TREATMENT OF REVERSE OSMOSIS BRINE THROUGH CHEMISTRY

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Abstract

Brine disposal is a unique and indispensable resource for reverse osmosis water treatment plants, allowing a facility to export high salinity waste from inland areas to the ocean, rivers, or groundwater recharge. This export is important for protecting water quality and meeting regulatory requirements. Unfortunately brine disposal also has a high incidence of scale due to long disposal lines, inconsistent flow or stagnation, and the introduction of air. This paper will walk through some common problems found in reverse osmosis brine disposal and the chemicals used to mitigate these issues. The Brine Line in the Inland Empire, concentrate tanks, and deep well injection will be discussed. Water treatment plants located throughout the US will provide as case studies for the effective treatment of reverse osmosis brine through chemistry.

Introduction

Waste disposal from reverse osmosis (RO) drinking water production is an ongoing challenge that continues to grow in complexity. As facilities work toward waste reduction through increased recoveries and concentrate recovery processes, the resulting waste becomes more difficult to store, handle, and transport. In many cases, customized chemistry offers the necessary support to advance toward smooth cradle-to-grave operation.[1]

Pretreatment chemicals have been in play for decades to minimize fouling and scaling throughout the RO process. However, as the concentrate stream exits the system, control of the supersaturated brine chemistry has a different nature and can require supplementary control. Chemical control to complete the brine discharge process is generally easy to dose and cost effective (reducing shutdowns and maintenance), and it extends equipment life and ensures a stable output capacity.

In this paper, we will discuss how to use the chemistry we know in brine water to solve scale build-up due to long retention time, inconsistent flow or stagnation, and the introduction of air. King Lee Technologies has worked extensively with two municipalities struggling with such issues, one that sends its discharge into the Inland Empire Brine Line, and the other who manages a concentrate tank followed by deep well injection in the City of Sterling. Evidence suggests that we have found a solution to some of the operational problems seen by both plants caused by inline scale accumulation.

Background

We will focus our experiments and discussions on two main brine discharge operations.

The Inland Empire Brine Line operated by the Santa Ana Watershed Authority (SAWPA)
To determine the control potential of various chemical treatments, we investigated the brine of an RO facility that is piped downstream for additional treatment. The concentrate stream passes through an air gap intended to prevent backflow contamination, then flows downstream in a pipeline that has maintenance access and therefore, exposed to air. Calcium carbonate and silica scale precipitate in the discharge lines and in the combined line due to sharp horizontal bends, elevation changes, air exposure, and periods of stagnation. As a result, costly periodic shutdowns are required to physically break apart the scale that precipitates in the pipeline.

The membrane process at the facility includes King Lee Technologies antiscalant injection ahead of the RO for successful operation with an incoming silica concentration of up to 51 ppm, recovery of 79%, and a resulting potential Langelier Saturation Index (LSI) value of 2.8. The antiscalant is dosed sufficiently to minimize scale for the retention time within the RO. However, due to the supersaturated nature of the brine, eventually precipitation occurs and crystallites of the scale are generated. Through further aging and agglomeration, crystals contribute to the formation of the adhering deposits.

Sterling Water Treatment Plant Concentration Tank/Deep Well Injection Operated by the City of Sterling
The Sterling Water Treatment Plant in Sterling, Colorado is a 9.6 MGD drinking water plant with a distribution blend that includes water purified through RO. Water chemistry analyses report up to 41 ppm reactive silica in the wells, and historically the system has operated at 82% recovery with a field-determined 2.2 brine LSI value and annual cleanings. This RO process results in up to 1.6 MGD of concentrate water whose supersaturated salts must be controlled sufficiently to allow for the retention time in an open-air 230,000-gallon concentrate storage tank, which then feeds two EPA Class 1 deep wells. The deep well injection process was initiated in 2013, and it was quickly met with the challenge of scale control. **Figure 1** shows the screen from one of the submerged concentrate discharge pumps after the first month of operation. Testing verified that the scale was comprised mostly of calcium carbonate. King Lee Technologies recommended an antiscalant, Pretreat Plus® 2000, which they have been using successfully since 2014. After continuous monitoring, it was believed improvement could still be made.

