# HIGH-PRESSURE REVERSE OSMOSIS SYSTEM TREATING WASTEWATER FROM A PHARMACEUTICAL PRODUCTION FACILITY AS PART OF A ZLD PROJECT

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## Abstract

As part of compliance requirements, a new pharmaceutical assay production facility in Shanghai, China, owned and operated by a major multinational pharmaceutical company, was required to implement a zero liquid discharge (ZLD) wastewater treatment system. The ZLD system incorporates high-pressure reverse osmosis (RO) with permeate RO polishing and an evaporator for brine concentration. With a large installed base globally, the high-pressure RO step was designed around spacer tube RO (STRO). The STRO has a proven track record of handling elevated organics, highly scaling feed, and high pressure in high recovery operations, all of which are present in this wastewater. While the Shanghai plant was under construction, it was decided to run a pilot trial at a similar pharmaceutical facility inside the corporation family, located in Massachusetts, United States. The pilot trial was run using disc tube RO (DTRO), which is a good representation of the STRO except that the DTRO has a more open feed flow path, requiring reduced pretreatment, allowing for simpler pilot trials. The feed wastewater presented high variability, with pH ranging from 8 to 10.5 and TDS from 1,000 ppm to 4,000 ppm, COD averaged 400 mg/l with peaks up to 2,900 mg/l, BOD average of approximately 200 mg/l. The operating pressures were between 900 psi and 1,320 psi. The permeate COD was approximately 25 mg/l, and the permeate TDS was always below 200 mg/l. Additionally, the pilot required antiscalant and pH control via acid addition to avoid scaling due to a high content of phosphates in the feed. Significant biofouling was experienced on the cartridge filter system, and a regime of biocide dosing as part of commercial system pretreatment was recommended. The pilot ran for ten weeks, and it achieved the objectives for removing LAS surfactants, Total Phosphorous, and SVOA surrogates. The pilot ran 95% recovery for different fluxes, finally recommending 5.6 GFD design flux. The STRO cleaning regime was refined during piloting as well, thereby confirming all key design parameters for the commercial system. The commercial system is currently under construction and will be operational by 2022.

## Introduction

A multinational pharmaceutical company is constructing a wastewater treatment plant in their new manufacturing facility in Shanghai, China. The wastewater from the planned Shanghai facility is expected to be similar to the Massachusetts facility's waste as the facilities operate similar production processes. The US facility discharges to a publicly owned wastewater plant for off-site treatment after adjusting pH to meet sewer requirements prior to discharge. The Shanghai wastewater requires additional treatment processes beyond pH control to comply with their wastewater disposal permit regulations. Shanghai's commercial wastewater treatment system design was developed based on water sampling from Massachusetts. One of the treatment steps for the Shanghai site includes a Crosstek STRO system. The STRO system reject or concentrate passes to a thermal evaporation step for further water recovery, and the STRO permeate passes to a polishing second pass conventional RO system. Ahead of the STRO is a dosing station with a mix tank, chiller for temperature control, inline acid dosing for pH reduction, sodium bisulfite (SBS) dose for removing residual bleach from upstream processes, and 50micron filtration for suspended solids management. Before initiating the pilot trial, the pharmaceutical company and its representatives provided the commercial project design information to use the commercial design to set up the pilot trial. A DTRO pilot was subsequently set up at the US pharmaceutical facility to validate the Shanghai wastewater plant design and verify the applicability of the Crosstek STRO membranes at the Shanghai facility. The objectives of the trial were the following:

1. Operate the Crosstek pilot system to collect hydraulic performance data for scale-up. This includes pressure, temperature, and flow rates
2. The pilot study is to be conducted over a 10-week testing period, operating 24-hours per day, seven days per week
3. The DTRO pilot operating parameters will remain constant at the commercial design conditions to evaluate the system performance over time
4. Demonstrate permeate water quality suitable for the downstream discharge and that the STRO reject will be suitable for additional evaporation treatment
5. Demonstrate design flux for the STRO membrane at the design recovery with design pretreatment
6. Demonstrate an effective chemical cleaning regime and determine expected cleaning frequency and type of cleaning for the commercial plant.

## Materials and Methods

### *Equipment*

The core of the STRO process is the membrane element selection. A seawater reverse osmosis membrane (CrossTek STRO4) was employed for the pilot project based on the commercial system design conditions and performance requirements. The membrane module used for the pilot contains a tailor-built DTRO4 5.17m^2 membrane area. This membrane module is rated 90bar / 1,305psig as per the commercial project design requirements. The test system employed was the cart-type CrossTek DTRO membrane pilot unit and a custom pretreatment cart unit, as shown in Figure 1. The DTRO pilot plant needed appropriate pretreatment to match the commercial system design, pH control for scale management based on the process design analysis.

