FIELD VALIDATION, TECHNICAL AND ECONOMIC PERFORMANCE FOR A NEW PRESSURE-DRIVEN SiC CERAMIC UF FOR DRINKING WATER PRODUCTION

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Introduction

Ceramic membranes have promise for drinking water production and wastewater reuse as they eliminate fiber breakage and offer enhanced flux that lead to footprint reduction. Potable water market adoption of pressure alumina ceramic products saw an uptick in the last five years. These alumina membranes have similar module size to incumbent hollow fiber membranes, and typically produce higher filtrate flow rate, thereby enabling retrofit of existing hollow fiber systems for increased production. This allows growing towns and cities across the Unites States to enhance production of drinking water assets for a fraction of the cost of a new plant.

A new encased silicon carbide (SiC) ceramic membrane for drinking water was piloted in 2022 at an existing alumina and polyvinylidene fluoride (PVDF) hollow fiber drinking water plant in Rapid Valley Sanitary District (RVSD) located near Rapid City, South Dakota. RVSD operates a surface water plant since 2007 that has inline coagulation and direct filtration with a two-stage UF system, where the primary and secondary filtrate is disinfected through a high strength UV. RVSD experienced population growth and used alumina UF to first debottleneck its secondary MF (PVDF) system in 2017 and then later in 2018 and 2020 to increase primary UF production in the existing facility footprint. The project team took advantage of 2022 with the final PVDF skid still operating to compare the three membrane materials for this study.

Membrane Type and Coagulation Pre-treatment

The SiC, alumina, and PVDF membranes have filtration area and pore size of 244, 261 and 538 ft^2 and 0.04, 0.03, and 0.1 micron respectively. The incumbent PVDF hollow-fiber membranes operated in crossflow configuration, while the alumina and SiC ceramic membranes operated in dead-end configuration. In terms of hydrophilicity ranking, from most hydrophilic to least, SiC > Alumina > PVDF, where the contact angles are 18º < 28-30º < 82-92º, respectively. The more hydrophilic a membrane surface is, the less energy is required to "push" a constant volume of water through the membrane surface, which results in a lower driving pressure or transmembrane pressure (TMP). Between the alumina and SiC, the iso-electric points (IEP) are at pH 9 and pH 4.3, respectively. This means that under typical drinking water treatment applications where pH of the feed water is between pH 6.5-8.5, the SiC membrane would be negatively charged, repelling negatively charged organic species in natural waters.

Coagulation is a critical component of surface water treatment plants in particulate removal and also organic reduction. Typical coagulant chemicals may include inorganic metallic salts, such as alum (aluminum sulfate) and ferric chloride/sulfate, organic coagulants (i.e., cationic polymers such as PolyDADMAC), or a blend of inorganic-organic coagulant chemistry. In general, coagulants carry a positive charge on their surface, and upon their addition in water and following their hydrolysis, negatively charged organic compounds are destabilized via charge-neutralization and form flocs which can be filtered/settled. At RVSD, due to cold water temperatures and turbidity fluctuations during seasonal changes, the coagulant formulation of choice is aluminum chlorohydrate (ACH) and ACH-polymer blends. The plant doses 13 – 13.5 ppm of coagulant dose year-round, utilizing ACH during late fall to late winter when surface water turbidity and TOC are relatively stable, and switches to a cationic polymer + ACH blend in spring to summer months when river turbidities vary due to higher organic loading and rainfall/flash flooding events. For the pilot trial at RVSD, aluminum sulfate was also tested for a short period of time for feasibility of application.

PRESSURIZED SiC MEMBRANE PERFORMANCE

Coagulant Types

Primary MF/UF skids at the plant operate at a nominal flux of 38 and 125 gfd, respectively, for the PVDF and alumina membranes. Initial startup flux testing was conducted at 125 gfd to baseline performance against incumbent alumina UF, and operation parameters such as production cycle, backwash and feed flush flowrate and duration were kept to the same bench mark. Due to the site's operation requirements needing different coagulant types at various times of the year, testing for 125 gfd was spread across the year when the opportunity for a different coagulant use arises. To compare the impact of coagulant type at 125 gfd, run times were normalized to duration (in seconds) and the normalized TMP to 20ºC was reported in Figure 1. Initial starting alum dose ranged between 0.5 - 1.0 mg/L as Al^{3+}, and stable performance at 125 gfd was achieved at 1.0 mg/L as Al^{3+}. Feed stream during the pilot test was common to all membranes.