Figure 1. Close-up of pump screen scaled with calcium carbonate.

Methods and Materials

Protocol Development

The goals of the initial investigation were to develop lab tests for simulating and accelerating the scale formation and to test various scale control formulations and dosages to minimize precipitation. Laboratory experiments conducted on various samples of the RO concentrate confirmed that air exposure and mixing increase the rate of precipitation. During air exposure, loss of CO_2 from brine raises the pH, thereby shifting equilibrium from bicarbonate (HCO_3^-) ions to carbonate (CO_3^{2-}) ions. The resulting reactions with calcium and magnesium ions initiates scale formation.

Several standard methods were proposed to reduce scale in brines with high scale formation. Some of these include: 1) Decrease pH to reduce the loss of CO_2 (add acid to the brine), 2) Increase or change antiscalant on the front end of the RO, 3) Keep the brine from ambient air exposure. After careful consideration and discussions with primary decision makers, each of these options had their own drawbacks, costs, or regulations preventing them from being viable options. Considering that an antiscalant injected directly into the brine could tackle the issue, we began lab testing several antiscalant formulations on brine water from each site.

Methods

Benchtop jar tests were conducted in the King Lee Technologies onsite lab. Using 1L brine samples in Nalgene bottles, a controlled dosage of antiscalant was added and allowed to stir using a multi-station hot plate accommodating 4 samples at a time. The sample bottles were provided with air exposure by a *ca.* 0.5” hole in the parafilm seal. Over the course of 1-4 days, the samples were allowed time to form scale. Visual observations were recorded, then the precipitate was manually filtered with a 0.7 µm Pall fiber filter. Scale was collected and dried in the oven at *ca.* 120^{o}C for 2 hrs, then weighed. Filtrate was then further analyzed by the methods described below. TDS and conductivity of the filtered solution was measured. Various antiscalant formulations were tested by addition to the same original brine and the masses of scale produced were compared.

Lab Results

The Inland Empire Brine Line
Improving Upon Current Scale Control
The root cause of heavy and thick scales on the pipe wall is mostly due to deposition of carbonate mineral scale. CO_2 escaping from the brine causes an increase in pH and results in $CaCO_3$ and $MgCO_3$ precipitation. Lab tests showed that 3N HCl can vigorously dissolve most of the precipitates, indicating likely composition of carbonates greater than 90% by weight. The 0.7 µm filter will have removed $CaCO_3$, as well as some colloidal silica. Nutreat™ 1700's performance showed a reduction in scale formation similar to the site's current methods at 20 ppm, but significantly improved control at 10 ppm (**Figure 2**).