*Figure 1:Crosstek Benchtop Disc-Tube Reverse Osmosis Pilot System*

The scale projection was a key aspect of the modified pH control for pretreatment and was based on the raw feed analysis provided as the pilot design basis. The projection was made using commercially available software, see Figure 2. CaPO4 was the main supersaturated scale former to be managed. The supersaturation with and without a dose of antiscalant is shown in Figure 2. This projection was used to develop the antiscalant dose concentration for the pilot and the acid dose / pH control. The iron was saturated and filtered out as a suspended solid in the pretreatment, hence not a real risk for the RO process. The pretreatment is summarized in Table 1.

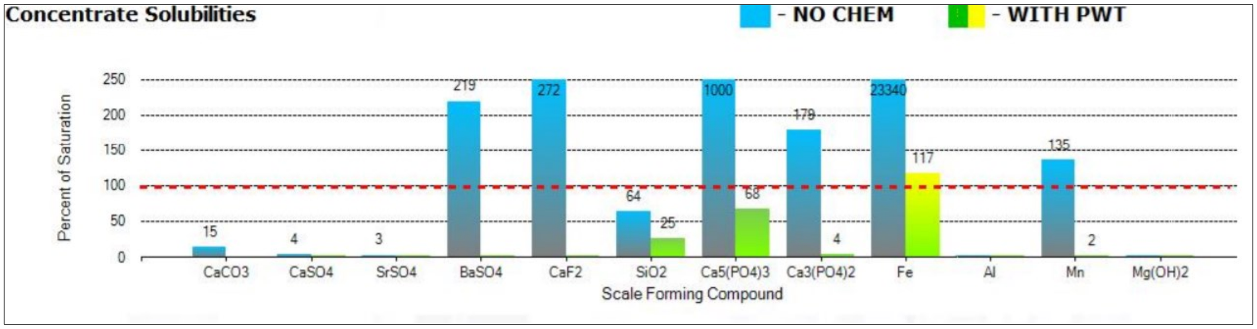

*Figure 2:Scale projection shows the efficiency of acid (sulfuric 7.1 ppm) and antiscalant (2.21 mg/l Spectraguard 300) dose for scale management.*

*Table 1: Pretreatment elements*

| Pretreatment | Characteristic | Design Basis | Performance |
|---|---|---|---|
| **Raw feed strainer 1** | 10 microns | 2.65 GPM/square foot | Added upstream the 5 um to the system to avoid rapid plugging |
| **Raw feed strainer 2** | 5 microns | 5.7 GPM/square foot | It was replaced after plunging without a 10 um filter upstream |
| **SBS dose** | Dose on ORP measurement | Destroys residual bleach | Found very little residual bleach in the typical wastewater |
| **Acid dose** | $H_2SO_4$ dosed to control pH | pH set at nominally pH6 to 6.4 in the feed to manage CaPO4 scale | pH control was not always easy as spikes occurred where feed pH went up to over pH 10 and was highly buffered |
| **Antiscalant dose** | SG300 dosed per scale projection (**Error! Reference source not found.**) | Dosed at 2.5 mg/l into feed to manage CaPO4 scale | Along with pH control, it appeared to work well as most fouling appeared to be related to organics (high pH cleaning was most critical) |

***Trial and sampling methodology:***

The DTRO pilot system was connected as a bypass to the wastewater treatment line at the pharmaceutical facility. CrossTek took the raw water feed and treated it to achieve a 95% recovery rate. The permeate and reject of the DTRO system were both returned to the wastewater discharge line on site. The performance parameters of the reverse osmosis system are calculated mainly using data from on-site instrumentation included with the pilot plant, together with a multimeter to measure pH, Conductivity / TDS, and temperature. As noted, the pretreatment skid was built to control pH with sulfuric acid, ORP (Chlorine) with Sodium bisulfite (SBS), and to dose antiscalant to the RO System feed line. This pretreatment system has a mixer tank with a residence time of nominally 25 minutes to allow acid dosing for pH control and SBS dosing before feeding to the RO system transfer pump. The on-site analytical data was as seen in Table 2. In addition to the on-site testing, weekly periodical samples for the pollutants of interest were sent to an external certified analytical laboratory. The extend of this test is shown in Table 3.

*Table 2: on-site data collection*

| **DTRO on-site data** | |
|---|---|
| Feed pump Pressure | Permeate Conductivity |
| Pressure pump Frequency | Permeate pH |
| Feed pressure | RO Feed ORP |
| Differential Pressure (Major and minor losses) | RO Feed Conductivity |
| System pressure | RO Feed pH |
| RO Feed Temperature | Raw Feed Conductivity |
| Permeate Flowrate | Raw Feed pH |
| Concentrate Flowrate | |

