ULTRA-HIGH PRESSURE REVERSE OSMOSIS (UHPRO) SYSTEM FOR TREATING PFAS/PFOA WASTEWATER FROM AN INDUSTRIAL FACILITY AS PART OF A ZLD PROJECT

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Summary

An industry was reducing their environmental footprint by implementing a ZLD system on a residual stream from their process water treatment. The UHPRO part of the ZLD was studied by developing a synthetic feed stream and performing a batch trial to determine design. The batch trial was run with a commercial AquaZoom 8040 DTRO membrane with pressure rating 1,740 psi with operating up to 1,700 psi. The data showed a flux range from 7.15 GFD down to 3.25 GFD, concentration ranged from 1wt% to 11wt% TDS, achieved chloride rejection of 98.6% at 10X concentration factor, and reported >99.2% rejection of PFAS/PFOA at 10X. The results allowed design of a practical commercial plant which is currently under construction

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of synthetic chemicals used to make fluoropolymer coatings and products that resist heat, oil, stains, grease, and water. PFAS has been manufactured and used worldwide since the 1940s and include over 3,000 different chemicals. Many PFAS, including perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), are a concern because they do not break down in the environment, can move through soils and contaminate drinking water sources, and build up (bioaccumulate) in fish and wildlife. Most people in the United States have been exposed to PFAS molecules. Evidence reports continued exposure to certain PFAS above specific levels may lead to adverse health effects, such as developmental effects, cancer, liver effects, immune effects, and thyroid effects. As a result, the characterization, regulation, remediation and destruction of PFAS has become a key focus of regulatory bodies around the world.

This paper discusses the use of ultra-high pressure reverse osmosis (UHPRO) for the removal of high concentration of PFAS contaminants from a wastewater stream as part of three ZLD remediation projects currently being implemented at major industrial facilities across the United States. The focus of the paper is on the fundamental pilot testing performed to form the basis for the design of the commercial equipment.

Goals of the project

The overall process entailed treatment of groundwater water, storm water, industrial waste water effluent, and various recycle streams around the plant, by conventional ultrafiltration (UF) and brackish water reverse osmosis (BWRO). The UF backwash is concentrated and filtered, and the solids recycled to the site wastewater treatment plant (WWTP) and the recovered water fraction is fed back to the BWRO. The BWRO permeate is reused on site, and excess is discharged. The nominally 15% BWRO concentrate contains ostensibly all of the raw water PFAS and is treated by granular activated carbon (GAC) for total organic carbon (TOC) removal, followed by SORBIX RePURE specialized regenerative ion exchange (RIX) for PFAS removal. The RIX effectively operates as a sequestration tool and the bulk of the PFAS from the source water is removed and captured by the RIX. Once depleted, the RIX is regenerated with a blended aqueous brine and solvent stream and the spent regenerant stream from the RIX comprises the feedstock for the UHPRO, after the solvent has been separated. The goal of the UHPRO was to further concentrate the PFAS into a brine stream of less than 30% of the feed stream to feed a zero liquid discharge (ZLD) thermal treatment system for final brine management. The UHPRO was designed at 120 bar / 1,740 psig to achieve nominally 11wt% total dissolved solids (TDS) concentration. Key performance indicators (KPIs) were developed for the UHPRO based on a whole plant materials balance, which targeted a minimum of 95% TDS removal and 98% PFAS removal by the UHPRO system at 90% recovery.

Salient process integration questions to address for the UHPRO design was to determine rejection of PFAS in the presence of elevated TDS by seawater RO (SWRO) membranes, and the ability of the membranes to produce permeate that can be recovered in the existing BWRO process on site. The UHPRO brine stream, targeting nominally 11wt% NaCl and 0.1wt% PFAS, would need to be more accurately quantified in order to proceed to design of the ZLD post-treatment, which will be the final fate of the PFAS as the site strives to reduce its environmental impact. Specific UHPRO design unknowns included flux versus recovery and fouling rate, but also less-known parameters such as PFAS rejection in high TDS, high pressure environments.