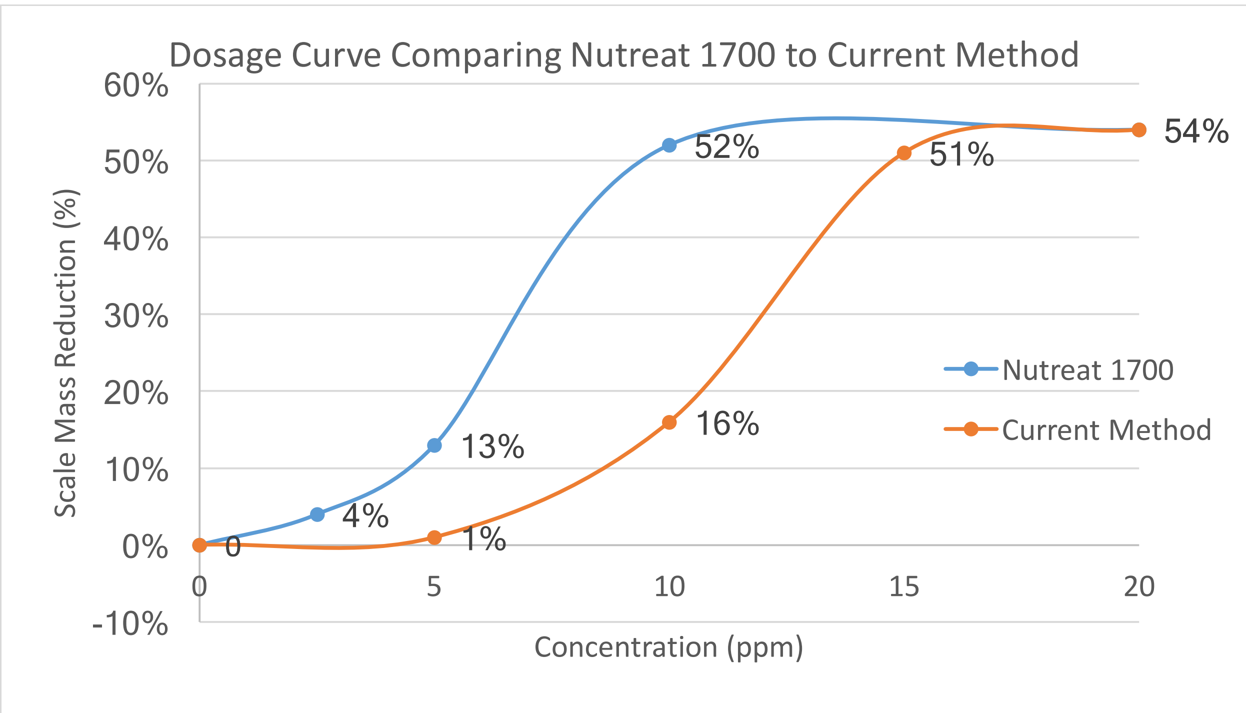


Figure 2. Dosage curve of Nutreat™ 1700 dosage and current methods used at the site.

The optimum dosage of Nutreat™ 1700 recommended was 10 ppm due to the plateauing scale control at dosage rates greater than 10 ppm (**Figure 2**). The scale produced in the presence of Nutreat™ 1700 is fluffier, finer, and less likely stick to the pipe wall, as seen in **Figure 3**.

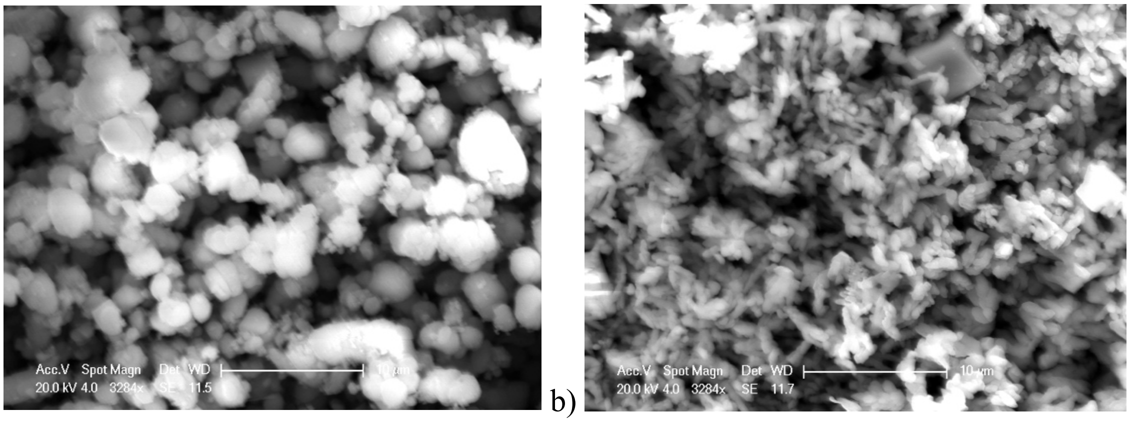
a) b)


Figure 3. SEM/EDX images of the filtrate a) with current methods used at the plant and b) with Nutreat™ 1700 antiscalant.

