary, which we can conveniently measure with a zeta potential meter.

Electrostatic repulsion becomes significant when two colloids approach each other and their charged double layers begin to interfere. Because of this mutual repulsion, coagulation and flocculation are difficult to accomplish and coagulants are often overfed into the RO system resulting in a positive zeta potential. Samples that show a near zero or neutral zeta potential represent the optimum coagulant dosage.

The zeta potential could not be determined as the foulant adhered too tightly to the membrane surfaces to collect a representative sample.



Image based on diagram from Particle Characterization Laboratories, Inc.



Fourier Transform Infrared Spectroscopy Analysis

Fourier Transform Infrared Spectroscopy (FT-IR) analysis identifies the functional groups of organic and inorganic foulant constituents. FT-IR is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation.

FT-IR spectrum of the membrane surfaces identified bands contributed by the membrane surface itself, multiple bands matching the spectra for calcium phosphate and weaker bands associated with organic material (primarily carbohydrates).



FT-IR spectral image of the membrane surface of SN#SOY35015

| Peaks | Yes | Weak |
|--------------------|-----|------|
| C-H | | X |
| C-N | X | |
| N-H | | X |
| C-C | | X |
| C=C | | X |
| H-C-OH | X | |
| N-H-C=O | | X |
| N-C=O | | X |
| C-O-C | X | |
| Ca-PO ₄ | X | |
| 19 | | |



Testing to Identify Inorganic Foulant Constituents

Energy Dispersive X-ray (EDX) analysis is conducted in conjunction with scanning electron microscopy (SEM) to identify inorganic foulant constituents. The electron beam in the microscope causes specimens to emit x-rays including those from the k, I and m atomic shells. Spectrometer counts of these x-rays, which are said to be "characteristic" of the elements present in the specimen, can be used to calculate composition for a full qualitative analysis.

| Elements | Feed End (150x) Average Weight Percent* | Concentrate End (150x) Average Weight Percent* |
|------------|--|---|
| Carbon | 54.01 | 52.38 |
| Oxygen | 34.01 | 35.10 |
| Sulfur | 2.25 | 2.14 |
| Sodium | 0.56 | 0.54 |
| Magnesium | 1.81 | 0.94 |
| Calcium | 4.63 | 5.60 |
| Phosphorus | 2.73 | 3.30 |

Inorganic Foulant Constituents Test Results

* Weight percentages based on average of four areas at magnification 150x from either the feed or concentrate end of the element





SEM image (500x) of the membrane surface on the feed end



SEM image (500x) of the membrane surface on the concentrate end



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Close up SEM image (5000x) of the membrane surface



Chromatic Elemental Imaging (CEI)

Chromatic Elemental Imaging (CEI) is an analytical technique used to resolve the spatial distribution of elements in a foulant sample. In this technique, a beam of focused electrons is accelerated across the surface of a foulant sample and interacts with the sample's inorganic elements by causing the elements to emit electrons. Since each element has its own unique atomic shell, a particular element's electron emission from its atomic shell generates a characteristic X-ray spectrum that allows for its identification. CEI assigns each element a color and provides a high resolution image of their exact location in a sample. An element's color intensity in a Chromatic Elemental Image is largely influenced by its concentration in the foulant sample; elements present in a higher percentage will be displayed with greater intensity in the image. CEI can uniquely identify the distinct elements in a mixed foulant sample containing a number of inorganic deposits. This technique also reveals the location and concentration of different elements relative to each other in a sample.



CEI image (1500x) of the feed end of the membrane surface





CEI image (1500x) of the concentrate end of the membrane surface



Testing Comments and Interpretation

The Energy Dispersive X-ray (EDX) analysis identified calcium and phosphorus as the primary inorganic contributors to the surface foulant material on both the feed and concentrate end. Trace amounts of salts including sodium and magnesium were also detected. The sulfur weight percentage represents the membrane material itself rather than the foulant layer.

The Scanning Electron Microscope (SEM) images showed a granular foulant layer covering the majority of the membrane surfaces on both ends. Dispersed particles were also observed across the membrane. Close up SEM (5000x) imaging also detected microorganisms above the even foulant layer.

Chromatic Elemental Imaging (CEI) identified the foulant on both ends of the element layer as calcium phosphate (yellow/green) with isolated calcium carbonate crystals (light blue-dark blue) and random spherical particles composed primarily of carbon (dark blue). Microorganisms were also coated with calcium phosphate. The membrane surface itself (represented by sulfur) was visible in the cracks of the dry foulant layer.



Cell Test & Laboratory Clean-in-Place Study

Flat sheet membrane samples harvested from the full element are placed in a cell test apparatus and cleaned with various Avista chemicals to determine the most effective cleaner combinations and the amount of time required for an effective cleaning.

The table below shows performance data before and after cleaning. Flat sheet samples harvested from the full element were cleaned using RoClean P303 followed by RoClean P111 (each cleaner 2% by weight), hydrochloric acid (HCl pH 2.5) followed by sodium hydroxide (NaOH pH 11.5) and citric acid (pH 2.5) followed by sodium hydroxide (pH 11.5). All cleaning solutions were heated to approximately 35°C and allowed to circulate for two hours.

| | Water Passage Constant | Salt Passage Constant | |
|---------------------------------|------------------------|-----------------------|--|
| SN# S0135015 | "A" Value* | "B" Value* | |
| Pre Clean-RoClean P303 | 0.51E-04 | 12.3E-06 | |
| | 38% of Normal | 174% of Normal | |
| Post Clean-RoClean P303 | 0.99E-04 | 10.1E-06 | |
| | 73% of Normal | 143% of Normal | |
| Pre Clean-HCl (pH 2.5) | 0.50E-04 | 11.5E-06 | |
| | 37% of Normal | 163% of Normal | |
| Post Clean-HCl (pH 2.5) | 0.97E-04 | 12.1E-06 | |
| | 72% of Normal | 171% of Normal | |
| Pre Clean Citric Acid (pH 2.5) | 0.51E-04 | 13.4E-06 | |
| | 38% of Normal | 191% of Normal | |
| Post Clean Citric Acid (pH 2.5) | 0.97E-04 | 14.0E-06 | |
| ч <i>ў</i> | 68% of Normal | 198% of Normal | |
| Manufacturer's Specifications | 1.35 to 1.83E-04 | 5.64 to 7.06E-06 | |
| · | Normal Range | Normal Range | |