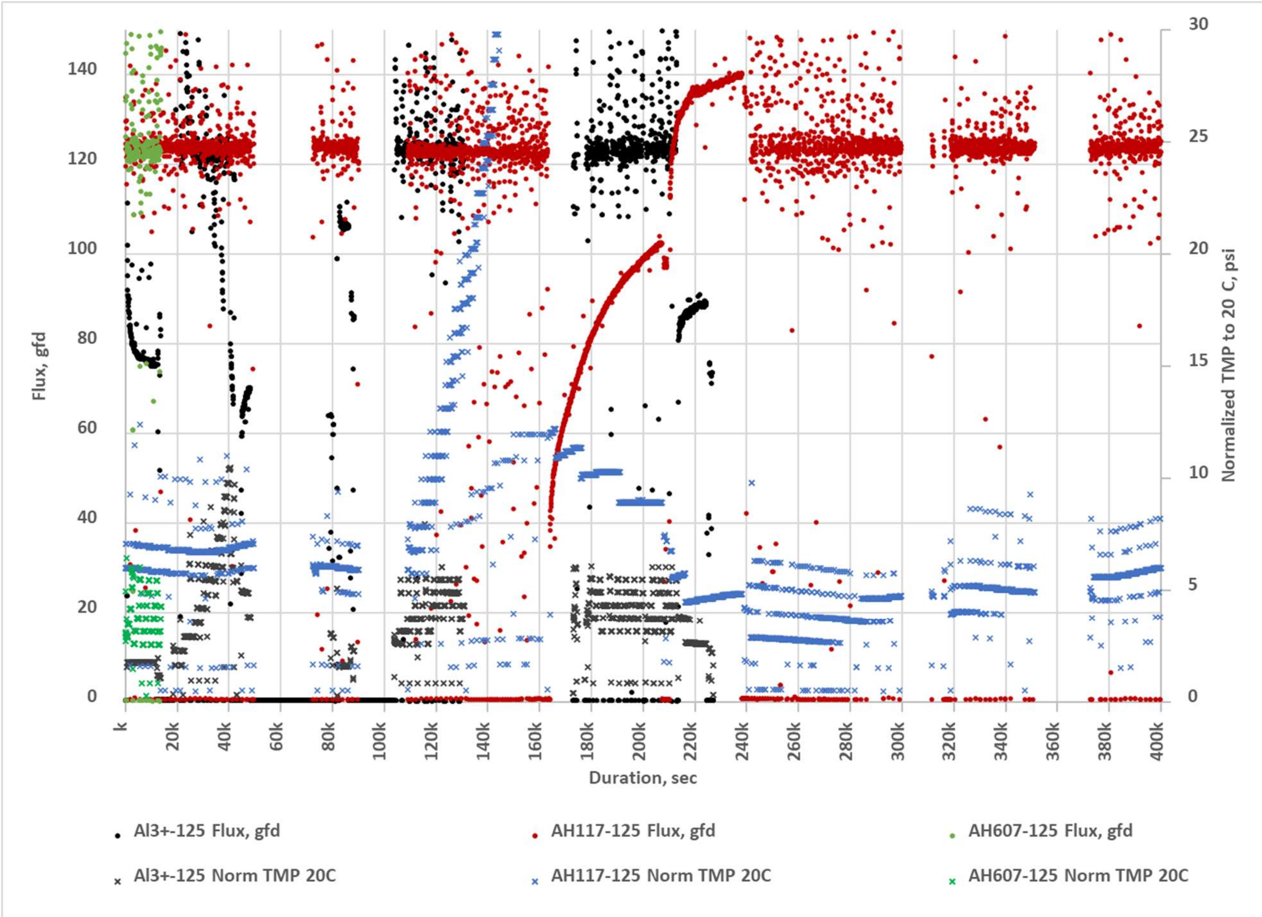

Figure 1. 125 gfd performance comparison against Alum, AH607, AH117 coagulants

As seen in **Figure 1**, the normalized starting TMP was 3.18-4.35 psi for 1.0 mg/L as Al^{3+}, 3.16-5.47 psi for AH607 (ACH only), and 4.04-5.77 psi for AH117 (ACH + 25% Cationic Polymer Blend) from post-CIP clean start conditions. The data suggests that cationic polymers on negatively charged SiC membranes would result in higher TMP, possibly due to electrostatic interactions, but operation stability can still be maintained. The spike in Figure 1 during the AH117 run was due to an overnight 200+ NTU spike in raw water, and TMP data during that time period was not considered as part of the typical starting TMP range. Typical post-coagulated feed turbidity is <20 NTU, and filtrate turbidity were < 0.1 NTU. The SiC pressurized membrane performs stably with alum