*Table 3: off-site analytical data collection*

| **Raw wastewater feed** | | |
|---|---|---|
| Total suspended solids (mg/l) | Silica (mg/l) | Potassium (mg/l) |
| Chloride (mg/l) | Carbonate alkalinity (mg caco3/l) | Zinc (mg/l) |
| Ammonia as N (mg/l) | Bicarbonate alkalinity (mg caco3/l) | BOD 5 (mg/l) |
| COD (mg/l) | Aluminum (mg/l) | TDS (mg/l) |
| Total Phosphorous as P (mg/l) | Barium (mg/l) | Nitrate as N (mg/l) |
| Sulfide (mg/l) | Calcium (mg/l) | Sodium (mg/l) |
| LAS Surfactants (MBAS) (mg/l) | Iron (mg/l) | Strontium (mg/l) |
| TPH GC/FID (ug/l) | Magnesium (mg/l) | Fluoride (mg/l) |
| Surrogate 2-Fluorobiphenyl (Range %) | Manganese (mg/l) | Sulfate (mg/l) |

| **Concentrate** | | **Permeate** |
|---|---|---|
| Chloride (mg/l) | LAS Surfactants (MBAS) (mg/l) | Total suspended solids (mg/l) |
| Total suspended solids (mg/l) | TPH GC/FID (ug/l) | Total Phosphorous as P (mg/l) |
| Ammonia as N (mg/l) | Surrogate 2-Fluorobiphenyl (Range %) | Total Phosphorous rejection |
| COD (mg/l) | BOD 5 (mg/l) | COD (mg/l) |
| Total Phosphorous as P (mg/l) | TDS (mg/l) | TDS (mg/l) |
| Sulfide (mg/l) | | |

# Results and discussion

## Feed quality

The feed presented significant variations along the pilot execution time. It consisted of representative wastewater effluent for the pharmaceutical facility processes. The abridged feed and permit values are summarized in Table 4.

*Table 4: Summarized feed conditions*

**Summarized Feed Conditions**

| | **pH** | **TSS** | **TDS** | **BOD5** | **COD** |
|---|---|---|---|---|---|
| | | ppm | ppm | ppm | ppm |
| **Average** | 7.2 | 39.5 | 4327 | 284 | 716 |
| **Max** | 10.5 | 55 | 11900 | 510 | 380 |
| **Min** | 6.9 | 23 | 1779 | 150 | 110 |
| | **Total Orthophosphates** | **Total phosphates** | **Surfactants (M.B.A.S)** | **Total Calcium** | **Temperature** |
| | ppm | ppm | ppm | ppm | Deg. Celsius |
| **Average** | 1158 | 760 | 0.9 | 13.25 | 27 |
| **Max** | 2040 | 1200 | 1.2 | 16.6 | 39 |
| **Min** | 530 | 396 | 0.5 | 11.6 | 21 |

## RO Pilot results

As mentioned before, the 95% recovery rate was important for this project as the RO reject was fed to a thermal evaporation process for additional treatment. Once tuned, the pilot achieved satisfactory reliability of operation at 95% recovery, as seen in Figure 3. It is relevant to mention higher recovery instances beyond the design recovery, as reported in Figure 3. Still, these excursions could lead to increased fouling, so exceeding the 95% recovery on the commercial system is not recommended.