*Pre and post clean data based on average of feed and concentrate samples



Cleaning Study Continued

| | Water Passage Constant | Salt Passage Constant "B" Value* | |
|-------------------------------------|------------------------|-------------------------------------|--|
| SN# SOY35015 | "A" Value* | | |
| Pre Clean | 0.50E-04 | 12.8E-06 | |
| RoClean P303/RoClean P111 | 37% of Normal | 181% of Normal | |
| Post Clean | 1.56E-04 | 12.5E-06 | |
| RoClean P303/RoClean P111 | Normal | 177% of Normal | |
| Pre Clean | 0.50E-04 | 13.3E-06 | |
| HCI (pH 2.5)/NaOH (pH 11.5) | 37% of Normal | 189% of Normal | |
| Post Clean | 1.20E-04 | 12.5E-06 | |
| HCl (pH 2.5)/NaOH (pH 11.5) | 89% of Normal | 177% of Normal | |
| Pre Clean | 0.51E-04 | 13.4E-06 | |
| Citric Acid (pH 2.5)/NaOH (pH 11.5) | 38% of Normal | 190% of Normal | |
| Post Clean | 1.15E-04 | 12.7E-06 | |
| Citric Acid (pH 2.5)/NaOH (pH 11.5) | 85% of Normal | 180% of Normal | |
| Manufacturer's Specifications | 1.35 to 1.83E-04 | 5.64 to 7.06E-06 | |
| | Normal Range | Normal Range | |

Note: Testing Conducted with dechlorinated city water from San Marcos, CA *Pre and post clean data based on average of feed and concentrate samples



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Certification by Laboratory

| Report Number | Report Content | Element Serial Number | Report Date |
|---------------|-------------------------|-----------------------|-------------------|
| WO#101614-2 | Standard Spiral Autopsy | 100930418 | November 07, 2014 |
| | | 101122325 | |
| | | SOY35615 | |
| | | SOY35015 | |

We the undersigned being the Technical Specialists in Membrane Autopsy and related testing procedures and protocol for Avista Technologies certify to the best of our knowledge and belief that the tests listed above have been conducted following Avista standard testing practices and that the results are accurate and complete.

By signing this certificate neither the laboratory employees nor their employer makes any warranty, expressed or implied, concerning the cleaning study results.

Date: 11/07/2014

Signed:

Sara Pietsch Laboratory Services Manager

Gull #

Erica Robles Laboratory Services Chemist





Membrane Autopsy Report

Completed for:

Trussell Technologies North City Water Reclamation Serial Number 100930418 Position B-3-7 (V20)-Tail Element Toray TML20-400

11/07/2014 WO#101614-2

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Executive Summary

Background

Trussell Technologies provided thirty-two reverse osmosis (RO) elements to Avista Technologies for wet testing with four of the elements designated for full membrane autopsy. Element Serial Number (SN#) 100930418 was removed from position B-3-7 (Vessel 20) in the RO system and was a Toray TML20-400.

Initial Element Testing

Element SN# 100930418 produced less than 1.0 GPM during baseline wet testing. New elements of this model type generally produce between 5.6 and 7.0 GPM.

External Inspection

The fiberglass casing, anti-telescoping devices (ATDs), permeate tube and brine seal were in good mechanical condition. The element also passed integrity testing indicating that there was no damage to the internal mechanical components of the spiral-wound element.

Internal Inspection and Testing

The scroll ends were discolored (brown) but free of large debris. Slight telescoping (shifting of internal components) and feed spacer extrusion were observed on the concentrate scroll end (opposite brine seal). The exposed membrane surfaces were evenly coated with a thin layer of white foulant material. The foulant adhered tightly to the membrane surfaces. The feed spacers and permeate spacers were in good condition. Black colored foulant was observed in the all but three of the glue lines. The black colored glue line area was swabbed and tested for the presence of heterotrophic bacteria and yeast/mold. Bacteria showed growth within 72 hours while the yeast/mold developed within 96 hours. Osmotic bubbling was also observed on the concentrate end of the element but remained on the outer edge of the glue lines. The element tested positive for the presence of halogens (e.g. chlorine) in the membrane structure.

Cell Testing Results

Flat sheet samples harvested from both the feed and concentrate ends of the element produced no water passage.



Foulant Analysis

The loss on ignition, foulant density measurement and zeta potential testing could not be performed due to the lack of removable foulant (adhered too tightly). Acid testing was negative, suggesting that any carbonates present were below the visual detection limit. Microscope analysis of foulant scraped from the membrane surface identified mainly amorphous material. Fungi, algae, Gram negative bacteria and fewer Gram positive bacteria were also detected. Fourier Transform Infrared (FT-IR) spectrum of the membrane surfaces identified bands associated with the membrane material itself and several bands matching the spectrum for calcium phosphate and weak bands associated with organic material.

The Energy Dispersive X-ray (EDX) analysis identified calcium and phosphorus as the primary inorganic constituents present on both the feed and concentrate ends. Sodium, magnesium and aluminum were also detected in lesser amounts. The Scanning Electron Microscope (SEM) images showed that the membrane surface was evenly coated with granular foulant material on both ends of the element (feed and concentrate). Randomly dispersed particles were also observed on the membrane. Close up SEM imaging (5000x) identified bacteria and microorganisms above the granular layer. Chromatic Elemental Imaging (CEI) identified the granular material on both the feed and concentrate ends of the element as calcium phosphate. The bacteria and microorganisms were coated in calcium phosphate.

Cleaning Study

Flat sheet samples harvested from the full element were cleaned using RoClean P303 (2% by weight), hydrochloric acid (HCl pH 2.5) and citric acid (pH 2.5). All cleaning solutions were heated to approximately 35 °C and allowed to circulate for two hours. The RoClean P303, hydrochloric acid and citric acid cleaners all restored water passage within the manufacturer's specified range.



Initial Element Test Results

Element Weight

Because element weight is often indicative of the degree of fouling, elements are weighed prior to the autopsy.

SN# 100930418 weighed 31 pounds; new eight inch elements weigh approximately 30 to 35 pounds.

Wet Test

The element was wet tested on dechlorinated San Marcos, CA city water. Wet test results were normalized to the manufacturer's published test conditions.

| Toray TML20-400 | Flow | Rejection | Pressure Drop |
|-------------------------------|--------------|-------------------|---------------|
| | (gpm) | (%) | (psi) |
| SN# 100930418 | | Less than 1.0 GPM | |
| Manufacturer's Specifications | 5.60 to 7.00 | 99.0 to 99.7 | ≤20 |



Element Wet Testing



Integrity Test

To determine if a membrane performance problem is possibly caused by mechanical damage, membranes are tested to check for vacuum decay that may indicate abnormal bypass.

In this test a vacuum of about 22 inches Mercury (in. Hg) is applied to the permeate side of the membrane for a duration of 120 seconds. If over 35% of the vacuum is lost within a 120 second period, then the membrane can be said to have severe physical damage.