Sterling Water Treatment Plant Concentration Tank/Deep Well Injection
Investigating Optimized Scale Control

The current scale control approach allowed successful operation for greater than 3 years. With a new antiscalant showing promise on brine treatment, further studies were initiated to determine whether a new formulation could provide incremental improvement for operations. A review of the Sterling Water Treatment Plant water chemistry revealed less of a dissolved silica burden than the previously tested brine, due to a maximum RO feed concentration of 41 ppm. Also, even with a higher recovery of 82%, the brine LSI is slightly lower than the other site tested, at up to 2.2.

Two tests were carried out, each with a control sample of 12.5 ppm of Pretreat Plus® 2000, which was the current concentrate tank dosage. The first test was designed to compare the current antiscalant dosage with a similar dosage of Nutreat™ 1700 to determine whether the formulation offered stronger control. The results of the 48-hour test, shown in **Figure 4**, revealed that even at a slightly lower dosage rate, Nutreat™ 1700 prevented an additional 20% of the scale formation.

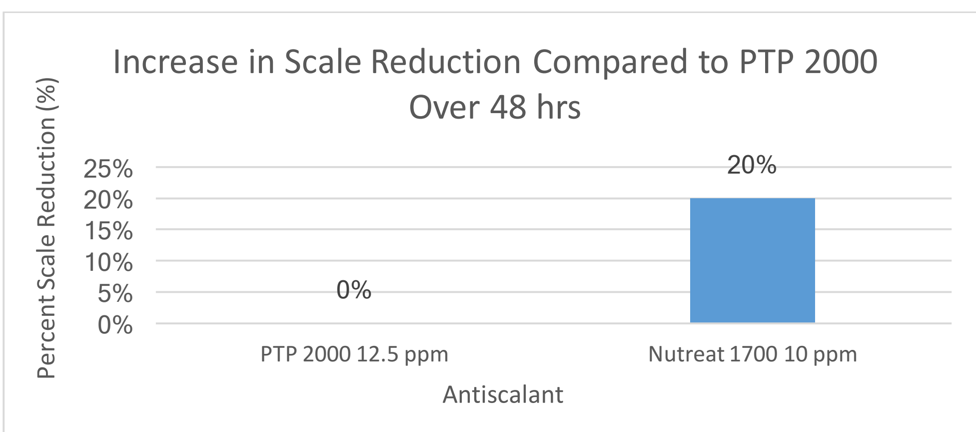


Figure 4. First Sterling brine test to determine relative control strength (Pretreat Plus has been abbreviated to PTP).

Due to the success of Nutreat™ 1700 in the first test, the second test was designed to evaluate a greater potential for scale control. Due to the concentrations of calcium and bicarbonate ions, two antiscalant formulations were considered in this round: Nutreat™ 1700 and Pretreat Plus® 3100. The current dosage rate of 12.5 ppm Pretreat Plus® 2000 was tested against 3 samples: a) 20 ppm Nutreat™ 1700 b) 20 ppm Pretreat Plus® 3100 and c) 10 ppm of Nutreat™ 1700 + 10 ppm of Pretreat Plus® 3100.

Figure 5 shows the results after 32 hours of test time. Nutreat™ 1700 dosed at 20 ppm resulted in the greatest scale reduction, with approximately half the precipitate of the control sample. This was greater than double the effect of the other test formulations.