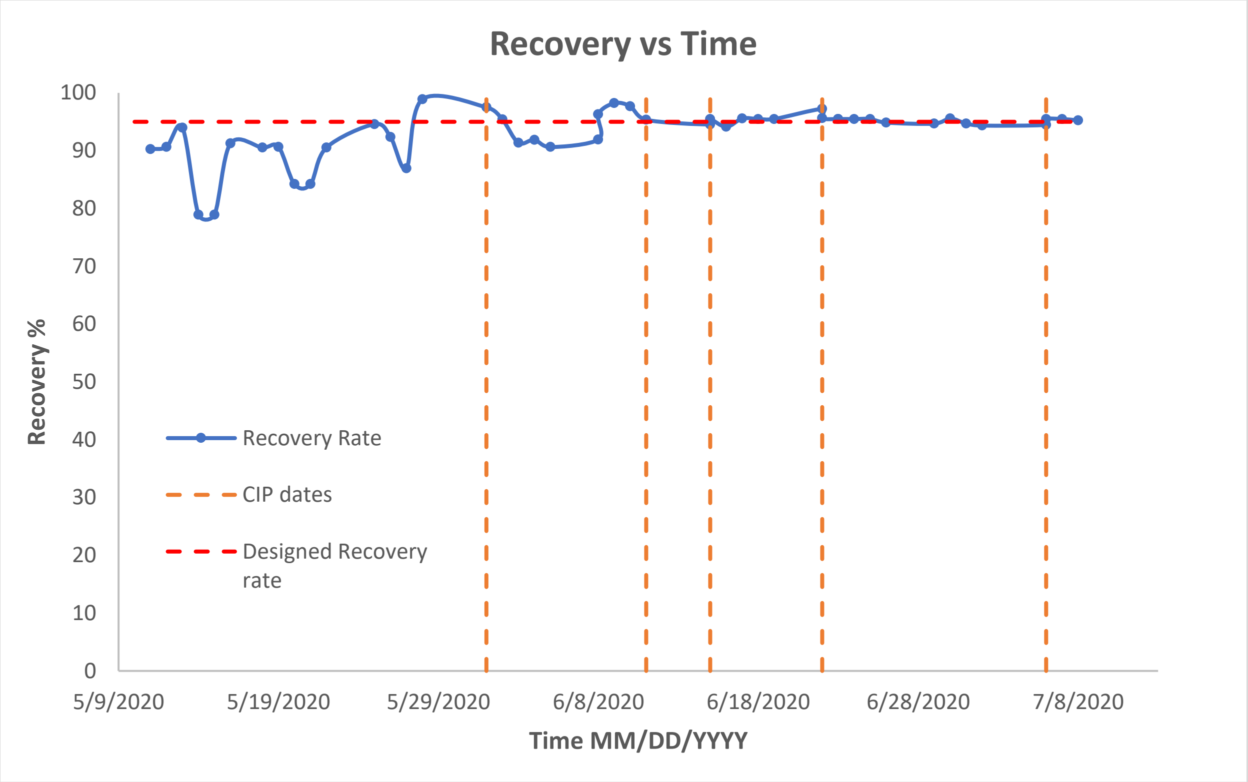

*Figure 3:Pilot trial recovery rate*

Due to variations in the pilot system temperature and its impact on the pilot plant control system, permeate flux and TDS had to be normalized. The normalized flux represents the measured flux at actual operation conditions, adjusted to standard operating conditions. The membrane can consistently achieve the desired flux under the normalized conditions, as seen in Figure 4. It is observable that the system can achieve the desired flow when operating conditions, primarily when the operating temperature is controlled effectively.

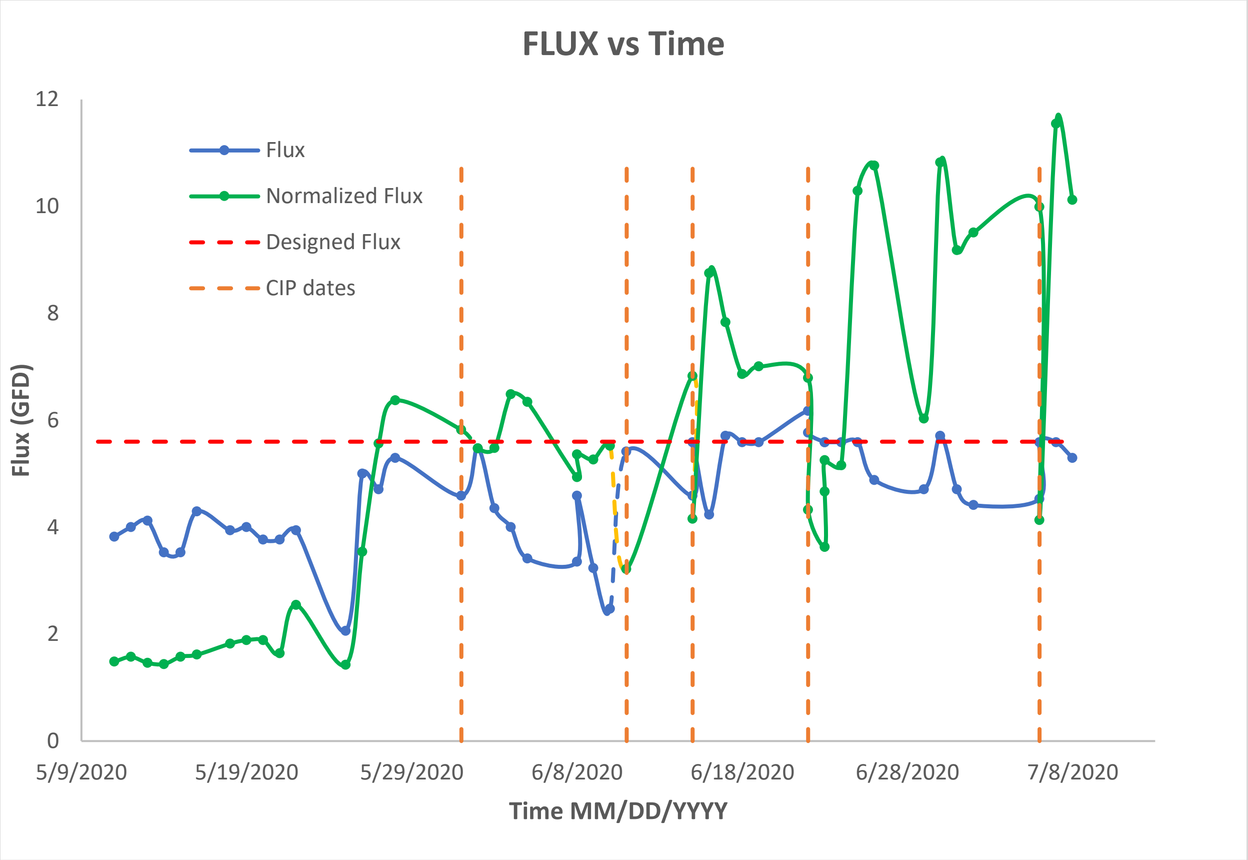

*Figure 4:: RO pilot Flux (GFD)*

The TDS rejection of the system is essential for the project, both for evaporator design and for effluent polishing RO system design. The project has a preferred TDS limit on the permeate of 100 mg/l and a discharge limit of 2,000 mg/l TDS. The normalized TDS and TDS are generally below the select limits of 100 mg/l after improved sampling methods. The system was finally operated at the appropriate flux and pressure starting 6/11/2020, as seen in Figures 5 and 6. As TDS rejection strongly depends on temperature, the variable temperatures in the project influenced actual permeate TDS.