SN# 100930418 passed integrity testing.



Integrity Test Results for SN# 100930418



External Inspection

The external inspection of a membrane element is an important step in the autopsy process. Physical damage to the exterior components can contribute to performance issues in the element or may yield clues as to the operating conditions of the membrane system that led to poor membrane performance. As most of the external components are damaged during the autopsy process, documenting any significant finds before further work is completed is essential.

This section covers the fiberglass casing, anti-telescoping devices (ATDs), permeate tube, and brine seal. In addition the scroll ends are also examined for any foulant/scale material that may be interfering with flow and for feed spacer extrusion also known as telescoping and gapping in the scroll end which may cause localized scaling (uneven hydraulics).

Spiral-Wound Membrane Element Construction







Fiberglass Casing

The fiberglass casing is an integral part of each element. The purpose of this wrap is to protect the element from external differential pressure, provide compressive strength to prevent telescoping and to ensure that the various membrane components are held in their correct position for optimum performance. Damage to the wrap can be an indication of rough handling or damage from excessive differential pressure across the membrane surface.

No damage to the fiberglass casing was noted during the external examination.



Fiberglass Casing for SN# 100930418

Brine Seal

The purpose of the brine seal is to seal against the inside diameter of the pressure vessels and the outside diameter of the membrane to ensure that all the feed water passes through the membrane element. Chevron type seals are used to aid in membrane loading and to seal to a variety of pressure vessel inside surfaces.

The brine seal was in good condition.

Permeate Tube

At the center of each membrane element is a round section of pipe that is called the permeate tube. Down the length of the tube, holes are drilled through the pipe wall to the tube center. This tube is bonded to the membrane leaves and permits water to flow from the leaves outward at each end of the full element and the through the holes for collection. To function properly, the permeate tube must be free from gouges or damage that can prevent proper o-ring sealing at each end. Poor sealing can result in bypass from the highpressure feed/concentrate flow into the permeate stream.

The permeate tube was free from damage which could allow for the bypass of feed water into the permeate stream.



Anti-Telescoping Device (ATD)

When assembled at the factory, membrane elements are commonly fitted with Anti-Telescoping Devices (ATDs) at each end of the element. These devices are designed to prevent telescoping of the membrane leaves under normal operating conditions that can cause membrane damage.

Both anti-telescoping devices (ATDs) were in good condition and free of mechanical defects.



Image of feed ATD (left) and concentrate ATD (right) for SN# 100930418



Internal Inspection & Testing

Scroll End Examination

Once the anti-telescoping devices are removed, the scroll ends of the membrane leaves are examined for presence of colloidal particles, biofouling, feed spacer extrusion and membrane gapping. In addition, each scroll end is examined for the gradual axial shift of the element leaves from outer diameter of the element towards the permeate tube. This type of damage is termed "telescoping" and is caused by the development of high differential pressure (usually greater than 10 psi) across the element.

The scroll ends were discolored (brown) but free of large debris. Slight telescoping and feed spacer extrusion were observed on the concentrate end.



Image of feed scroll end (left) and concentrate scroll end (right) for SN# 100930418

Membrane Surface Visual Examination

When assembled, the surface of the membrane is a uniform, shiny surface with no visual contamination or impurities. Although the membrane surface contamination can be sometimes hard to detect visually many times contamination is very visible and easy to detect with the naked eye.

The exposed membrane surfaces were evenly coated with a thin layer of white foulant material. The foulant adhered tightly to the membrane surfaces.





Exposed membrane surface for SN# 100930418



Exposed membrane surface from feed end for SN# 100930418



Feed Spacer Visual Examination

The feed spacer is a plastic net material designed to separate membrane surfaces to form a flow path and to promote turbulence within feed water channel.

The feed spacers of the element were virtually free of foulant material.



Image of feed spacer



Glue Line Integrity Examination

Membrane leaves are glued on three sides to separate feed and permeate streams. Glue lines are inspected to ensure that there are no sections of unbounded material referred to as glue flaps that may block the feed channel into the element module. In some worst case situations, glue lines may fail at the feed end of the membrane permitting contamination. The glue lines are also inspected for pouching and delamination which often occur on the concentrate end of last stage elements. This type of physical damage may indicate permeate backpressure caused by positive pressure on the permeate side of the membrane.

Black colored foulant was observed in all the glue lines except for three membrane leaves. The black colored area in the glue line was swabbed to test for heterotrophic bacteria and yeast/mold. The samples were incubated and growth observed every 24 hours. Bacteria showed growth within 72 hours while the yeast/mold developed within 96 hours. Osmotic bubbling was also observed on the concentrate end of the element but remained on the outer edge of the glue line.



Image of black foulant observed within the glue lines (left) image of foulant observed when the glue lines were pulled apart (right)

Permeate Spacer Visual Examination

Permeate spacer provides a path for permeate flow to channel towards the central permeate tube which minimizes permeate-side pressure losses.

The permeate spacers were in good mechanical condition and free of visible foulant contamination.

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Testing for the Presence of Oxidizing Halogens

The Fujiwara test is used to confirm that a polyamide (PA) thin-film membrane has been exposed to an oxidizing halogen, such as chlorine, bromine, or iodine. This test analyzes whether halogens have become part of the polymer structure through oxidative attack. Please note that the Fujiwara test is a qualitative test and that any color change indicates the presence of a halogen in the membrane structure. However the test does not quantify the amount of exposure or which exact halogen is attached.

Fujiwara testing was positive for the presence of halogens (e.g. chlorine) in the membrane structure.



Example of negative (left) and positive (right) Fujiwara color change



Cell Test for Permeate Flow & Salt Passage

To determine membrane performance characteristics membrane samples are tested in a cell test apparatus (CTA). The water passage constant is expressed as the "A" value, and the salt passage constant is expressed by a "B" value. Both constants are functions of the chemical-physical properties of the membrane plus any fouling layer present.

"A" and "B" value constants are also independent of operating parameters such as pressure, temperature, and salt content of the feed stream. "A" value units are cm/sec/atm. "B" value units are cm/sec. The table below shows baseline performance data before cleaning.

Comparing cell testing of the membrane material to the original specification for the full spiral membrane element is a useful comparison tool. This data is collected in order to factor out any additional mechanical aspects the element construction may have caused in the spiral configuration.

| SN# 100930418 | Water Passage Constant "A" Value* | Salt Passage Constant "B" Value* | |
|---|--------------------------------------|-------------------------------------|--|
| Flat Sheet Membrane-Feed End | No Water Passage | | |
| Flat Sheet Membrane-Concentrate End | No Water Passage | | |
| Manufacturer's Specifications | 0.90 to 1.22E-04 | 4.31 to 14.5E-06 | |
| | Normal Range | Normal Range | |
| Note: Testing Conducted with dechlorinated city water from San Marcos, CA | | | |

*Average value based on six flat sheet samples tested


Foulant Analysis

Organic Content Testing

Loss on ignition (LOI) testing gives an approximation of the organic content of the foulant. Values in excess of 35% typically represent the presence of organic content.

