RECOVERY ZONE SPRING 2023

PFAS Removal From Surface Water with Nanofiltration and Treatment of Membrane Concentrate

Authors: Samantha Black, PhD, PE (HDR), Katie Walker, PE (HDR), Haley White, PhD (HDR), Dell Harney (City of Greensboro)

Introduction

The City of Greensboro, NC (City) operates the Mitchell Water Treatment Plant (WTP), a 24 million gallon per day (MGD) conventional treatment facility. One of the City's long-term goals is to provide a robust and flexible advanced treatment process capable of treating both emerging and regulated contaminants. One family of emerging contaminants includes per- and polyfluoroalkyl substances (PFAS). The Environmental Protection Agency (EPA) has established a lifetime health advisory level of 70 nanograms per liter (ng/L) for the sum of two PFAS, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). The EPA will publish draft regulations for PFOS and PFOA in 2023.



PFAS have been detected in the City's water supply for the Mitchell WTP. For this reason, the City operates a powdered activated carbon (PAC) system at the Mitchell WTP for a portion of the flow on an as-needed basis. However, identifying a permanent and more sustainable technology for PFAS removal is a priority. Granular activated carbon (GAC) and ion exchange (IX) are two proven advanced treatment technologies for PFAS removal from drinking water supplies. Additionally, novel sorbents (NS) are emerging on the market and show promise for reducing PFAS in drinking water. Reverse osmosis (RO) and nanofiltration (NF) membranes are other proven PFAS treatment alternatives. However, one major drawback is that membranes produce a continuous concentrate stream, which requires disposal. There are options for concentrate treatment, including GAC, IX, and NS. Additionally, the waste stream can be further concentrated using other separation technologies such as foam fractionation (FF).

MESSAGE FROM OUR PRESIDENT

Welcome to the year of the Water Rabbit in Chinese cosmological terms . . . 2023! The Rabbit represents peace and prosperity which creates something to look forward to in this fast-paced society. Looking back to 2022, we worked through challenges such as supply chain uncertainties, hiring workers and high inflation. It does not seem things will return to the way they used to be. The good news is professionals in the water treatment industry have been progressively adapting to these challenges thanks to the comradery and engagements with associations like SEDA.

In 2022, the SEDA Training Committee offered four Membrane Operator Certification (MOC) courses and five Technical Workshops. A total of 273 MOC certificates were issued and 100 people attended workshops. The certificates earned are a great feather in the cap for professionals in the water treatment industry. Once again, I would like to thank all the utility's folks, administration, sponsors, presenters and the Board of Directors for participating in our educational events. The membership collaboration at these events creates synergy by providing more learning opportunities and networking.

Looking forward to June of 2023, the Annual Symposium will be held in Delray Beach, Florida. The uncertainty of Hurricane Ian landfall led the Program Committee to revert to the east coast again. The event dates a week before the Fourth of July Holiday. SEDA will unveil a most fitting association slogan originating from the membership at the venue.

I hope you all received a digital version of the Recovery Zone newsletter in your email. For some of us, the digital version is a perfect fit while other folks prefer the paper version as their norm. I assure you; the Board of Directors are frequently discussing how to measure the effectiveness of paperless outreach to continue to better our environment. The digital format is printer friendly so it can be hard copied in the plant operator's control room. You also may have noticed the delivery of the publication is from the Newsletter Chair, creating a personalized touch. If you would still like to receive a hard copy by mail please email admin@ southeastdesalting.com.

As always, SEDA is here to help you to be successful in overcoming new challenges in 2023. The prosperity of the Water Rabbit has already influenced a great lineup of early training opportunities for anyone in need of CEU's for the quickly approaching April cycle. Please feel free to drop a line to anyone on the Board of Directors for help, opinions, or just to express an idea or new goal for the membership. The Board's knowledge bank is an added value of your SEDA membership bundle.

I hope the year of the Water Rabbit is prosperous for all of us in 2023!