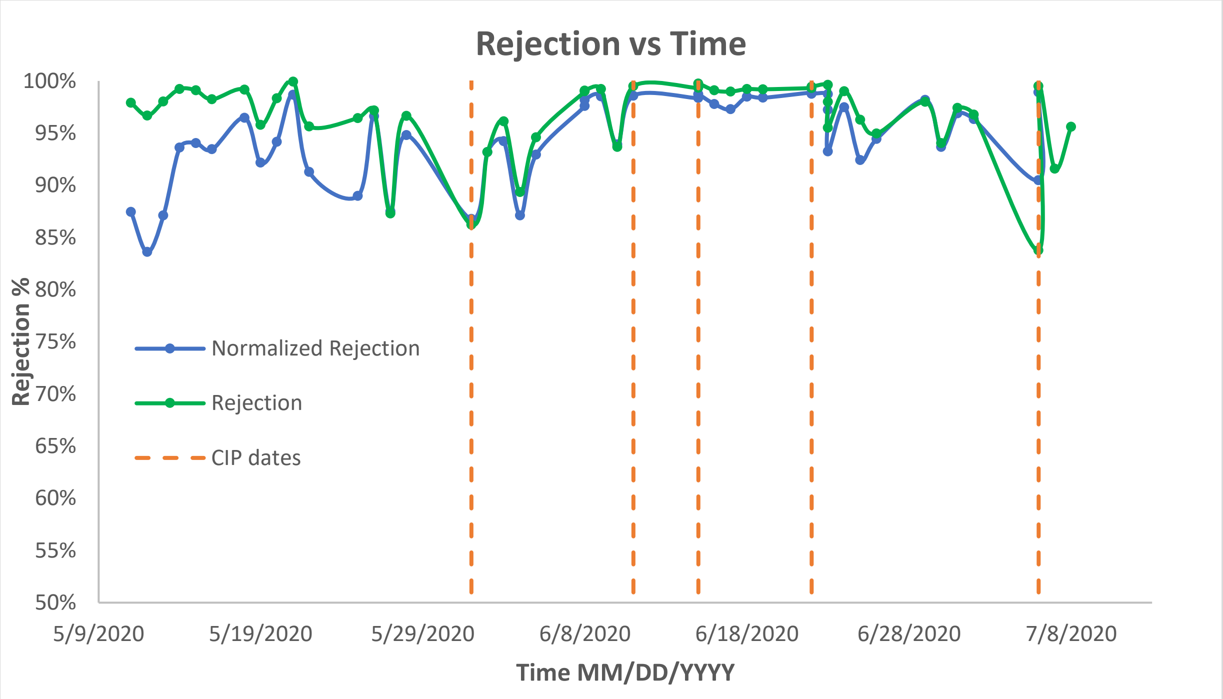

*Figure 5: Pilot's Rejection % over time*

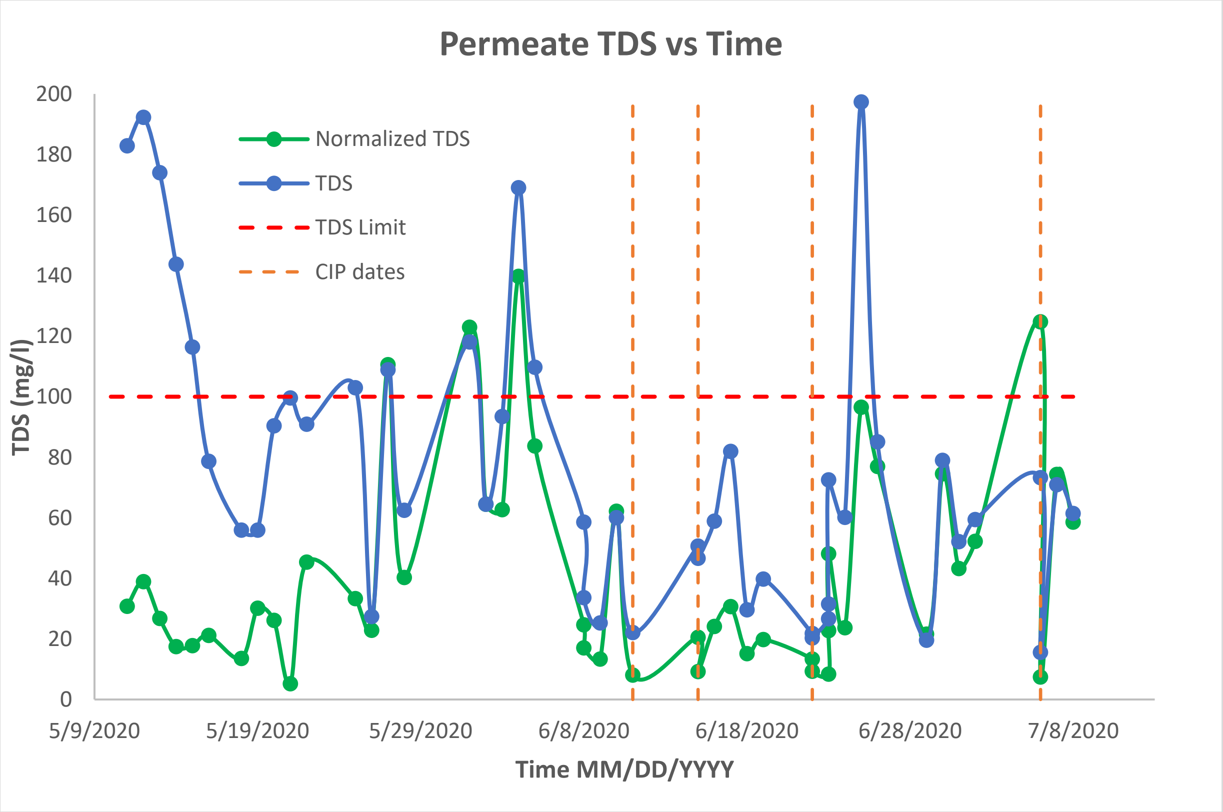

*Figure 6: Permeate TDS*

Due to the required feed acid dose for pH control to control scaling, the permeate pH is below the targeted 6-9 pH requirement in values around 5.5 pH, as seen in Figure 7. Since the RO permeate is relatively unbuffered, pH adjustment should require small amounts of caustic or soda ash addition.