Organic content could not be determined as the foulant adhered too tightly to the membrane surface to obtain a representative sample.

Foulant Density Measurement

Membrane foulant density is the weight of dry foulant per area of membrane surface. Foulant densities determined from past autopsies range from 0.02 to 1.84 mg/cm² and average 0.51 mg/cm².

A representative sample could not be removed from the membrane surfaces to determine the foulant density.

Testing for the Presence of Carbonates

Acid testing is used to determine the presence of carbonates on the membrane surface. In this test, several drops of dilute hydrochloric acid were placed on the foulant surfaces. Effervescing indicates a positive test result.

No effervescing was observed as acid was applied to the active membrane surfaces indicating any carbonates present were below the visual detected limit.



Testing for the Presence of Microbiological Organisms

Foulant samples were stained and examined with a light microscope at 1000x using an oil immersion lens. Gram positive bacteria are stained blue while Gram negative bacteria are stained red.

Foulant scraped from the membrane surface contained mainly amorphous material. Fungi, algae, Gram negative bacteria and Gram positive bacteria were also detected.



Light microscope images (1000x) of foulant scraped from SN#100930418



Testing for the Presence of Coagulant

Zeta potential testing of the membrane surface foulant can determine the presence of excess coagulant by measuring the charge associated with the surface colloids. Most naturally occurring colloids are negatively charged and surrounded by a double layer of counter ions. Zeta potential is the charge that resides at the double layer boundary, which we can conveniently measure with a zeta potential meter.

Electrostatic repulsion becomes significant when two colloids approach each other and their charged double layers begin to interfere. Because of this mutual repulsion, coagulation and flocculation are difficult to accomplish and coagulants are often overfed into the RO system resulting in a positive zeta potential. Samples that show a near zero or neutral zeta potential represent the optimum coagulant dosage.

The foulant adhered too tightly to the membrane surface to collect a representative sample for zeta potential testing .



Image based on diagram from Particle Characterization Laboratories, Inc.



Fourier Transform Infrared Spectroscopy Analysis

Fourier Transform Infrared Spectroscopy (FT-IR) analysis identifies the functional groups of organic and inorganic foulant constituents. FT-IR is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation.

FT-IR spectrum of the membrane surfaces identified bands associated with the membrane surface itself, several bands matching the spectrum for calcium phosphate and weak bands associated with organic material (proteins and carbohydrates).



| Peaks | Yes | Weak |
|-------------------|-----|------|
| C-H | | X |
| C-N | | X |
| N-H | | X |
| C-C | | X |
| C=C | | X |
| Н-С-ОН | X | |
| N-H-C=O | | |
| N-C=O | | X |
| C-O-C | X | |
| CaPO ₄ | X | _ |

| FI-IR Spectral image of the membrane surface of SN#1009504 | FT-IR | spectral | image | of the | membrane | surface | of | SN#10093041 |
|--|-------|----------|-------|--------|----------|---------|----|-------------|
|--|-------|----------|-------|--------|----------|---------|----|-------------|

Testing to Identify Inorganic Foulant Constituents

Energy Dispersive X-ray (EDX) analysis is conducted in conjunction with scanning electron microscopy (SEM) to identify inorganic foulant constituents. The electron beam in the microscope causes specimens to emit x-rays including those from the k, I and m atomic shells. Spectrometer counts of these x-rays, which are said to be "characteristic" of the elements present in the specimen, can be used to calculate composition for a full qualitative analysis.

| Elements | Feed End (150x) Average Weight Percent* | Concentrate End (150x) Average Weight Percent* |
|------------|--|---|
| Carbon | 60.09 | 51.19 |
| Oxygen | 25.68 | 34.57 |
| Sulfur | 4.71 | 4.22 |
| Sodium | 0.19 | 0.59 |
| Magnesium | 0.93 | 0.94 |
| Calcium | 5.35 | 5.25 |
| Phosphorus | 2.86 | 3.00 |
| Aluminum | 0.19 | 0.24 |

Inorganic Foulant Constituents Test Results

* Weight percentages based on average of four areas at magnification 150x from either the feed or concentrate end of the element





SEM image (500x) of the membrane surface on the feed end of the element



SEM image (500x) of the membrane surface on the concentrate end of the element





Close up SEM image (5000x) of the membrane surface



Chromatic Elemental Imaging (CEI)

Chromatic Elemental Imaging (CEI) is an analytical technique used to resolve the spatial distribution of elements in a foulant sample. In this technique, a beam of focused electrons is accelerated across the surface of a foulant sample and interacts with the sample's inorganic elements by causing the elements to emit electrons. Since each element has its own unique atomic shell, a particular element's electron emission from its atomic shell generates a characteristic X-ray spectrum that allows for its identification. CEI assigns each element a color and provides a high resolution image of their exact location in a sample. An element's color intensity in a Chromatic Elemental Image is largely influenced by its concentration in the foulant sample; elements present in a higher percentage will be displayed with greater intensity in the image. CEI can uniquely identify the distinct elements in a mixed foulant sample containing a number of inorganic deposits. This technique also reveals the location and concentration of different elements relative to each other in a sample.







CEI image (1500x) of the membrane surface on the concentrate end



Testing Comments and Interpretation

The Energy Dispersive X-ray (EDX) analysis identified calcium and phosphorus as the primary inorganic constituents present on both the feed and concentrate ends. Sodium, magnesium and aluminum were also detected in lesser amounts. The sulfur weight percentage represents the membrane material itself rather than the foulant layer.

The Scanning Electron Microscope (SEM) images showed that the membrane surface was evenly coated with granular foulant material on both ends of the element. Randomly dispersed particles were also observed on the membrane. Close up SEM imaging (5000x) also identified bacteria and microorganisms above the granular layer.

Chromatic Elemental Imaging (CEI) identified the granular material on both the feed and concentrate ends of the element as calcium phosphate. The bacteria and microorganisms were also coated in calcium phosphate. The membrane surface denoted by sulfur was visible in the cracks of the dried foulant layer.



Cell Test & Laboratory Clean-in-Place Study

Flat sheet membrane samples harvested from the full element are placed in a cell test apparatus and cleaned with various Avista chemicals to determine the most effective cleaner combinations and the amount of time required for an effective cleaning.