Yours truly,

Pierre







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The Mitchell WTP is undergoing renovations to improve plant performance, which will likely result in improved organics removal and a reduction in the formation of DBPs upstream of the future advanced treatment process. GAC and RO / NF membranes can reduce organics and potentially minimize the formation of unregulated DBPs, but IX and novel sorbents typically do not remove organics.

The ultimate goal of this project is to identify a successful, cost-effective, sustainable, and flexible technology that will be implemented at the Mitchell WTP for PFAS and emerging contaminant treatment. The project team has established a series of events to meet this goal as shown in Figure 1. At the current stage of the project, water quality review, goal setting, bench-scale testing, and now pilot-scale testing have been completed.



Figure 1. Steps to Meet Greensboro Project Goals

Figure 2 presents a simplified Mitchell WTP process flow diagram. Lake Brandt is the sole water source for the Mitchell WTP. Sodium permanganate is added at the Lake Brandt Pump Station then water is pumped to the Air Harbor Reservoir. With the recent replacement of a broken valve at the Air Harbor Reservoir, this 20 million-gallon (MG) structure is expected to provide two to three days of storage, turbidity settling, and possibly settling of precipitated iron and manganese under normal flow conditions. Reservoir effluent travels by gravity to the Mitchell WTP and splits into two process trains just prior to

entering the facility. One process train is referred to as the Seminole train and is located on the southwest side of the site, and the other is referred to as the Battleground train and is located on the northeast side of the site.

The Seminole train contains the PAC system, which is used intermittently as needed for PFAS removal. Lime, polymer, caustic, and ferric sulfate are added as pre-treatment chemicals prior to rapid mix, flocculation, and sedimentation. Caustic and pre-chlorine are used upstream of dual-media filters, which contain sand and anthracite. Seminole filter effluent is then combined with Battleground filter effluent for post-treatment.

The Battleground train utilizes polymer, caustic, and ferric sulfate upstream of rapid mix, flocculation, and sedimentation. Similar to the Seminole train, caustic and pre-chlorine are applied upstream of dual-media filters containing sand and anthracite. Battleground filter effluent is then combined with Seminole filter effluent.

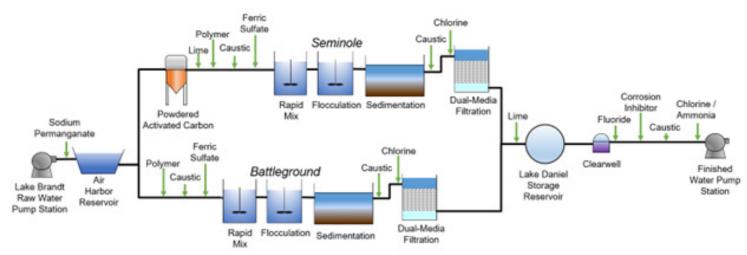


Figure 2. Mitchell WTP Process Flow Diagram

Post-treatment of combined filter effluent includes lime then storage at Lake Daniel and an on-site clearwell. The City has the ability to inject fluoride, although this has not been done at the Mitchell WTP in the last five years. Orthophosphate is added for corrosion control and caustic is added for final pH adjustment. Chlorine and ammonia to form chloramines are the final chemicals added prior to distribution for disinfection.

The primary goal of the pilot-scale testing was to test advanced technologies for PFAS treatment. These technologies included GAC, IX, NF, NS, and FF. The top two GAC medias and top two IX resins during bench-scale testing were selected for pilot-scale evaluation. Two novel sorbents that have recently emerged in the drinking water industry were tested – one treating filtered water and the other treating NF concentrate.

Media, resin, and sorbents are impacted by various water quality parameters, such as total organic carbon (TOC) and metals as well as pretreatment chemicals; therefore, one year of pilot testing was conducted to capture seasonal variations and expected plant chemical use.