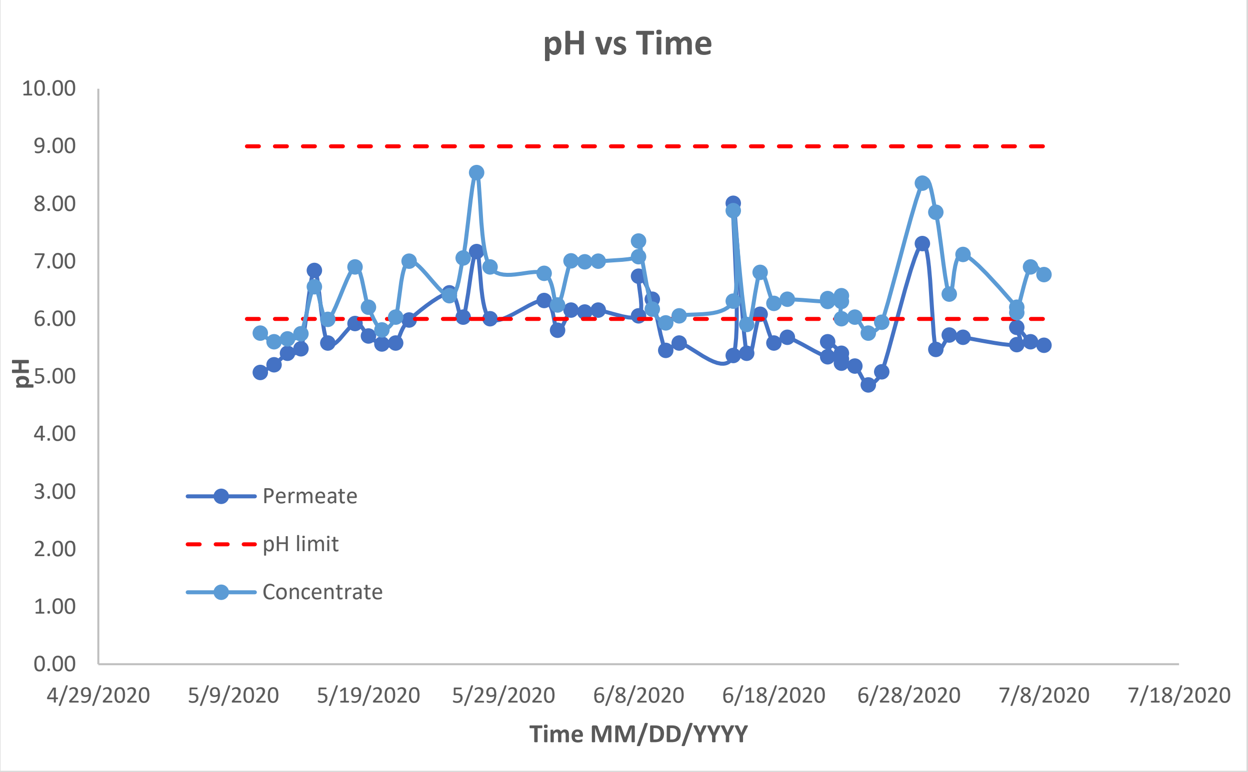

*Figure 7: Permeate and concentrate pH*

The analytical data allows for comparing the permeate quality with desired discharge limits. Table 5 shows the permeate analytical data for phosphates, COD, and TDS. It should be noted that COD and phosphate analytical data were not normalized, and generally, lower permeate values would be expected when normalized, as is the case for TDS. Permeate quality (average) showed good compliance with desired standards for COD and TDS but showed elevated phosphates. Phosphate rejection was 96.82%, which was good. Still, with high feed phosphates levels, the permeate phosphate exceeded the desired 5 mg/l by an average of 9 mg/l and certainly needed the polishing RO system to reduce the final discharge permeate below the 5 mg/l phosphate targeted. The reject quality is relevant to the project as it is to be the feed for an evaporator within the ZLD design. The reject information is summarized in Table 6.

*Table 5:Analytical parameters of the permeate compared to the desired effluent limits*

**Permeate /discharge parameters**

| | Total Phosphates | COD | TDS Normalized/Standard |
|---|---|---|---|
| **Average mg/L** | 13.95 | 27.2 | 41.2/76.4 |
| **STD** | 14 | 16 | 33.9/37.4 |
| **Desired effluent Limits mg/L** | 5 | 100 | 100 |
| **Rejection% Average** | 96.81% | 87.57% | 97% |

*Table 6:summarized reject conditions at 20x Concentration factor*