The commercial system (UF, BWRO, GAC, RIX, UHPRO, ZLD) was still in design phase at the time of studying the UHPRO design, and so the feedstock for the UHPRO was not readily available. However, due to the number of unknowns and the importance of getting a design basis for the integration of the UHPRO into the downstream permeate and concentrate management systems, it was decided that a pilot trial needed to be performed with a representative simulated feed to progress design as far as possible. The synthetic feed was prepared to match projected feed

for the UHPRO from the overall site process materials balance. Fouling and scaling parameters were not sufficiently defined by the process projection at the time of pilot trial design, and hence the study focused on correlating flux, rejection (TDS and PFAS), recovery, and pressure impacts. Additional studies were planned to consider a more complete feed analysis for a second potential simulated feedstock and a plan was developed to potentially generate representative real world feed using pilot BWRO, GAC and RIX equipment.

After modeling the UHPRO process, considering the design KPIs, the unknowns in the feed definition, and taking all design factors into consideration, it was decided to operate the UHPRO system as a batch process inside the commercial plant. The disadvantages of batch processes involve tankage for inventory management, which adds some process complexity, but the advantages were felt to provide risk mitigation and enable the ability to achieve the KPIs identified for the UHPRO process. A major factor enabling practical batch UHPRO design in this project, stemmed from 85% reduction of raw feed flow prior to the RIX, followed by additional 95% flow reduction by sequestration of the PFAS by the RIX. An overall greater than 99.25% volume reduction of the PFAS feed to the UHPRO. The main impacts of the selected batch design approach are outlined below:

1. The fouling and scaling compounds contained in the feed, are retained inside the membranes for reduced periods of time, thereby reducing the risk of deposit on the membrane
2. Reduced fouling and scaling risk, reduces the frequency of chemical cleaning. This saves the owner significant operating costs as it pertains to chemicals, and reduces downtime associated with cleaning
3. The average osmotic pressure inside the system is significantly less than that for a system that operates at a fixed, final recovery, thereby reducing energy use in the system
4. The average contaminant concentration on the feed side of the membrane is lower than a conventional system and this results in a reduced concentration on these contaminants permeate side, therefore batch systems exhibit improved overall rejection of contaminants
5. Two batch tanks are to be considered, one filling while the other is being concentrated, batched down. This enables sequential operation of batches, reducing fill and drain downtimes, stopping only for clean-in-place.

A process block flow diagram of the commercial UHPRO system is shown in Figure 1, which shows the key features of the design concept developed for the project.