The purpose of this paper is to focus on the Membrane Pilot and Membrane Concentrate Pilot. Some GAC and IX Pilot discussions are included since they relate to the overall project goals, but further information related to the GAC and IX Pilots are available upon request.

Pilot Set Up

Test water to the Membrane Pilot was transferred from the combined filter effluent (CFE) basin. As shown previously in Figure 2, CFE has been treated with chemicals including lime, polymer (as needed), ferric sulfate, caustic, and pre-filter chlorine. Because pilot influent has been pretreated, turbidity is low (< 0.1 NTU) and TOC has been partially removed. Figure 3 presents a simplified schematic of the pilot process flows.



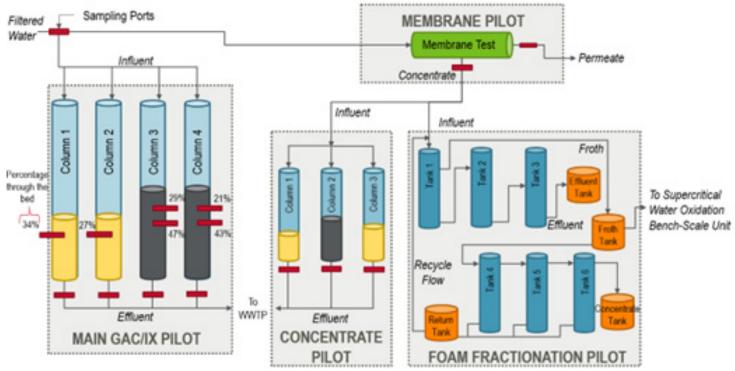


Figure 3. Pilot Process Flow Diagram

The Membrane Pilot was provided by Harn R/O and treated filtered water, and the Concentrate Pilot skid is owned by the City. The pilots are shown Figure 4. The Membrane Pilot is a 2:2:1:1 array, which simulates a full-scale 2:1 array. NF270 membranes, manufactured by DOW, were tested during this study. For this study, the pilot was operated at recoveries of 80%, 85%, and 90% and the concentrate valve was adjusted to make recovery changes.

The Concentrate Pilot treated concentrate from the Membrane Pilot and contained IX (column 1), GAC (column 2), and a NS (column 3). The Concentrate Pilot columns were 6" in diameter and media depths and flow rates varied depending on desired empty bed contact times (EBCTs). The IX EBCT was 2 minutes, two GAC EBCTs of 10 minutes and 20 minutes were tested, and the NS EBCT was 5 minutes.



Figure 4. Membrane Pilot and Membrane Concentrate Pilot



A suite of water quality parameters was evaluated throughout this study. For brevity, only a portion of the data are presented. Test water results are summarized in Table 1 for the CFE (Membrane Pilot feed water). In addition to determining treatment capabilities, monitoring feedwater can indicate operability of a system. Membrane feedwater parameters such as anions, metals, and pH can indicate the propensity of membrane elements to scale or foul, affecting performance and membrane longevity.

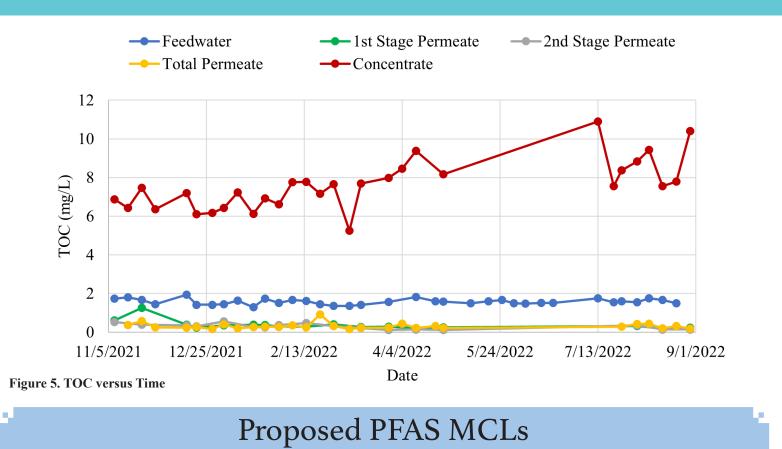
Parameter	MIN	AVG	MAX
Field Parameters			
pH	6.0	6.6	7.9
Temperature	4.8	16	30
Turbidity	0.052	0.44	1.2
Conductivity	6.39	148	561
Laboratory Parameters			
TOC	1.38	1.58	1.94
Total Iron	< 0.025	0.070	0.41
Dissolved Iron	< 0.025	0.029	0.042
Total Manganese	< 0.005	0.011	0.027
Dissolved Manganese	< 0.005	0.0055	0.008
TDS	68	89	126
Chloride	7.25	16.9	124
Sulfate	20	24	37
Nitrate	0.090	0.24	0.60
Calcium	7.2	8.1	10
Magnesium	2.48	2.76	3.01
External Laboratory Parameters			
Total PFAS 1	42	72	125