and ACH (optimized dosage for the feed water), and reports slightly higher normalized TMP with ACH + cationic polymer coagulant blends. Typical starting normalized TMP for the alumina UF is reported to be 7-8 psi (8-10 psi for non-normalized TMP). Given the lower starting TMP and lower contact angle (i.e., more hydrophilic) for SiC membranes, the SiC membrane is able to operate at higher flux (i.e., more filtrate production) at the same TMP compared to alumina membranes.

Flux Stepping with ACH Coagulant

Flux stepping experiments were conducted at 150 gfd and 165 gfd for AH607 (ACH only) at longer durations, with CIP in between to validate membrane recovery after fouling. **Figure 2** summarizes the impact of (a) flux increase on TMP, (b) Specific Flux.

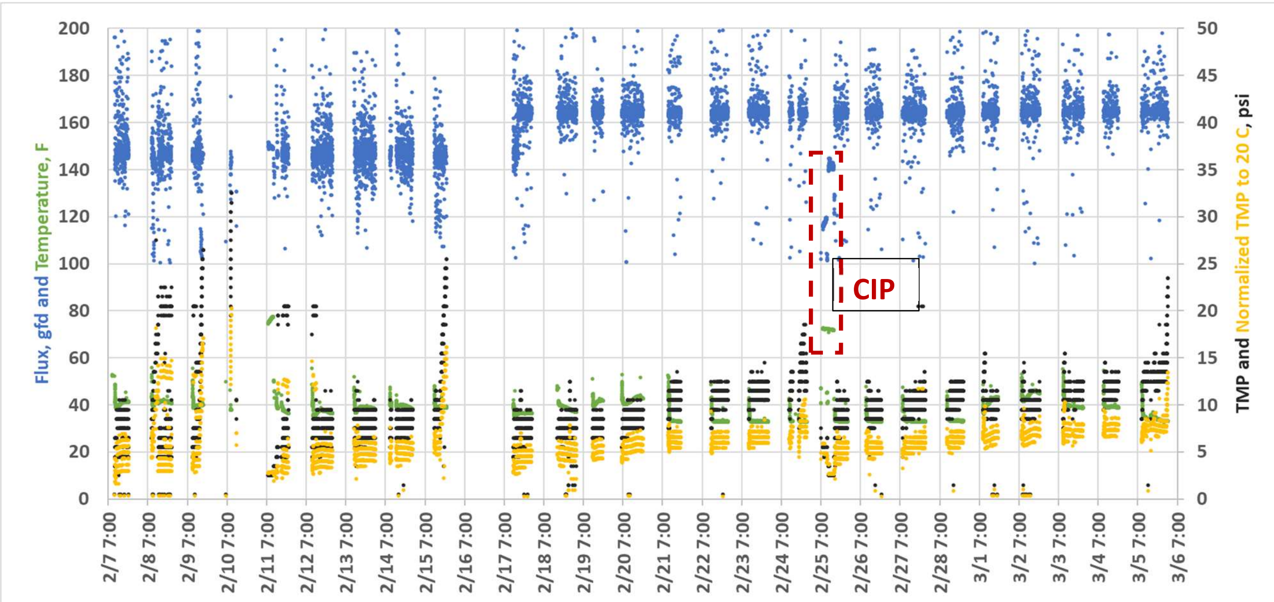

Figure 2a. ACH Flux Step Runs at 150 gfd and 165 gfd (CIP conducted 1/31 and 2/16)