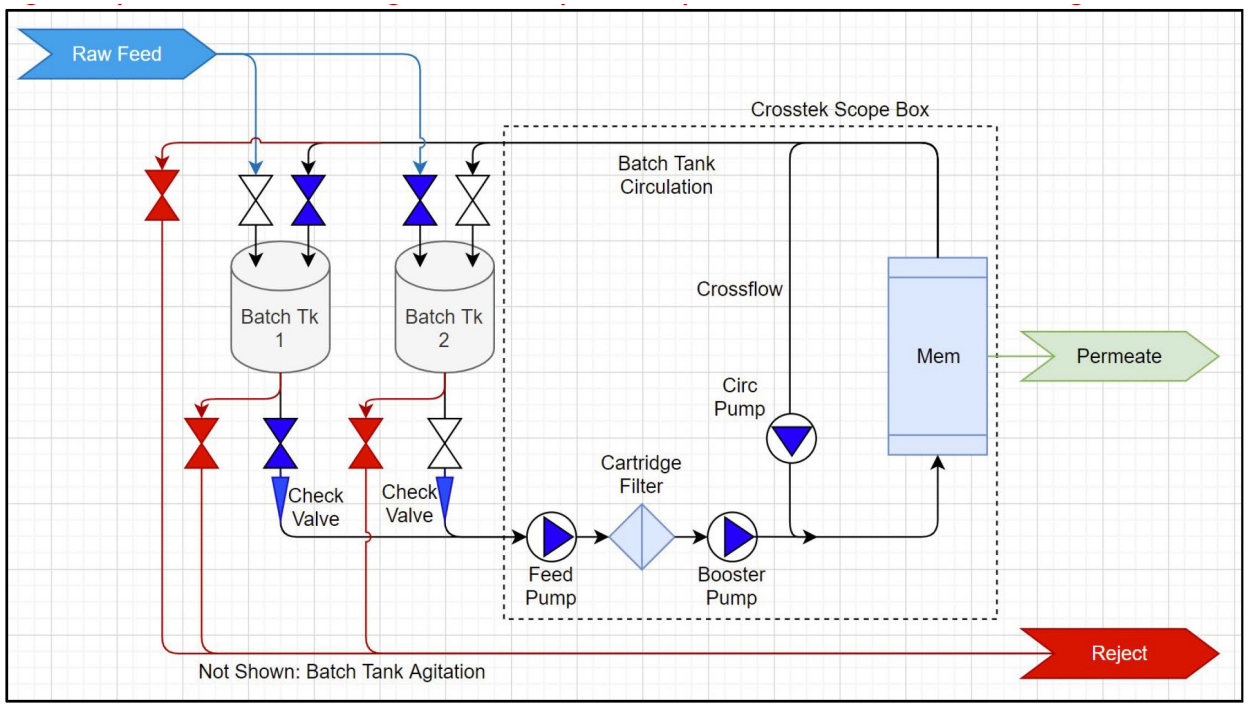

Figure 1. Process block flow diagram of the commercial UHPRO system showing key features

The process design informed the pilot trial design and the pilot trial design and execution is described next.

Pilot Trial

Materials and methods

A block flow diagram of the pilot plant is shown in Figure 2. The pilot system included a batch tank of 100 gallons volume, a batch tank circulation pump to ensure mixing and avoid stratification of the batch tank and that also served as the feed transfer pump to the booster / circulation pump, which in turn set the required pressure for the SWRO membrane for the trial. The trial was run with an AquaZoom® 8040 disc-tube reverse osmosis (DTRO) membrane in batch operating mode with concentrate recycle to the batch tank, as per the process design selected for the project.