 Table 1. CFE Water Quality Summary

15 PFAS were detected during this study.

Figure 5 presents TOC data collected from the Membrane Pilot. TOC was relatively consistent in the feedwater. TOC rejection ranged from 37% to 88% with an average value of 80%. This translates to TOC in the permeate stream ranging from 0.17 to 0.91 mg/L, which would significantly reduce DBP formation. TOC in the concentrate stream ranged from 5.25 to 10.9 mg/L.





Who: The United States Environmental Protection Agency

What: Per- and Polyfluoroalkyl Substances (PFAS), specifically perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorononanoic acid (PFNA), hexafluoropropylene oxide dimer acid (HFPO-DA, commonly known as GenX Chemicals), perfluorohexane sulfonic acid (PFHxS), and perfluorobutane sulfonic acid (PFBS). These substances are deviations of the PFAS family and were widely used substances in manufacturing products in the early 1900's

Author: Allyson Felsburg, Town of Jupitar

When: The EPA released new Maximum Contaminant levels on March 14, 2023. Finalization of the proposed rule is anticipated by the end of 2023.

Where: PFAS have been found around the nation in drinking water, stormwater and wastewater. There are higher concentrations observed in the vicinity to some manufacturing facilities and airports. However, these new MCLs will apply to all drinking water facilities.

Why: The rule is intended to prevent PFAS-attributable illnesses and promote public health.

How: There has been multiple means of treatment that have proven effective for removal of PFAS compounds from drinking water which include membrane treatment, granular activated carbon, and ion exchange. *also expressed as ng/L

Compound	Original Health Advisory Limit	Previous Health Advisory Limit	Proposed MCLG	Proposed MCL (enforceable levels)	Method Detection Limit
PFOA	70 ppt	0.004 ppt	Zero	4.0 ppt*	2.0 ppt
PFOS	70 ppt	0.020 ppt	Zero	4.0 ppt	2.0 ppt
PFNA			1.0	1.0	
PFHxS			(unitless)	(unitless)	
PFBS		2,000 ppt	Hazard	Hazard	
HFPO-DA		10 ppt	Index	Index	



Figure 6 presents average PFOS results from Membrane Pilot samples. PFOS was selected to present since it was present in the highest concentrations in test water. Results are shown for operation at both 80% and 85% recoveries. Data from the 90% operating recovery was not received back from the laboratory at the time of this paper development. PFOS rejection was > 90%, with levels near or below the detection limit. PFOS measured in the concentrate stream were on average around 100-107 ng/L. This stream supplied the Concentrate Pilot influent.