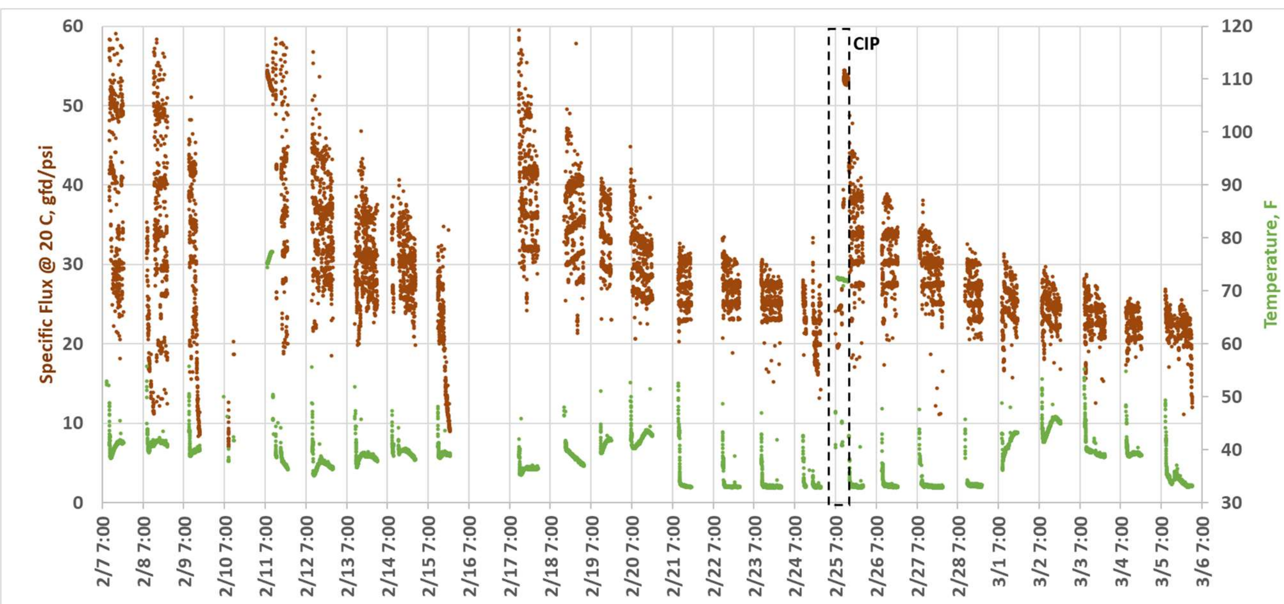

Figure 2b. ACH Flux Step Runs: Specific Flux during Operation at 150 gfd and 165 gfd

At 150 gfd, normalized starting TMP was 3-6 psi on 2/7, and gradually increased over the 5 day run period to 7 psi on 2/14. Flux was increased to 165 gfd on 2/17, at a normalized TMP of 4.5 – 13.5 over 7 days, and a maintenance CIP was conducted on the 8th day (2/25) to illustrate that permeability can be recovered in between runs. The typical maintenance CIP onsite is a 2-step process, sodium hypochlorite followed by citric acid plus hydrochloric acid. Following the weekly maintenance clean, another 8-day run was conducted at 165 gfd with a normalized TMP of 4.5 – 13.5 psi from start to end. These results show that for cold waters at temperatures between 34-40 degrees Fahrenheit, stable operation can be achieved at 150 – 165 gfd at optimized ACH dosages for direct filtration of surface waters.