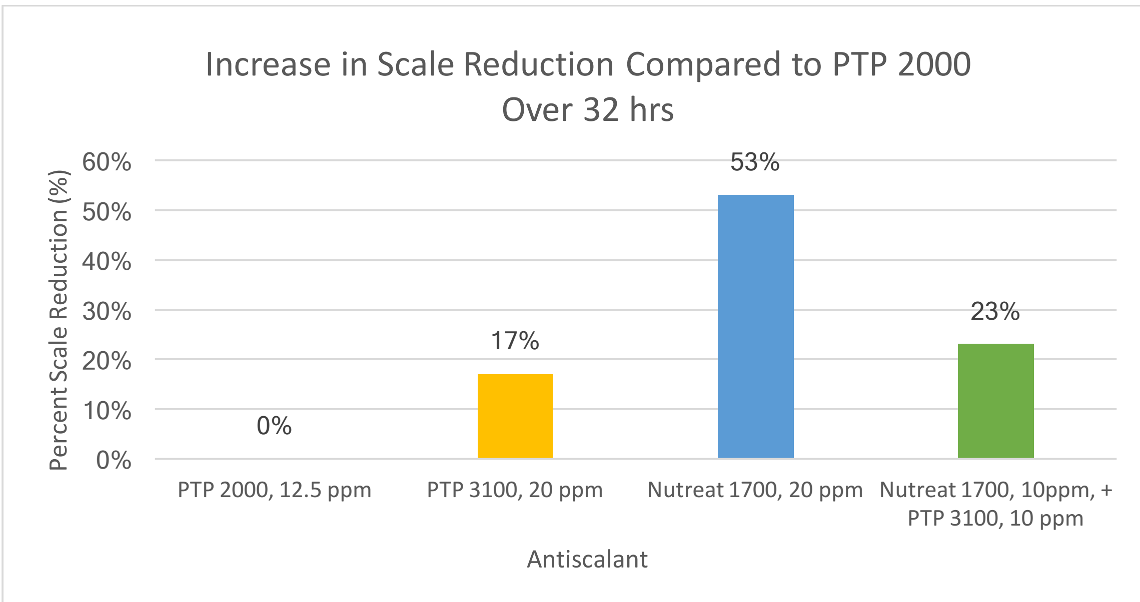


Figure 5. Second Sterling brine test to determine greater potential for scale control.

Observations throughout the testing showed that the morphology of the $CaCO_3$ is modified so the precipitates are fluffier, less densely packed, and less likely to adhere. Samples of the filtered solid are shown in **Figure 6**.

Figure 6. Filtered precipitate from the control sample (left) vs. reduced mass and altered morphology of the sample dosed at a similar rate with Nutreat™ 1700 (right).

Sterling Water Treatment Plant: Case Study and Expanded Application

Operation Interrupted

From the initial transition to a reverse osmosis facility, Lead Operator, David Beck, has been part of the team pursuing successful operation and optimization. The deep well injection process was initiated in 2013, and it was quickly met with the challenge of scale control. "A few weeks after RO system startup, a calcium carbonate scaling problem in the concentrate removal system halted operations. Chemical dispersants used in the RO process are designed to keep minerals in solution. 'We quickly found out that these dispersants were not designed to overcome the time the brine was in the storage tank,' says Beck. 'No one foresaw this issue because deep injection is not common for RO facilities. The only other RO facility in Colorado with a deep injection well[3] does not have a brine storage tank.'"[2]

Figures 1 and **7** show the screen from one of the submerged concentrate discharge pumps after the first month of operation. Testing verified that the scale was comprised mostly of calcium carbonate.

Figure 7. Deep well injection pump screen.

Sustaining Operation with Scale Control

After successful removal of the scale from the pumps and pipes, the Operations Team worked with King Lee Technologies toward a solution. The addition of 10 ppm Pretreat Plus® 2000 was implemented in the concentrate storage tank, and scale control was evident immediately. Over time, sodium hypochlorite dosing was also implemented to help control biogrowth in the open-air tank and to minimize automatic backwashes triggered by the 25 micron stainless steel filters before the deep well injection.

Figure 8 shows two of the concentrate discharge pumps in the storage tank. The pump on the right has scale that remains from the first month of operation without antiscalant injection in the concentrate tanks. The pump on the left was installed after the dosing of Pretreat Plus® 2000 was implemented, and the photograph was taken after 10 months of operation with no evidence of scale.

Figure 8. Discharge pumps after 10 months operation with Pretreat Plus® 2000 in concentrate tank. Right pump has some scale that remains from original operation without antiscalant in the concentrate tank.

Verifying Optimized Scale Control: Automatic Backwash
Within two months of reported brine test results, the Sterling Water Treatment Plant replaced Pretreat Plus® 2000 with Nutreat™ 1700 in the concentrate storage tank. One of the markers that would be used at the facility to monitor field success for the new approach is automatic backwash operation to address the 25 micron filter prior to the deep well injection.