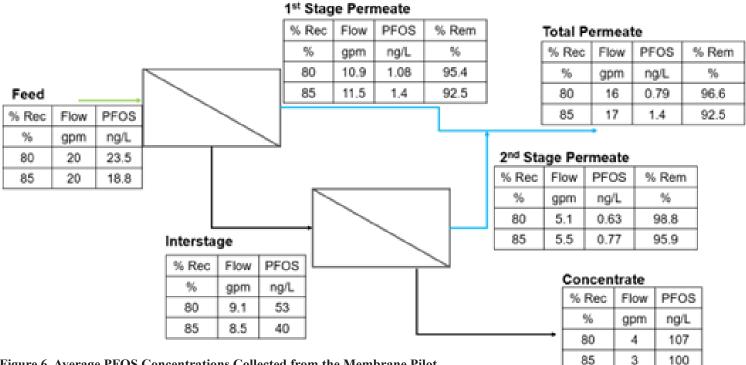


Figure 6. Average PFOS Concentrations Collected from the Membrane Pilot

The Concentrate Pilot influent contained high PFAS concentrations since PFAS were rejected from the Membrane Pilot. Concentrate Pilot total PFAS influent ranged from 200 ng/L to 662 ng/L. A majority of the total PFAS in Concentrate Pilot influent was PFOS and PFHxS. Figure 9, 10, and 11 present PFAS data for the IX, GAC, and NS columns, respectively.



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In Figure 7, sulfonic acid PFAS (e.g. PFOS, PFHxS, and PFBS) are removed better than carboxylic acid PFAS (PFOA, PFHpA, and PFHxA) with the same number of carbons. At the beginning of the study, each of the six PFAS presented in Figure 9 are removed by > 95%. At operation continues, the carboxylic acid-type PFAS begin to breakthrough first and reach 50% breakthrough after about 35,000 bed volumes. Removal is largely dependent on influent PFAS concentration, which is the cause for the increase in PFAS removal between 50,000 and 100,000 bed volumes. After almost 100,000 bed volumes, PFOS and PFHxS are still below detection limits in the IX effluent and PFBS has only slightly broken through the IX resin bed.

IX is a viable technology for PFAS treatment from membrane concentrate, if membranes are installed at the full-scale and concentrate treatment is desired. IX change-out will occur based on feedwater PFAS levels and target treated water PFAS concentrations.

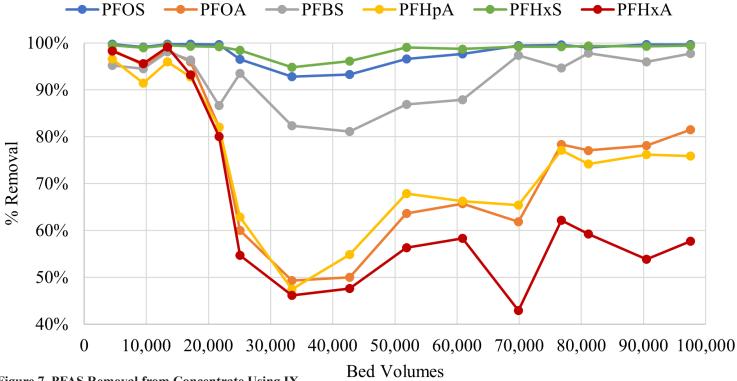


Figure 7. PFAS Removal from Concentrate Using IX

In Figure 8, the sulfonic acid PFAS (black and green data in the figure) are removed better than the carboxylic acid PFAS (shown in blue and orange), similar to what was observed for IX treatment. This figure demonstrates the impact that EBCT can have on PFAS treatment. The carbon operating with a higher EBCT of 20 minutes took longer to reach PFAS breakthrough compared to the same type of carbon operating with an EBCT of 10 minutes.

Additionally, this figure shows the impact that other constituents such as TOC can have on PFAS removal from GAC, since GAC is not PFAS-specific. Breakthrough began relatively quickly compared to IX, which is PFAS-specific and operates at a lower EBCT.