Anionic Polymer Stress Test

At the end of the 165 gfd AH607 flux step experiments, a stress test was conducted by injecting 0.5 mg/L anionic polymer (flocculant) at the intake 2-feet upstream of the coagulant dosing point to simulate a stress test condition. The results of the stress test are shown in **Figure 3**. Within the first production cycle, TMP drastically increased from 5.5 to 18.5 psi. After a backwash, the second cycle started at 10.5 psi and rose to 19.5 psi at the end of cycle. Increasing the backwash flowrate from 40gpm/module to 55 gpm/module was able to stabilize the run for a few additional cycles, but unable to lower the TMP.

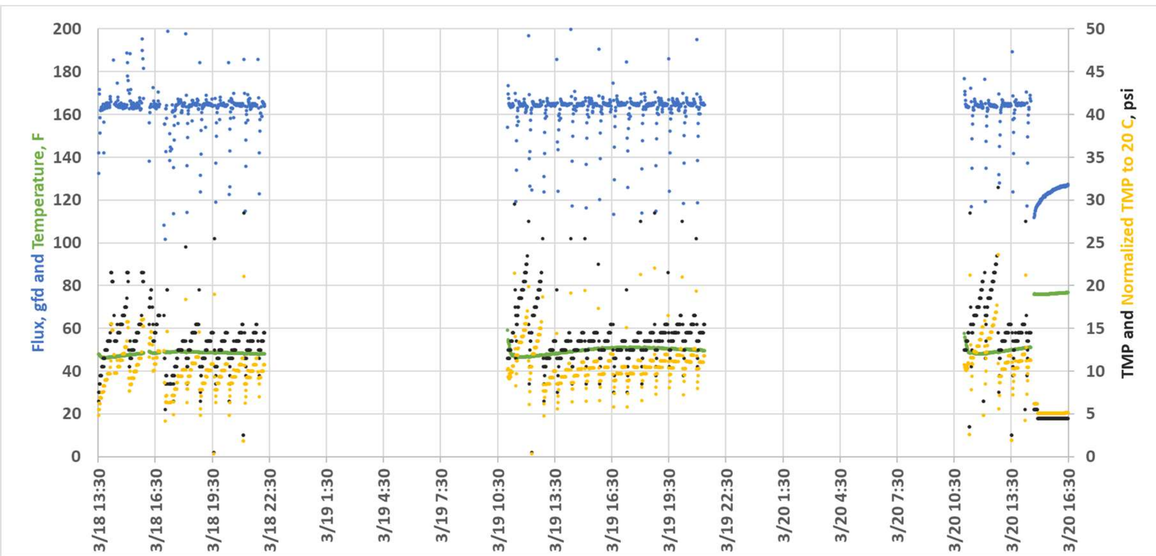

Figure 3. Anionic Polymer Stress Test at 165 gfd

Several extended CIP cycles were conducted, using NaOCl at pH 9 and Citric Acid + HCl at pH < 2 with 3 hours of recirculation at each step, and a final CIP conducted using NaOH at pH 12.5 and low pH clean recovered the starting TMP of the SiC to 3.5 psi. The anionic polymer stress test suggests that even though the SiC membrane surface is negatively charged, long chain high molecular weight polymers can still foul membranes and is difficult, albeit possible, to clean at pH 12.5.

Flux Stepping with ACH + Cationic Polymer Blend

As the plant transitions to the spring-summer seasons where raw water turbidity is less stable and tends to spike due to seasonal events, a coagulant change-over from strictly ACH (AH607) to ACH + Cationic Polymer blend (AH 117) was needed. The initial starting flux was 165 gfd (last highest stable flux point with ACH), and normalized TMP rose quickly from 4.5 psi to 10 psi in the first cycle and required a more aggressive backwash flowrate (60 gpm/module as opposed to 40 gpm/module) to stabilize the run at 11-12 psi TMP. The results are shown in **Figure 4**.