The improvement due to Nutreat™ 1700 on the backwash operation can be revealed by first understanding the history. The screenshot in **Figure 9** shows two key factors of the backwash process for Deep Well 1 during the week of November 3-10, 2016. The first is the effluent valve position, which is represented by the line height on the graph, with the peak representing the backpressure valve being 100% open. The second is the frequency of the automatic backwashes, each of which is represented by the drop to 5% on the graph due to the valve being mostly closed during a backwash. As mentioned earlier, when Pretreat Plus® 2000 was dosed alone for scale control, organics were still a concern for the 25 micron filters downstream, and this is represented here. On 11/3, multiple consecutive automatic backwashes occurred until the filter was manually cleaned on 11/4. By 11/6, the backpressure valve reached the 100% open position, with consecutive automatic backwashes occurring again by 11/8. During this time period, the Sterling Operations Team was manually cleaning the filters 1-2 times per week because the automatic backwashes alone were not fully effective.

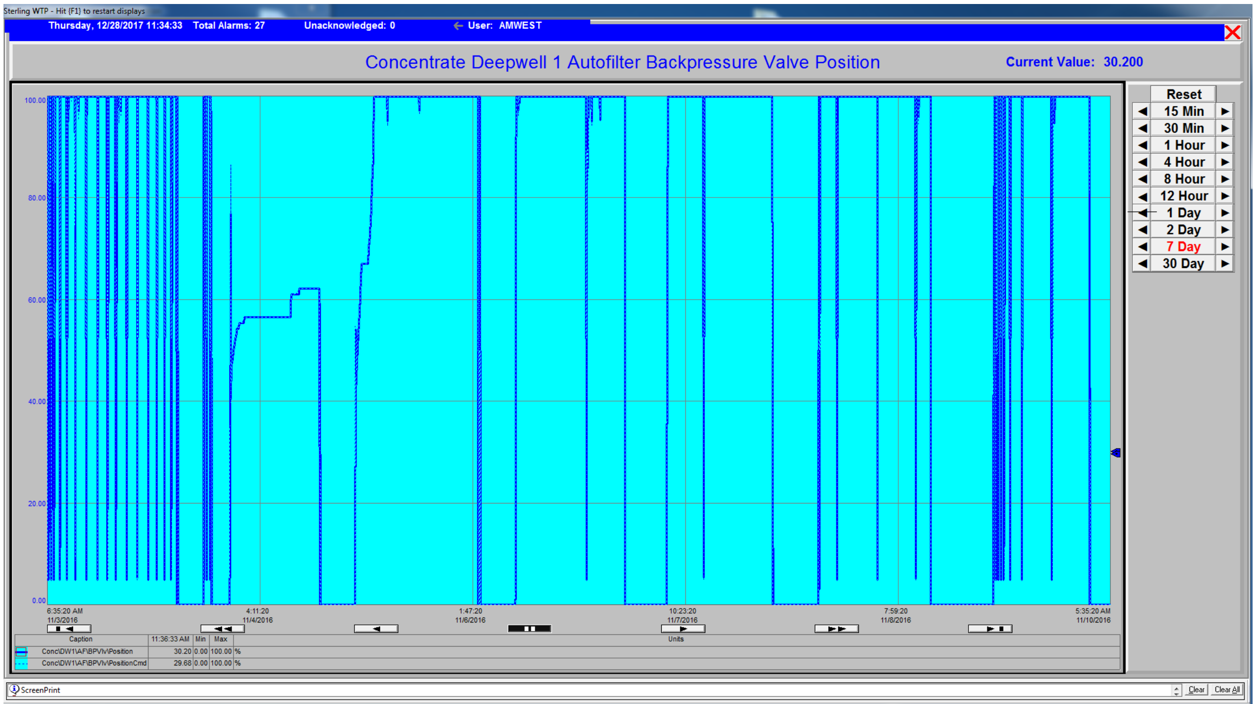


Figure 9. Deep Well 1 backpressure valve position during Nov. 3-10, 2016 with scale control only. Consecutive automatic filter backwashes remedied by once- or twice-weekly manual cleanings.