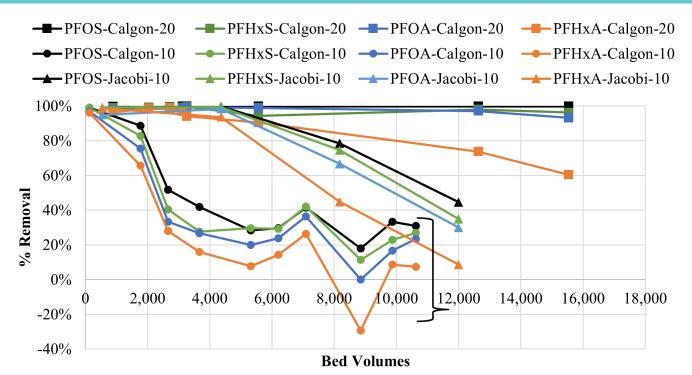


Figure 8. PFAS Removal from Concentrate Using GAC

Table 2 presents a summary of benefits and challenges associated with each of the technologies tested. Any of the technologies evaluated could be viable for PFAS treatment at the City's Mitchell WTP, but they each have challenges that must be addressed and considered during design. These challenges will be evaluated during the next phase of the project to determine the process ultimately installed at the full-scale.







Table 2. Technology Benefits and Challenges Observed as a Result of Pilot Testing

Fechnology	Benefits	Challenges
• NF •	Consistently achieves > 90% PFAS removal Consistently results in TOC < 1.0 mg/L	 Produces continuous waste stream that requires PFAS treatment Susceptible to iron fouling at the Mitchell WTP Requires two pretreatment chemicals (antiscalant and dechlorination) Operates at feed pressures higher than existing technologies Will require some post-treatment for permeate to match existing finished water
٠	PFOS and PFHxS, the two main contributors to the total PFAS concentration, were still at or near detection limits after one year of pilot operation	
GAC •	(> 20,000 bed volumes treated) for one of the GAC media For the other GAC, PFOS and PFHxS broke	Requires more contactors compared to IX due to a longer EBCT
Une	through early on in the study and were at around 60-80% removal after 24,000 bed volumes	Requires one pretreatment chemical (dechlorination)
•	Provides partial TOC removal Minimal headloss challenges due to larger media compared to IX resin	
• IX	PFOS and PFHxS, the two main contributors to the total PFAS concentration, were still at or near detection limits after one year of pilot (> 110,000 bed volumes treated) operation for one of the GAC media	 Fouling was observed, which may or may not occur at the full-scale No additional water quality benefit
•	Depending on resin type, chemical pretreatment (dechlorination) may not be required	

The following conclusions were developed after a review of pilot results.

- The NF270, a relatively loose membrane, provides substantial PFAS removal (> 90%) from filtered water.
- Membrane pretreatment required dechlorination and antiscalant dosing to reduce membrane damage. Despite this, the membranes still experienced scaling due to iron accumulation. Clean-in-place (CIP) events restored membranes to original performance, but frequent CIPs are not a viable operational strategy.
- Membrane concentrate treatment by IX was the superior treatment technology due to the high organic loading to the Concentrate Pilot columns. GAC is a viable option but would require more frequent change-outs compared to IX.

Next steps for this project include a complete analysis of these treatment technologies. This analysis will include a PFAS treatability review, a secondary water quality benefits (e.g. TOC removal) assessment, a cost analysis (capital, operational, and life cycle), an operational requirements review, site plan layout development, and an integration with existing facilities evaluation. Ultimately this will lead to final technology selection, followed by preliminary design of the full-scale treatment facility.

RECOVERY ZONE - 11 🛌

Anatomizing of 2020 Lead and Copper Rule Revisions

Author: Pierre Vignier, City of Port St. Lucie

Lead Service Line Inventory

- Information required: Material classification, all service lines and ownership, Information used to identify material
- Deadline for submission: October 16, 2024
- Must be publicly accessible

Sampling and Monitoring Program

- For verified LSL the 1st liter sampled will be analyzed for copper and the 5th liter collected will be analyzed for lead.
- Schools and childcare facilities must be sampled at a rate of 20% per year over the span of 5 years.
- A new Tier system will be implemented

Optimization of Corrosion Control Treatment and WQPs

- Orthophosphate inhibitors exceed calcium hardness indicators as part of corrosion control.
- PWS with and without corrosion control treatment may need to evlaute current corrosion studies for deficiencies.
- New sampling and testing requirments for 20% of the schools and daycare's children per year.