The table below shows performance data before and after cleaning. Flat sheet samples harvested from the full element were cleaned using RoClean P303 (2% by weight), hydrochloric acid (HCl pH 2.5) and citric acid (pH 2.5). All cleaning solutions were heated to approximately 35°C and allowed to circulate for two hours.

| CN# 100020410 | Water Passage Constant | Salt Passage Constant |
|---------------------------------|------------------------|-----------------------|
| SN# 100930418 | "A" Value* | "B" Value* |
| Pre Clean-RoClean P303 | No water | passage |
| Post Clean-RoClean P303 | 1.04E-04 | 10.8E-06 |
| | Normal | Normal |
| Pre Clean-HCl (pH 2.5) | No water | passage |
| Post Clean-HCl (pH 2.5) | 1.17E-04 | 13.6E-06 |
| | Normal | Normal |
| Pre Clean Citric Acid (pH 2.5) | No water | passage |
| Post Clean Citric Acid (pH 2.5) | 1.07E-04 | 15.3E-06 |
| | Normal | 106% of Normal |
| Manufacturer's Specifications | 0.90 to 1.22E-04 | 4.31 to 14.5E-06 |
| | Normal Range | Normal Range |

Note: Testing Conducted with dechlorinated city water from San Marcos, CA *Pre and post clean data based on average of feed and concentrate samples



Certification by Laboratory

| Report Number | Report Content | Element Serial Number | Report Date |
|---------------|-------------------------|-----------------------|-------------------|
| WO#101614-2 | | 100930418 | |
| | Standard Spiral Autopsy | 101122325 | No |
| | | SOY35615 | November 07, 2014 |
| | | SOY35015 | |
| | | | |

We the undersigned being the Technical Specialists in Membrane Autopsy and related testing procedures and protocol for Avista Technologies certify to the best of our knowledge and belief that the tests listed above have been conducted following Avista standard testing practices and that the results are accurate and complete.

By signing this certificate neither the laboratory employees nor their employer makes any warranty, expressed or implied, concerning the cleaning study results.

Date: 11/07/2014

Signed:

Sara Pietsch Laboratory Services Manager

Guill Robles

Erica Robles Laboratory Services Chemist





Appendix B: Membrane Autopsy Reports by NMSU

Analytical Report Submitted to

Dr. Aleks Pisarenko

Trussell Technologies, Inc.

Characterization of Membrane Fouling

Submitted by

Dr. Pei Xu Department of Civil Engineering New Mexico State University Las Cruces, NM 88003 Phone 575-646-5870 E-mail: pxu@nmsu.edu

December 8, 2014

1. OBJECTIVES

The objective of the study is to characterize membrane fouling of the elements taken from a brackish groundwater treatment plant to identify the types and extent of foulants/scalants using a suit of advanced analytical techniques.

Four membrane samples were received on October 17 (S/N SOY35015, S/N SOY35615, S/N 101122325, S/N 100930418). The membrane samples were stored in a refrigerator after receiving. Middle sections of the samples were taken for characterization of membrane fouling, including:

- Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) to observe and identify fouling and scaling on membrane surface;
- Quantify membrane foulants and scalants by extraction methods followed by elemental analysis using inductive coupled plasma (ICP) mass spectrometer (MS), ion chromatography, total organic carbon analyzer, as well as using F-EEM to measure proteins and humic acids.
- Dye tests to detect membrane damage or leaking
- Fujiwara test to determine the exposure of the membranes to halogens

2. RESULTS AND DISCUSSION

2.1 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscope (EDS) Examination of Membrane Surface

The SEM technique provides direct observation of a sample, including membrane morphology and fouling layer. The SEM in combination with an energy-dispersive X-ray spectroscope (EDS) enables analysis of elemental composition of a grain, a spot, or a whole area, being imaged by the SEM. It provides detailed information on the size, shape, structure, and chemical composition of membrane material and foulants. SEM-EDS may also be used to characterize very thin fouling layer, such as microbiological fouling, membrane scaling, or membrane degradation and defects.

Below summarizes the characterization results of the SEM and EDS.

| Analysis | S/N SOY35615 | S/N SOY35015 | S/N 101122325 | S/N 100930418 |
|----------|--------------------|--------------------|-----------------------|--------------------|
| ESEM/EDS | Membrane | Heterogeneous | Membrane surface | Heterogeneous |
| | surface is clean. | fouling layer with | is clean. Few small | fouling layer with |
| | Few small Al- | patches of thick | Al-silicate particles | patches of thick |
| | silicate particles | fouling layer. EDS | were observed on | fouling layer. EDS |
| | and a very thin | indicates calcium | membrane surface. | indicates calcium |
| | layer of | phosphate | | phosphate |
| | aluminum | deposition on | | deposition on |
| | silicates were | membrane surface | | membrane surface |
| | observed on | with small amount | | with small amount |
| | membrane | of magnesium and | | of magnesium |
| | surface. | aluminum. | | |
| | | | | |

Figure 1. SEM micrographs and EDS spectra of S/N SOY35615 membrane.









Figure 1.8. SEM and EDS mapping of the scalants.

Figure 2. SEM micrographs and EDS spectra of S/N SOY35015 membrane.





Figure 2.7. EDS spectrum of the foulants in Figure 2.6.



Figure 2.8. SEM and EDS mapping of the foulants.



Figure 2.9. SEM and EDS mapping of the foulants.

Figure 3. SEM micrographs and EDS spectra of S/N 101122325 membrane.







Figure 3.8. SEM and EDS mapping of the foulants in S/N 101122325 membrane.

Figure 4. SEM micrographs and EDS spectra of S/N 100930418 membrane.





Figure 4.7. EDS spectrum of the foulants S/N 100930418 membrane.



Figure 4.8. SEM and EDS mapping of the foulants.

2.2 Quantitative Elemental Measurement of Organic and Inorganic Substances in Fouling Layer

In addition to EDS which characterizes the chemical composition of foulants on the membrane surface, foulants were extracted from membrane surfaces to quantify the elements of the foulants and scalants on a larger area than EDS scanning. Deionized water, 0.8M HNO₃ solution, and 0.1 M NaOH solution were used as extractants. Membrane specimens (50 cm²) taken from the middle section of each membrane sample were cut into small pieces, soaked in 100 mL deionized water, 100 mL of 0.8 M HNO₃, and 100 mL of 0.1 M NaOH. These were then sonicated for 30 min in a typical laboratory sonication bath. Standard inorganic elements of the extracted solutions were analyzed using inductive coupled plasma (ICP) mass spectrometer (MS) and ion chromatography (IC). Total organic content of the solutions was analyzed using a total organic carbon (TOC) analyzer. Protein and humic or fulvic-like substances were analyzed using F-EEM spectroscopy.