**Summarized Reject Conditions**

| | pH | TSS | TDS | BOD5 | COD | Total Phosphorous | Surfactants (M.B.A.S) |
|---|---|---|---|---|---|---|---|
| | | ppm | ppm | ppm | ppm | ppm | ppm |
| **Average** | 6.8 | 300 | 60000 | 1900 | 4722 | 15625 | 4.8 |
| **Max** | 8.4 | 610 | 75000 | 2300 | 15000 | 29000 | <1.2 |
| **Min** | 5.9 | 470 | 34000 | 1600 | 2200 | 12000 | NA |

Figure 8 shows the fouling pressure trend vs. time. The fouling pressure is determined by removing osmotic pressure and membrane inherent (clean water) pressure from total pressure. Figure 9 shows the total pressure and each of the components of the total pressure, including fouling, osmotic, and membrane clean water permeability (CWP) pressure. Fouling pressure is the sum of organic fouling, scaling, and concentration boundary layer effects. The fouling pressure picked up significantly after May 26th. This was when flux was increased toward a design flux of 5.6GFD. The fouling pressure showed a non-linear increase in pressure with flux when increasing flux closer to 5.6GFD, indicating that the design flux of 5.6GFD was above the critical flux for the system. Green dashed lines in Figure 8 show the reduction in fouling when performing a CIP and reinforce the CIP's reliability developed in the pilot program.

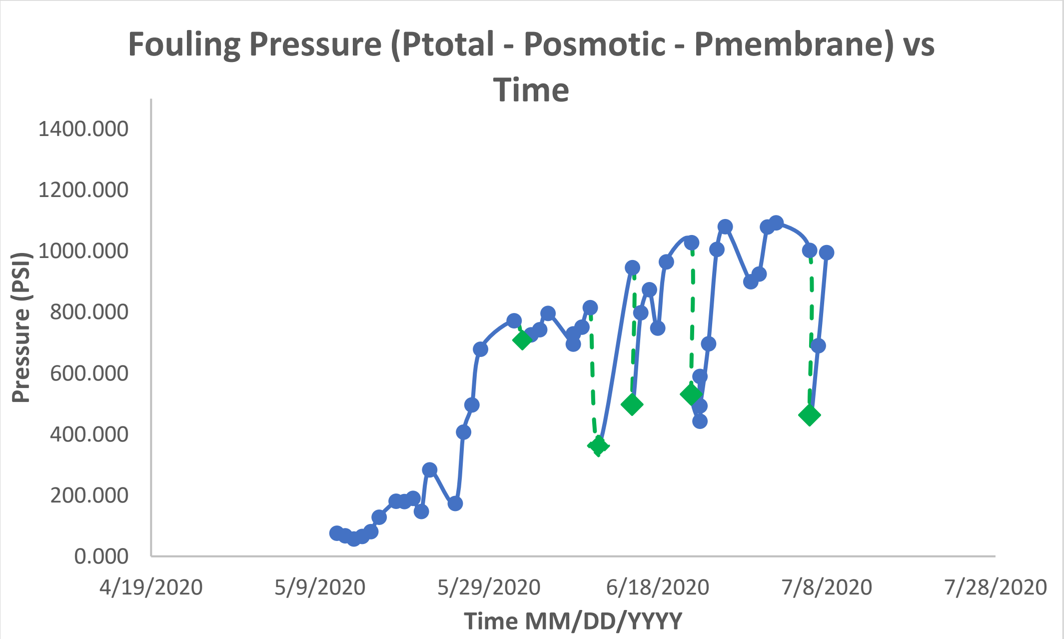

*Figure 8: Fouling pressure versus time. Green dash lines show the impact of CIP on reducing fouling*