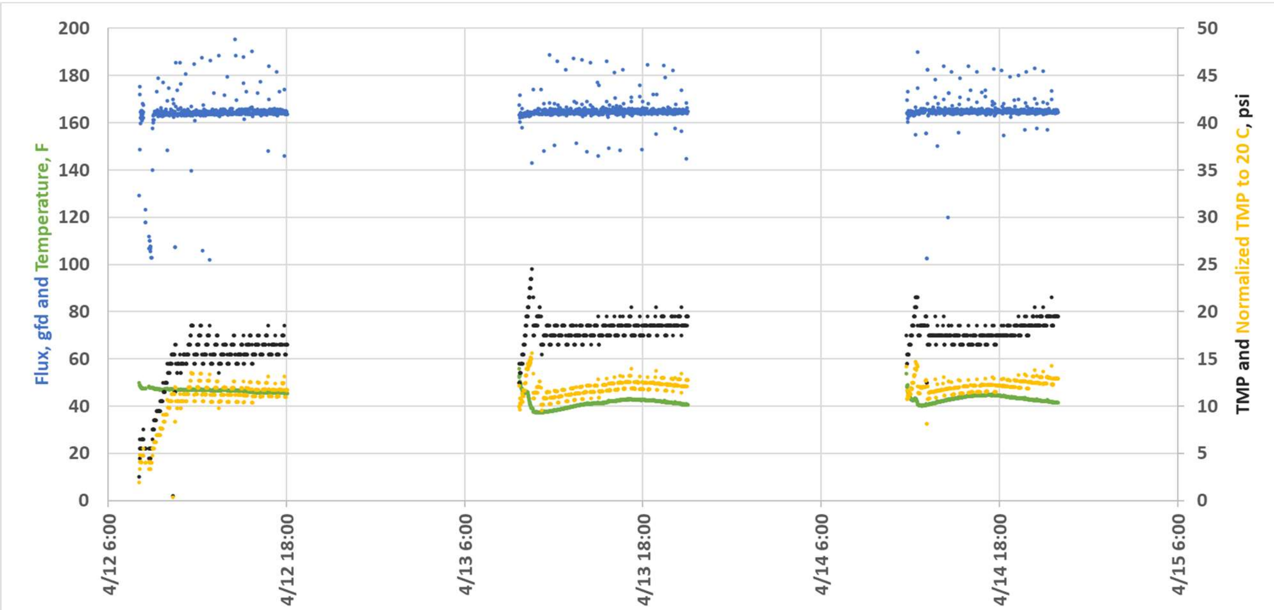

Figure 4. 165 gfd with AH117 (Cationic Polymer + ACH blend)

After a CIP was conducted and restored the membrane to clean-start conditions, the 165 gfd run was repeated before stepping up to 175 gfd. After CIP, the normalized TMP at the beginning of the 165 gfd run started at 3.5 psi and rose to 10-11 psi, agreeing with what was previously observed in **Figure 4**. Increasing the flux up to 175 gfd as seen in **Figure 5** showed that the TMP was not stable at the same backwash conditions for 165 gfd, and increasing the backwash flowrate beyond 60 gpm/module was considered impractical.