Acid and base solutions extracted more organic and inorganic foulants than DI water (Table 1). The TOC and ICP-MS results are consistent with SEM and EDS analysis that membranes SOY35615 and 101122325 have much less organic fouling and inorganic scaling than SOY35015 and 100930418. Membranes of the tail-end elements are mainly fouled by the precipitation of calcium phosphate with small amount of magnesium and trace amount of Al, Sr, Ba (Table 2).

| Serial No. | DI Water Extraction | 0.1M NaOH Extraction | 0.8M HNO3 Extraction |
|---------------|---------------------|----------------------|----------------------|
| S/N SOY35615 | 3.7 | 22.6 | 5.5 |
| S/N SOY35015 | 6.9 | 26.0 | 28.0 |
| S/N 101122325 | 2.6 | 22.1 | 22.1 |
| S/N 100930418 | 4.2 | 23.7 | 20.0 |

Table 1. TOC Analysis (µg/cm²)

| | 0.8M HNO3 Extraction | | | | DI Water | Extraction | | |
|-----|----------------------|--------|-------|--------|----------|------------|-------|-------|
| | 615 | 015 | 325 | 418 | 615 | 015 | 325 | 418 |
| Ca | 3.699 | 73.196 | 0.996 | 64.755 | 1.379 | 14.742 | 1.312 | 9.836 |
| std | 0.149 | 1.659 | 0.261 | 1.774 | 0.194 | 0.300 | 0.371 | 0.636 |
| Р | 0.182 | 48.954 | 1.282 | 45.465 | 0.000 | 11.401 | 0.120 | 6.668 |
| std | 0.395 | 4.359 | 1.452 | 1.474 | 0.000 | 0.479 | 0.315 | 0.300 |
| Mg | 0.325 | 8.336 | 1.215 | 7.711 | 0.000 | 2.344 | 0.208 | 2.188 |
| std | 0.194 | 0.925 | 1.560 | 0.420 | 0.000 | 0.242 | 0.240 | 0.375 |
| Al | 0.029 | 1.052 | 0.080 | 1.083 | 0.000 | 0.212 | 0.013 | 0.063 |
| std | 0.030 | 0.231 | 0.063 | 0.056 | 0.000 | 0.060 | 0.049 | 0.020 |
| Sr | 0.021 | 0.838 | 0.024 | 0.788 | 0.020 | 0.165 | 0.020 | 0.122 |
| std | 0.006 | 0.033 | 0.004 | 0.009 | 0.001 | 0.002 | 0.002 | 0.001 |
| Ba | 0.010 | 0.313 | 0.009 | 0.254 | 0.005 | 0.027 | 0.005 | 0.010 |
| std | 0.010 | 0.030 | 0.001 | 0.012 | 0.000 | 0.003 | 0.001 | 0.002 |
| Cu | 0.000 | 0.021 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| std | 0.000 | 0.024 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Fe | 0.003 | 0.031 | 0.014 | 0.027 | 0.000 | 0.010 | 0.000 | 0.000 |
| std | 0.008 | 0.013 | 0.023 | 0.003 | 0.000 | 0.003 | 0.000 | 0.000 |

2.4.2 F-EEM Results

Membrane extractions performed with acid did not find significant peaks, except small protein-like peaks near em/ex 375/260 nm (Figure 5). The florescence intensities of the peaks are summarized in Table 3. The base and DI extractions found significant peaks for protein-like substances, indicating biofouling. Results did not show significant difference in fluorescence peaks between the lead and tail elements. It infers that organic adsorption occurs throughout the membrane elements.



Figure 5. F-EEM spectra of the membranes



Table 3. Summary of F-EEM peaks

| Extraction | Serial number | Peak 1 (Em/Ex) | Peak 2 (Em/Ex) |
|-----------------------------|---------------|-----------------|-----------------|
| DI extraction | SN#SOY35015 | 0.081 (370/210) | 0.037 (375/270) |
| | SN#SOY35615 | 0.044 (370/225) | 0.032 (360/295) |
| | SN#101122325 | 0.038 (335/215) | |
| | SN#100930418 | 0.043 (350/230) | 0.028 (375/280) |
| NaOH extraction | SN#SOY35015 | 0.045 (380/235) | 0.032 (360/295) |
| | SN#SOY35615 | 0.047 (370/240) | 0.032 (370/280) |
| | SN#101122325 | 0.044 (330/230) | 0.039 (375/275) |
| | SN#100930418 | 0.040 (375/240) | 0.036 (375/275) |
| HNO ₃ extraction | SN#SOY35015 | 0.069 (360/265) | |
| | SN#SOY35615 | 0.012 (370/260) | |
| | SN#101122325 | 0.022 (360/260) | |
| | SN#100930418 | 0 | |

2.3 Dye Test

Dye testing showed that none of the membrane elements experienced mechanical damages (Figure 6). After the Rhodamine B was applied to the active layer, the support layer was completely clean for all of the element samples, indicating that no leakage occurred.

2.4 Fujiwara Test

Fujiwara test was conducted to determine if the membrane samples had been exposed to an oxidizing halogen, such as chlorine, bromine, or iodine. The test analyzes qualitatively whether halogens have become part of the PA polymer structure through oxidative attack. The test results were positive, color of the pyridine layer (upper) changed to brown, indicating that the membranes had been exposed to some type of halogen (Figure 7).

| Serial Number | Active Layer | Support Layer |
|---------------|--------------|---------------|
| SN#SOY35015 | | |
| SN#SOY35615 | | |

Figure 6. Dye test using Rhodamine B solution





Figure 7. Pictures of membrane samples after Fujiwara test. The far left bottle is blank.



Appendix C: RO Cleaning Study by King Lee Technologies

Reverse Osmosis Membrane Element

Cleaning Study Report

for

Trussell Technologies, Inc.: Advanced Water Purification Facility

October 2014

Subject: Reporting Results of Membrane Cleaning Study

October 24, 2014

Aleks Pisarenko, Ph.D. Trussell Technologies, Inc. 380 Stevens Avenue, Suite 308 Solana Beach, CA 92075 858-458-1030 x124 aleksp@trusselltech.com

Dear Mr. Pisarenko:

We are pleased to report our Cleaning Study findings on two membrane elements submitted on 10/16/2014.

This report was done per your verbal PO.

Background

This cleaning study is part of the harvested membrane analysis done by Trussell Technologies, Inc. at the test Advanced Water Purification facility. The test facility currently processes tertiary treated sewage water for non-potable use. The process includes feed through a pretreatment MF/NF filtration system, followed by two Reverse Osmosis trains fed in parallel, and finally through UV disinfection.