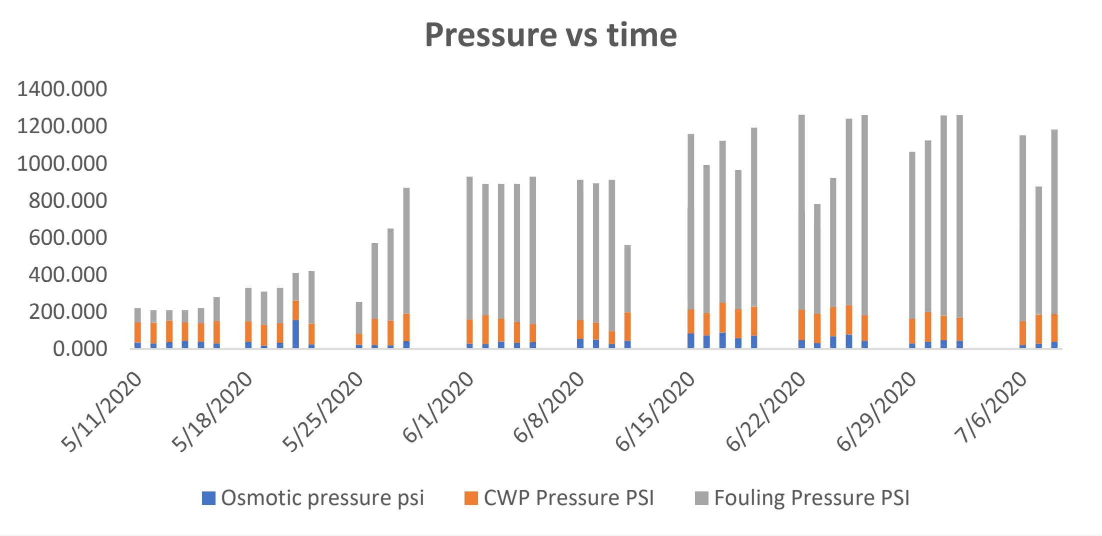

*Figure 9:Filtration pressure of the STRO versus time, and broken down into key components of pressure*

The system presents a significant amount of organic fouling based on:

- Feed BOD data
- Observations of biofilm formation in the pilot system components, especially the filters.
- Observed membrane permeability decline when feed was left in contact with membranes over a weekend
- The fact that CIP primarily required caustic cleaning rather than acid cleaning for membrane permeability recovery
- The smell of anaerobic biofilm existence in the equipment

## Conclusions

Crosstek performed the following recommendations for the commercial systems.

### *Total Suspended Solids*

**CrossTek advises considering ultrafiltration (UF) or 1-micron or smaller pore size disposable media filtration to remove TSS from the STRO feed.** The UF reject can be recycled to UF feed storage tanks and potentially extracted as sludge via a sludge disposal service. UF will additionally reduce biofouling by removing bacteria and viruses to slow bio-growth in the RO.

### *BOD and Biofouling*

Bio growth can be a risk with an average 284 mg/l BOD in the RO feed. Since bleach is sometimes present in the raw RO feed, it could be worthwhile to consider adding a 5 to 10-minute bleach contact time mix tank ahead of the standard pretreatment into which bleach is dosed under controlled conditions to act as a biocide. A commercial biocide can be considered additionally for RO feed side dose. Still, compatibility between biocide and membrane should be tested in field RO testing if this path is to be considered.

### *RO Design*

The pilot plant showed that it was possible to achieve the commercial design. The design for the commercial RO based on pilot results:

- Maintain 95% recovery so that the same evaporator system is installed as per the original design.
- The design flux is achievable with 90bar/1340psi STRO4 modules
- This fouling rate would require at least one full CIP (caustic+acid step), possibly two CIP cycles per week. In the worst case, a short daily caustic flush could be required. As such, automated CIP should be incorporated into the STRO system

### *CIP Conditions*

As noted elsewhere, highly caustic CIP is required to clean the membrane from organic and biofilm fouling. Several CIP conditions were studied. The high pH at high-temperature conditions, followed by an acid CIP, showed the best and most consistent results. As mentioned earlier, the frequency of the caustic CIP should be considered to be twice a week depending on fouling conditions, and a daily acidic flush could be required. CIP should be automated for the commercial system. The recommended CIP conditions are mentioned in Table 6:

*Table 7: Recommended CIP conditions*

**CIP Conditions**

| **Description** | **pH feed** | **pH reject** | **Temperature** |
|---|---|---|---|
| **Caustic: PWT Opticlean B** | 11.5-12 | 11-11.5 | 100 F |
| **Acid: Citric acid** | 2.5-3.0 | 3.0-4.0 | 80 |

### *Other suggestions*

- Consider a blend tank for the RO concentrate to stabilize feed parameters for the evaporator.
- The antiscalant in the RO concentrate should be considered as it pertains to evaporator design.