Customer Outreach and Education

- Within 30 days of completing your LSL inventory any customer with a LSL, GRR, or lead status unknown must be notified and this notification must be completed annually. This notification must include:
- Statement about service material
- Lead health effects
- Steps to minimize lead exposure in drinking water

Lead Service Line Replacement Program

- Maximum Containant Level Goal of zero for lead
- Lead trigger above level of 10 ppb requires to set annual goal for replacing known lead services.
- Above 15ppb requires full repalcement of pipes of three percent of known or potential services annually



Sampling Header



Optimization Header



Customer Outreach Header



Lead Service Inventory Header



Lead Service Replacement Header



SEDA QUIZ

By: Fred Greiner, JEA H2.0 Purification Manger

- During sample collection you experience a significant pH drop in your contact chamber. You checked your caustic feed, and it is dosing correctly. What is the most probable cause?
 - A. Sudden change in source water quality
 - B. Extreme biofouling in the second stage elements
 - C. A broken degassifier belt
 - D. Extreme biofouling in the first stage elements
- 2. Which of the following membranes are chlorine tolerant?
 - A. Cellulose Acetate
 - B. Thin Film Composite
 - C. Hollow fiber
 - D. No membrane process can handle chlorine
- 3. Which of these are considered a colloid or fouling index using a .45 micron filter?
 - A. LSI
 - B. Ryznar index
 - C. SDI
 - D. Aggressive index
- 4. In the membrane treatment process what describes the pore size or rejection capability of a membrane?
 - A. Concentration polarization
 - B. μ mhos/cm
 - C. MWCO
 - D. SDI
- 5. What is the main benefit of an EDR unit?
 - A. Reversing polarity every 15 minutes aids in reducing scale formation
 - B. Acts as a powerful disinfectant
 - C. Acts as a booster for DC system
 - D. Reduces gases in the separator tank

- 6. Select the mg/l of chlorine that it takes to theoretically takes to oxidize 1 mg/l of hydrogen sulfide to sulfate.
 - A. 4.0 mg/l
 - B. 6.5 mg/l
 - C. 2.08 mg/l
 - D. 8.32 mg/l
- 7. What concentration (in ppm) of chlorine gas will cause death after a few deep breaths?
 - A. 10 ppm
 - B. 30 ppm
 - C. 100 ppm
 - D. 1000 ppm
- 8. If a new or altered well or a well that has been out of operation for more than.....a biological survey is required (increased bacti-sampling regiment)?
 - A. 30 days
 - B. 6-months
 - C. 12-months
 - D. 3-years
- 9. What term is used to express the measure of pipe wall roughness that retards the flow because of friction?
 - A. C factor
 - B. Correlation efficiency
 - C. Tubercles
 - D. Corrosion factor
- 10. Which of the (4) trihalomethanes s the most volailte?

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- A. Bromoform
- B. Dibromochloromethane
- C. Bromodichloromethane
- D. chloroform

Answers can be found on the SEDA website at http://www.southeastdesalting.com/members-only/quiz/



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> May MOC I Melbourne, FL

July MOC I Collier County, FL

Aug MOC I Mt. Pleasant, SC

MOC III Palm Coast, FL

Sept MOC II Orlando, FL

Dates to be determined - Keep up to date on: https://seda.memberclicks.net/calendar-of-events Pretreatment for RO/NF Workshop Clearwater, FL

> Autopsy Workshop Plant City, FL

Scaling and Fouling Palm Beach County, FL

> **Post-treatment and Corrosion Control** Pompano, FL

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Proposed PFAS MCLs

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