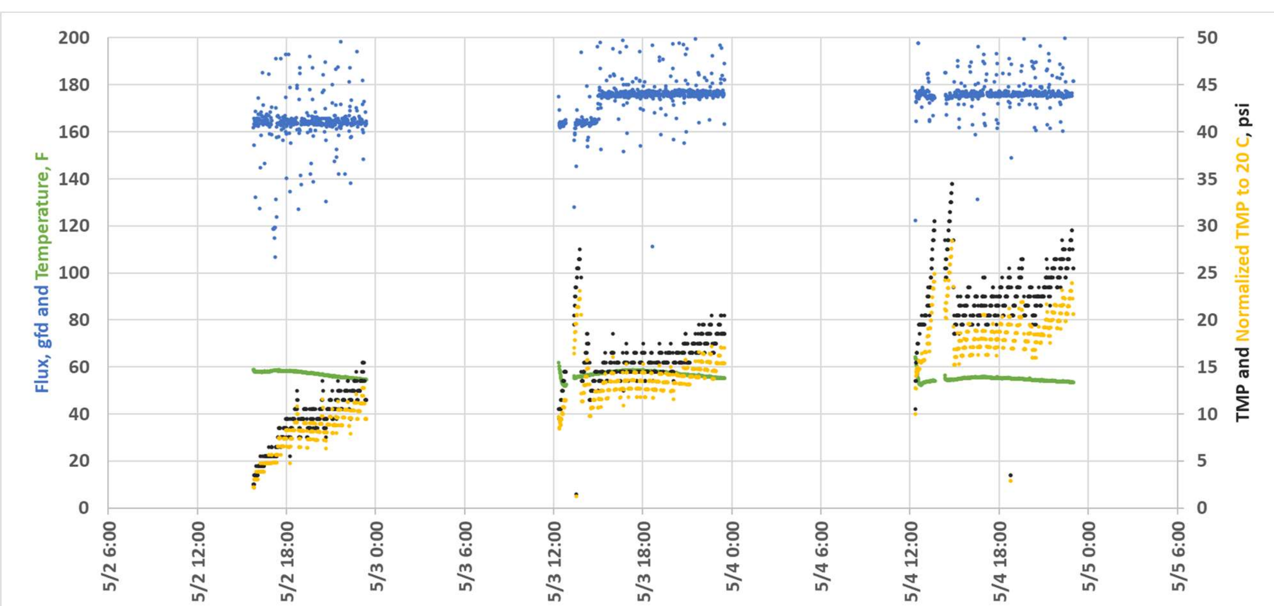

Figure 5. 175 gfd with AH117 (Cationic Polymer + ACH blend)

The impact of coagulant formulations with cationic polymer blends on SiC are clearly illustrated in this experiment. At 165 gfd, the presence of cationic polymers in coagulant blended increased the normalized TMP 35-50% over pure ACH coagulant, and required a higher backwash flowrate to combat the charge attraction between the polymer and membrane surface to stabilize the membrane operation. This experiment shows the importance of coagulant charge interactions with membrane surface. RVSD reported that SiC membrane operated more stably with ACH + Cationic Polymer coagulant blend when the TOC levels in the raw waters are higher, which indicated that the cationic polymer was able to charge-neutralize the TOC, resulting in less available positively charged polymer attachment to the SiC membrane surface.

Integrity Testing

Membrane integrity testing was conducted for the SiC module intermittently during the pilot testing period, and the resulting calculated LRV were > 4 during the year-long test period. Between June and July, the plant converted integrity testing methods from the feed side to the filtrate side. Feed side pressurization during the integrity testing may push foulants further into the membrane channels, and the potential plugging may cause the dP measurements during to be artificially better. The piping volume for the filtrate side still needs to be updated, but preliminary calculations indicate that the pressurized SiC module will be able to achieve LRV > 4 through aggressive backwash conditions, high TMP stress test conditions, and aggressive chemical cleaning at pH 12.5. **Figure 6** summarizes the calculated LRV from the dP measured during IT testing at the plant.