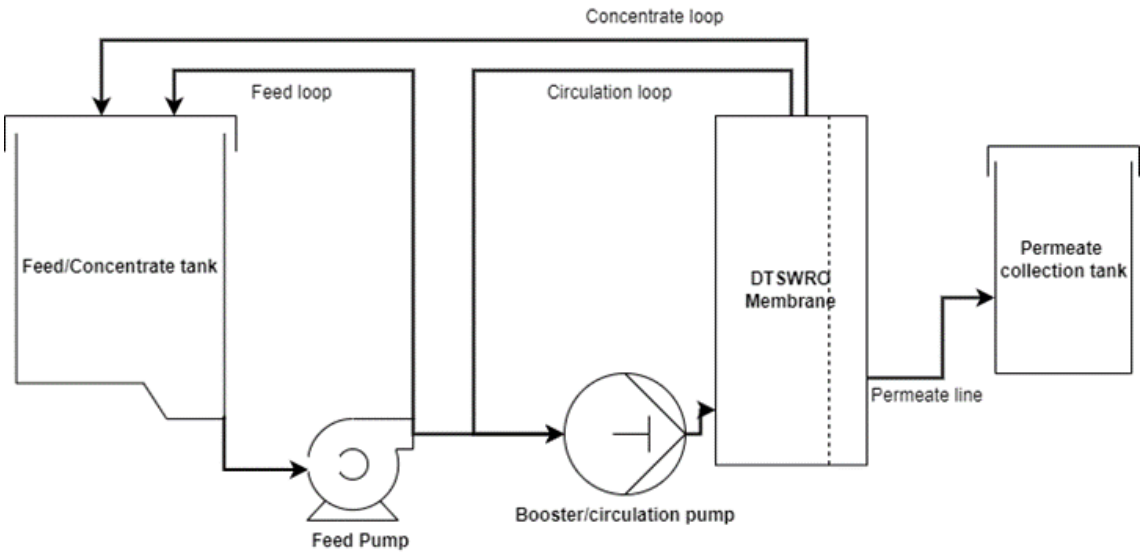

Figure 2. AquaZoom® DTRO pilot plant schematic showing key process equipment

The DTRO product is a plate-and-frame RO module which comprises up to 208 doughnut shaped membrane cushions stacked with alternating flow spacers with seals in between, to form the membrane element, which is then enclosed inside a pressure vessel. The Crosstek AquaZoom product line comprises spiral and plate and frame (i.e DTRO) membrane designs. The DTRO handles higher amounts of suspended solids (TSS) versus the spiral products. However, Crosstek had developed a procedure for scaling up successfully from a DTRO pilot trial to either of our spiral or DTRO products. This procedure was followed for this current project as well. The simplicity and flexibility of DTRO piloting was the main driver. DTRO pilots can be adjusted for membrane area and allowed for simplifying pilot trials through use of smaller pumps, lower feed volume, ease of studying membrane surface impacts of piloting in a non-destructive manner by sampling selected membrane cushions, and even replacing those if destructive studies need to be performed without sacrificing the entire element as typically is required for spiral membranes.

The test methodology was to mimic the commercial system, in that the initial process flux was determined based on experience with similar TDS and organic loaded feeds, and this flux was to be maintained until the membrane inlet pressure reached nominally 1,700 psig, after which the system would be switched from flux control to membrane inlet pressure control to avoid activation of the relief valve set at 1,740 psig, the membrane design pressure limit.

A number of feed, reject and concentrate samples would be collected throughout the batch trial to verify performance across the entire batch run, and the final concentrate and blended permeate would be collected for mass balance analysis. The pressure, temperature, pH, and flow rates were collected throughout the batch trial to track performance of the membrane system. The analytical test matrix for the pilot trial is outlined in Table 1 . Pure PFAS compounds and various commodity additives including salts used for preparing the simulated feedstock were acquired from Sigma-Aldrich.

Table 1: Sampling streams and test matrix for the pilot trial

Sampling streams			
Initial Feed	Final concentrate (10X+)	Initial permeate (1X)	Blended permeate (batch)
Permeate (2X)	Permeate (5x)	Final Permeate (10X+)	
Wet chemistry Analytical Test (All Streams)			
Chlorides	Sodium	Sulfates	Bromide
PFAS Analytical Test (All Streams)			
PFBA	2,3,3,3 TFPA	PFPA	TFMS
PFBS	HQ-115	TFA	

Compound Name	Abbreviation	CAS	Sigma Aldrich SKU
Unnamed PFAS Type 1	NoName1	Not shown	Not shown
perfluorobutanoic acid/ Heptaflouro butyric acid	PFBA	375-22-4	52411-5ML-F
Unnamed PFAS Type 2	NoName2	Not shown	Not shown
Trifluoroacetic acid	TFA	76-05-1	T6508-25ML
Unnamed PFAS Type 3	NoName3	Not shown	Not shown
Unnamed PFAS Type 4	NoName4	Not shown	Not shown
Perfluorobutanesulfonic acid	PFBS	375-73-5	562629-5G

Pilot results

Analytical analysis of the feed. The feed solution recipe and analytical measurements of this recipe are reported in Table 2. The feed solution was prepared by adding the recipe components from Table 2 into lab RO permeate. The pH was found to be 4.0 pHU once blended, and pH was raised to 7.9 pHU by adding NaOH to the blended solution. Samples of the feed were sent to two independent 3rd party laboratories to perform analytical analysis – the results from this analytical analysis are reported in Table 2.

Table 2: Feedstock preparation recipe and analytical measurement of component

Full Name	Abbreviation	Recipe (mg/L)	Analytical (mg/l)
Unnamed PFAS Type 1	NoName1	558.74	349.00
perfluorobutanoic acid/ Heptaflouro butyric acid	PFBA	155.94	<191.00
Unnamed PFAS Type 2	NoName2	98.08	110.00
Trifluoroacetic acid	TFA	42.98	64.20
Unnamed PFAS Type 3	NoName3	34.71	31.90
Unnamed PFAS Type 4	NoName4	31.96	58.40
Perfluorobutanesulfonic acid	PFBS	11.02	7.74
Sulfates added as MgSO4	SO4	300.00	2.3
Bromide added as NaBR	Br	100.00	0.00
Ethanol	Ethanol	10.00	NA
Sodium Chloride	NaCl	10,000	9,500

After a number of analysis iterations and calibrations by the lab, there we still some significant differences between the recipe and the analytical data, as shown in Table 2. The analytical analysis was conservative in some cases, close in other cases, or over-estimated in other cases, largely due to the the presence of high chlorides in the feedstock. This has ramifications for reliability of measurements from commercial labs, and is an area worth studying further in the industry as we develop regulations around PFAS in public water systems, especially with regards to discharge permits for industrial operations.