Goal of the Study

Cleaners are being tested on membrane elements to determine an optimum cleaning procedure.

RO Membrane Elements Specifications

| | Element 1 | Element 2 | | | | | | | | | |
|-------------------------------|---------------------------|---------------------------|--|--|--|--|--|--|--|--|--|
| Manufacturer | Hydronautics | Toray | | | | | | | | | |
| Model No. | ESPA2-LD | TML20-400 | | | | | | | | | |
| Serial No. | SOY34435 | 100930385 | | | | | | | | | |
| Position | next-to-last in 2nd stage | next-to-last in 3rd stage | | | | | | | | | |
| Train | А | В | | | | | | | | | |
| MANUFACTURING SPECIFICATIONS: | | | | | | | | | | | |
| Productivity (GPD) | 10,000 | 10,200 | | | | | | | | | |
| Salt Rejection (%) | 99.6 | 99.7 | | | | | | | | | |

Cleaning Study

Wet Test

Upon arrival the test elements were weighed, then characterized using the manufacturer's wet test conditions.

The first table in Appendix A shows the Cleaning Study data for the SOY34435 element. The nominal productivity specified by the manufacturer is 10,000 gallons per day, and the nominal salt rejection is 99.6%. This element had a wet test normalized flow of 91% of nominal and a normalized salt rejection of 98.9%. Because the flow is within 15% of nominal and the salt rejection is above 98%, this element likely is not fouled significantly.

The second table in Appendix A shows the Cleaning Study data for the 100930385 element. The nominal productivity specified by the manufacturer is 10,200 gallons per day, and the nominal salt rejection is 99.7%. This element had a wet test normalized flow of 28% of nominal and a normalized salt rejection of 99.5%.

Cleaning Test

The tables in Appendix A show the cleaning formulations through which the membrane elements were cycled and the resulting test data. Each cleaner was circulated for approximately 30 minutes at ambient temperature.

The SOY34435 normalized productivity as a percentage of nominal is shown in the final column of the first table. This relative flow decreases with the low pH cleaners (Diamite LpH, KL-1000, and KL-1050) and increases with the high pH cleaners (KL-2000 and Diamite BFT). The salt rejection remained relatively consistent, as shown in the next-to-last column in the table.

The 100930385 normalized productivity as a percentage of nominal is shown in the final column of the second table. The element began at a normalized productivity that was 28% of nominal. Normalized productivity of 147% of nominal was achieved with acid cleaner KL-1000. The formulations circulated following KL-1000 did not increase the percent of nominal flow. The normalized salt rejection decreased following each cleaning.

Discussion, Conclusions, and Recommendations

As previously mentioned, the wet test indicated that the SOY34435 membrane element from Train A was not fouled significantly. Therefore, the minimal changes in normalized productivity for this element can be attributed, at least in part, to the loosening and tightening of the membrane as a result of the cleaning solutions.

Significant fouling of the third-stage membrane is typical for three-stage systems due to the lower bulk flow and lower level of control over the third stage. During the cleaning test, the increase in normalized productivity for element 100930385 from 28% to 147% of nominal indicates that the low pH cleaner KL-1000 is effective for removal of the colloidal calcium phosphate membrane foulant. The decrease in normalized salt rejection can be expected due to

removal of the foulant layer during cleaning. The post-cleaning productivity of 139-147% exceeds the standard allowance of 15% variation from nominal for a healthy membrane. Multiple factors can contribute to this, for example, frequent cleanings. Exposure to halogens can also cause membrane damage. However, the normalized salt rejection above 98% implies that this is not the cause.

Please contact King Lee Technologies if you have questions or concerns.

Sincerely,

Amy C. Nowlin

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Appendix A

Wet Test and Cleaning Results

King Lee Technologies Cleaning Data Sheet

| Commercial Informati | on | Technical Information | Manufacturing Test Specifications | | | | | | | |
|-----------------------------|--------------------------|-----------------------|-----------------------------------|---------------|------|-------|------------|-----|------|--|
| Date Element Rec'd | 10/16/2014 | Element Manufacturer | Hydronautics | Pressure | Net: | 132.4 | psig Test: | 150 | psig | |
| Client | Trussell Technologies | Element Model | ESPA2-LD | Recovery | | 15% | | | | |
| Contact | Aleks Pisarenko | Productivity, GPD | 10,000 | Temperature | | 77 | °F = 25 °C | | | |
| PO# | verbal & email per Aleks | %Rejection | 99.6 | Test Solution | | 1500 | ppm NaCl | | | |

| Date | S/N | Cleaner | Soak Time | Circ Time | Differential Pressure | Perm Pressure | Feed Pressure | Feed Temp | Perm Flow | Conc Flow | Feed Cond. | Perm Cond. | Norm GPD | Norm %Rej | % Spec Flow |
|--------------------------------------|----------|------------|--------------|--------------|--------------------------|------------------|------------------|--------------|--------------|--------------|---------------|---------------|-------------|--------------|----------------|
| | | | | | UP | Рр | Pc | Tf | Fp | Fc | Cf | Ср | | | |
| | SOY34435 | Pre-test | | | 1.5 | | 150 | 75.2 | 6.03 | 17.5 | 800 | 9 | 9,113 | 98.9% | 91% |
| | | | | | | | | | | | | | | | |
| | | D-LpH | | 30 | 1.5 | | 150 | 75.2 | 5.7 | 17.5 | 800 | 9 | 8,619 | 99.0% | 86% |
| | | KL-1050 | | 30 | 1.0 | | 150 | 75.2 | 5.95 | 17.5 | 800 | 9 | 9,009 | 98.9% | 90% |
| | | KL-2000 | | 30 | 1.0 | | 150 | 75.2 | 6.30 | 17.5 | 800 | 9 | 9,534 | 98.9% | 95% |
| | | KL-1000 | | 30 | 1.0 | | 150 | 75.2 | 5.34 | 17.0 | 800 | 9 | 8,096 | 99.0% | 81% |
| | | Diamite BF | T | 30 | 1.0 | | 150 | 75.2 | 7.62 | 17.0 | 800 | 9 | 11,511 | 98.7% | 115% |
| Notes: Pre-test weight: 31.70 lbs | | | | | | | | | | | | | | | |
King Lee Technologies Cleaning Data Sheet