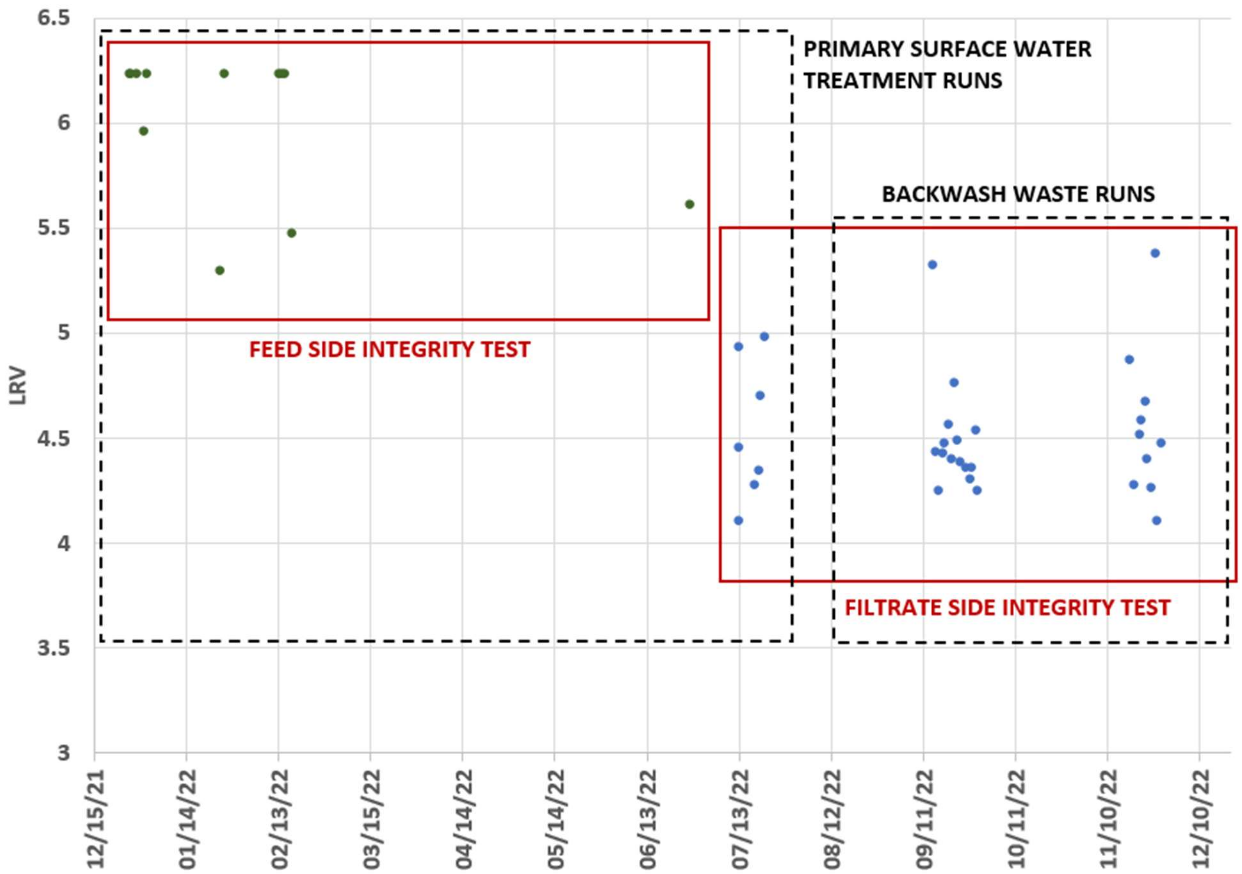

Figure 6. LRV for SiC pilot module

SUMMARY AND ECONOMIC EVALUATION

Using the performance data for SiC at 165 GFD, a payback analysis was performed for an upgrade from PVDF to alumina and SiC membranes, showed that production rate increased 54% and 106%, installed capital cost for the upgrade was \$0.25/gpd and \$0.24/gpd, and payback was 0.59 and 0.43 years respectively. The analysis considered water and wastewater (backwash) rates of \$3 and \$5/1,000 gallons respectively and used the pre-treatment chemistry, pressure and recovery from the field trial.

The study showed that: (1) flux was increased at RVSD from 38 gfd for PVDF MF Hollow Fiber membranes, to 125 gfd for ceramic alumina membranes, and up to 165 gfd for silicon carbide pressurized membranes within the same plant footprint; (2) SiC pressure decay rates were below 0.04 psid/minute were likely to comply with EPA LT2 requirements; (3) alum was the preferred pre-treatment chemistry for SiC membranes but some other chemistries were workable; (4) SiC would compete favorably with alumina for retrofit projects, achieving 50% more production with preferred paybacks. Following these successful field trials and successful bench scale 3rd party cryptosporidium and giardia testing, the SiC membrane was optimized to 269 ft^2 filtration area in the same vessel, subsequently certified to NSF61, and obtained an NSF419 in November 2022.