Batch test performance data. Data was collected at four instantaneous points in the batch and then also for the average of the run using the blended permeate and concentrate, as reported in Table 3.

Table 3: Batch trial key performance data over the course of the trial

Sample:	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Type	Instant 1	Instant 2	Instant 3	Instant 4	Blend
time (minutes)	0.00	105.45	161.82	190.91	190.91
Concentration Factor Based on CL	1.00	2.00	5.00	12.73	12.73
rejection (1-P(tds)/C(tds))	99.4%	99.6%	99.7%	93.5%	99.8%
Mass removal TDS	99.4% (inst.)	99.1% (inst.)	98.6% (inst.)	30.4% (inst.)	97.7%
Flux (gfd)	7.16	7.16	7.16	3.25	7.16 (ave)
Pressure (PSI)	250.00	400.00	550.00	1700.00	NA
Temperature Celsius	22.50	22.10	28.60	30.00	26.00
pH Batch tank	7.90	6.40	8.80	8.07	8.10
Conductivity (uS/cm) Batch tank	17380.00	39900.00	69400.00	151800.00	151800.00
TDS (mg/l) Batch tank	10418.00	25727.00	46977.00	111415.00	111415.00
Concentration Factor based on TDS	1	2.47	4.51	10.69	10.69
pH Permeate	5.30	5.72	9.70	8.14	9.20
Conductivity (uS/cm) Permeate	150.00	228.00	352.00	12450.00	550.00
TDS (mg/l) Permeate	59.00	93.00	150.00	7247.00	243.00
Chloride (mg/l) Permeate	41.00	62.00	150.00	4700.00	130.00
Sulfate (mg/l) Permeate	<5	<1	1.50	66.00	1.20
Bromide (mg/l) Permeate	0.07	1.80	3.60	83.00	2.30
Sodium (mg/l) Permeate	30.00	43.00	110.00	3000.00	91.00
PFBA (mg/l)	0.00	0.00	0.00	0.00	0.00
PFBS (mg/l)	0.06	0.03	0.08	11.90	0.17
NoName3	0.1	0.1	0.3	40.4	0.4
Chloride (mg/l) Batch tank	5500.0			70000.0	70000.0
Sulfate (mg/l) Batch tank	300			2	2
Bromide (mg/l) Batch tank	100			<0.02	<0.02
Sodium (mg/l) Batch tank	4000.00			0.02	0.02
PFBA (mg/l) Batch tank	156.00			<191.00	< 191.00
PFBS (mg/l) Batch tank	11.10			149.00	149.00
PFBS mass removal	99.4% (inst.)	99.7% (inst.)	99.2% (inst.)	-7.2% (inst.)	98.5%
NoName3 (mg/l) Batch tank	31.9			280.0	280.0

The instantaneous samples were taken at concentration factor (based on Cl-) of 1.00, 2.00, 5.00 and 12.73X. The run was ended at 12.73X concentration factor, which was higher than the minimum target of 10X / 90% recovery. It is often difficult to end a pilot batch trial at the exact end recovery. Performance at 10X concentration factor was interpolated from pilot data. The commercial system will have accurate recovery controls. It is worth noting the value of designing a batch commercial system, which is clearly displayed by the enhanced mass removal of TDS between the 12.73X instantaneous and 12.73X batch blended removal of 30.4% and 97.8% respectively. The poorer permeate quality at the end of the batch is blended with the initial better permeate quality at the start of the batch, to enable significantly improved TDS mass removal over the batch on average. Similarly, looking at PFBS for PFAS rejection determination, a similar trend is observed, where batch treatment improves the ability of higher water recovery while achieving rejection goals, emphasizing the value of the batch process design for this project.

Also, of note is that the end of a batch pilot trial can prove challenging for temperature control. As fluid volumes decline and pumping energy increases, process water temperatures rise throughout the batch cycle, as was the case in this trial (see Table 3). This process challenge was anticipated

early on, and adequate temperature control was included in the commercial system design to mitigate this limitation.