| Commercial Information | | Technical Informati | Manufacturing Test Specifications | | | | | | |
|------------------------|--------------------------|---------------------|-----------------------------------|---------------|------|-------|------------|-----|------|
| Date Element Rec'd | 10/16/2014 | Element Manufacture | er_Toray | Pressure | Net: | 201.5 | psig Test: | 225 | psig |
| Client | Trussell Technologies | Element Model | TML20-400 | Recovery | | 15% | | | _ |
| Contact | Aleks Pisarenko | Productivity, GPD | 10,200 | Temperature | | 77 | °F = 25 °C | | |
| PO# | verbal & email per Aleks | %Rejection | 99.7 | Test Solution | _ | 2000 | ppm NaCl | | |

| Date | S/N | Cleaner | Soak Time | Circ Time | Differential Pressure | Perm Pressure | Feed Pressure | Feed Temp | Perm Flow | Conc Flow | Feed Cond. | Perm Cond. | Norm GPD | Norm %Rej | % Spec Flow |
|--------|-------------|---------------|--------------|--------------|--------------------------|------------------|------------------|--------------|--------------|--------------|---------------|---------------|-------------|--------------|----------------|
| | | | | | DP | Рр | Pc | Tf | Fp | Fc | Cf | Ср | | | |
| | 100930385 | Pre-test | | | 1.5 | | 225 | 75.2 | 1.88 | 21 | 800 | 12 | 2,819 | 99.5% | 28% |
| | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| | | KL-1000 | | 30 | 1.5 | | 225 | 75.2 | 10.20 | 21 | 800 | 9 | 14,974 | 98.3% | 147% |
| | | KL-1050 | | 30 | 1.5 | | 225 | 75.2 | 9.88 | 21 | 800 | 10 | 14,513 | 98.2% | 142% |
| | | KL-2000 | | 30 | 1.5 | | 225 | 75.2 | 9.65 | 21 | 800 | 8 | 14,183 | 98.6% | 139% |
| | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| Notes: | | | | | | | | | | | | | | | |
| | Pre-test we | ight: 30.95 I | lbs | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |

Appendix B

Product Information

Diamite[™] Series

Liquid Membrane Cleaners

The Diamite Series is a line of liquid membrane cleaners designed to remove a variety of organic and inorganic foulants. All Diamite cleaners are highly concentrated and easy to use.

| Product | Ideal For | Membrane | Mixing Ratio | pH |
|------------------------|--|---------------------|-------------------------------------|------|
| Diamite ACA | Microbiological Matter, Silt, Organics, Particulates, Colloids, Acid Insolubles. | Cellulose Acetate | l gallon to 40 gallons of water. | Med. |
| Diamite LpH and ZpH | Fe, CaCO3, Metal Oxides, Inorganic Salts, Acid Solubles. | All Types | l gallon to 40 gallons of water. | Low |
| Diamite AFT and BFT | Silt, Organics, Particulates, Colloids, Microbiological Matter, Acid Insolubles. | Thin Film Composite | l gallon to 40 gallons of water. | High |

Diamite ACA

Diamite ACA was designed to optimize cellulose acetate membrane performance by effectively removing microbiological foulants, organics, silt, and particulates from the membrane surface. It is buffered to not cause hydrolysis of cellulose acetate.

Diamite LpH and ZpH

Diamite LpH and ZpH are ideal for the removal of acid soluble scale including iron, calcium carbonate and metal oxides. They are compatible with thin film composite and cellulose acetate membranes. The mild acidic liquids are convenient and safe to use.

Diamite AFT and BFT

Diamite AFT and BFT were designed to aggressively remove silt, organics, particulates, colloids and microbiological foulants from thin film composite membranes. The unique formulations include a highly effective sanitizing agent that eliminates the need for hydrogen peroxide, formaldehyde, and other membrane disinfectants as a post or pretreatment to membrane cleaning.

Cleaning Procedures

- Prepare system for cleaning and fill cleaning tank with good quality water.
- Use 1 gallon of Diamite Cleaner for every 40 gallons of cleaning solution mixed.
- Re-circulate the cleaning solution for a minimum of 1 hour. Heavily fouled membranes may require a static soak.
- For best results:
 - *Temperature* elevated, but should not exceed 110°F.

Pressure – minimal (not to exceed 60 psig).

Flow rate per unit – 4 inch diameter membrane 9 gpm

- 8 inch diameter membrane 35 gpm
- Rinse system with good quality water for a minimum of 30 minutes at low pressure.
- Discard system product water for a minimum of 15 minutes after system start-up.

*MSDS available upon request.

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KL[™] Series Powder Membrane Cleaners

KLIMSeries are heavy duty action cleaners that quickly and easily mix with water to make an easy to use cleaning solution that safely and effectively remove a wide range of membrane foulants from polyamide thin film (TF), cellulose acetate (CA) and ultrafiltration (UF) membrane elements.

| Product | For Removing | Membrane Type | Solution pH |
|---------|--------------------------------|---------------|-------------|
| 1000 | Hardness Scale | TFC, CA & UF | 2 |
| 1010 | Metallic Oxide Scale | TFC, CA & UF | 2 |
| 1050 | Silica | TFC, CA & UF | 4 |
| 2000 | Organics | TFC & UF | 11 |
| 2010 | Biofoulants | TFC & UF | 11 |
| 2020 | Barium/Strontium Sulfate Scale | TFC & UF | 11 |
| 2030 | Calcium Sulfate Scale | TFC & UF | 11 |
| 2040 | Sulfur | TFC & UF | 11 |
| 3000 | Iron | TFC, CA & UF | 6 |
| 3030 | Hardness Scale | TFC, CA & UF | 2 |
| 7000 | Biofoulants | TFC, CA & UF | 8 |
| 7020 | Barium/Strontium Sulfate Scale | TFC, CA & UF | 4 |
| 7330 | Organics | TFC, CA & UF | 7 |

*MSDS available upon request.

Cleaning Procedure

- 1. A) When the system's normalized flow and/or salt rejection has decreased up to 15% or delta P has increased up to 15%; mix cleaner in the ratio of 11b to 15 gallons of clean water. B) When the system's normalized flow and/or salt rejection has decreased by more than 15% or delta P has
- increased by more than 15%: mix cleaner in the ratio of 11b to 10 gallons of clean water. 2. Cleaning solution temperature must not exceed the maximum allowed by the membrane manufacturer. The minimum temperature for maximum effectiveness is 86°F (30°C).
- 3. Recirculate cleaning solution through each section of system for a minimum of 50 minutes. For heavily fouled membranes a static soak is beneficial.
- Cleaning pump pressure: less than 60 psi Flow rates per element: 4 inch diameter @ 7-12 gpm 8 inch diameter @ 25-35 gpm
- 5. Flush system after cleaning with feed or permeate water. Typical rinse time is 15 to 30 minutes.

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