Based on the pH behavior reported in Table 3, which was non-monotonic, and the unknowns of the actual feed constituents the UHPRO system would receive, pH control as well as antiscalant dose was to be included in the commercial system design.

As reported in Table 2, Permeate Flux was 7.16 GFD at 250 psig membrane inlet pressure at the start of the run through the flux control portion of the trial, and ended at 3.25 GFD at 1,700 psig membrane inlet pressure, at 12.73X concentration factor / end of run, where operation was pressure limited. The hydraulic performance data generally verified the design projection developed for the project that considered flux, temperature, recovery and pressure limits, for example the model project 451 psig feed pressure for 25,180 mg/l membrane inlet TDS, which compared well with the 400 psig feed pressure at the 25,727 mg/l in Table 4. However, without fouling or scaling components in the pilot feedstock, the design and piloting flux had to be conservative to allow for reliable scale up due to uncertainty of ultimate feed quality.

An approximate average membrane inlet pressure for the batch run was 645 psig using the four instantaneous sample point pressure values. This is 62% of the 1,700 psi pressure if operating constant feed pressure at the final point of the batch. However, since the average flux is also higher for the batch operation, additional power savings may be achieved for a batch design as a higher number of membranes (lower flux) may require higher pump flow rates, depending on system design.

Table 4 shows the key performance values relating to the project KPIs, which targeted a minimum of 95% TDS removal and 98% PFAS removal by the UHPRO system at 90% recovery. The 90% recovery ~10X concentration factor case was interpolated from the data generated in the pilot trial.

Table 4: Batch blended average trial key performance indicator with interpolation to 10X

	Batch average rejection and values				
Compound	**Feed (mg/l)**	**Blended permeate (mg/l) 12.73X**	**Rejection 12.73X**	**Blended permeate est. (mg/l) 10X**	**Rejection 10X**
Chloride	5500	130	97.64%	77	98.6%
Sulfate	*300*	1.2	99.60%	0.6	99.8%
Bromide	*100*	2.3	97.70%	1.3	98.7%
PFBA	156.0	0.0443	99.94%	< 0.0443	> 99.94%
PFBS	11.1	0.166	98.5%	0.085	99.2%

In Table 4, the UHPRO permeate PFAS values were accurate due to reduced chloride concentration and resulting reduced interference with analytical methods. The measured chloride rejection was nominally 98.6% blended average over 10X concentration factor, which meets the KPI for TDS mass removal (>95%). Likewise, PFBS mass removal was 99.2% and PFBA rejection was > 99.9%, both met the > 98% mass removal requirement at 10X concentration factor. The pilot trial proved that the KPIs were achieved with batch system design.

It is worth noting that a follow-on trial was performed just prior to completing this paper, that used actual feedstock produced at the client site from pilot-sized equipment. The data from this follow-on trial confirmed the need for antiscalant, proved the TDS rejection to be similar to the trial simulated feedstock trial, and confirmed design permeate flux. Other data is yet to be determined, such as PFAS rejection, but there is no reason to expect differences in performance. The membrane surface was studied under SEM as part of the follow-on study, concluding that fouling was not significant.

Summary and Conclusions

The design data generated in this trial allowed the project team to: (1) prove commercially reasonable flux and recovery were achieved; (2) confirm salt rejection was accurately predicted by commercial SWRO projection tools for the UHPRO system; (3) develop an improved analytical measurement method for PFAS in 1wt% to 11wt% NaCl brine; (4) determine that PFAS rejection met project goals of >98% mass removal; determine that TDS mass removal met project goals of > 95% mass removal. In addition, the data allowed for the development and validation of an accurate batch system design at commercial scale that allowed project capital and operating cost development, leading to a number of commercial projects that are under execution at the time of submitting this paper. The first project is expected to go into production mid-2023.

The combination of highly selective regenerable ion-exchange to sequester PFAS into small volumes of regeneration wastewater, combined with UHPRO to concentrate and reduce volume of this regeneration waste, is a promising approach for managing PFAS in ZLD and/or PFAS destruction projects. This project served to develop evidence of performance and develop a design approach for projects based on this technology.