By disinfecting the concentrate with sodium hypochlorite, the Sterling Team greatly increased the effectiveness of the disposal process, as can be seen in **Figure 10**, which shows operation during the week of March 3-10, 2017. In this case, the red line represents the backpressure valve position, and the blue line represents the injection of sodium hypochlorite. Consecutive automatic filter backwashes were practically eliminated.

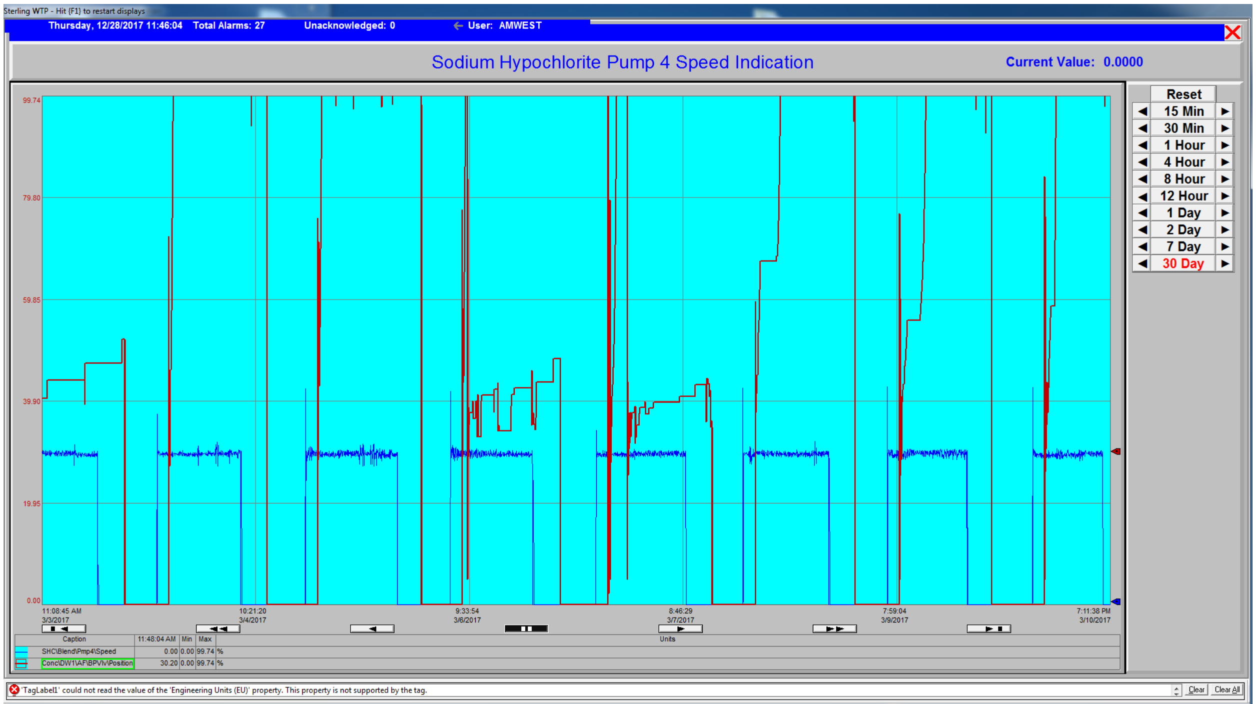


Figure 10. Deep Well 1 backpressure valve position (red) and sodium hypochlorite pump speed (blue) during March 3-10, 2017. Consecutive automatic filter backwashes practically eliminated.

Typical operation eventually consisted of sodium hypochlorite being dosed intermittently in two-week intervals. This is shown in **Figure 11**, which shows the same data as **Figure 10**, but for the entire month of March 5 – April 4. No consecutive backwashes, and only one manual filter cleaning during this period on April 2.

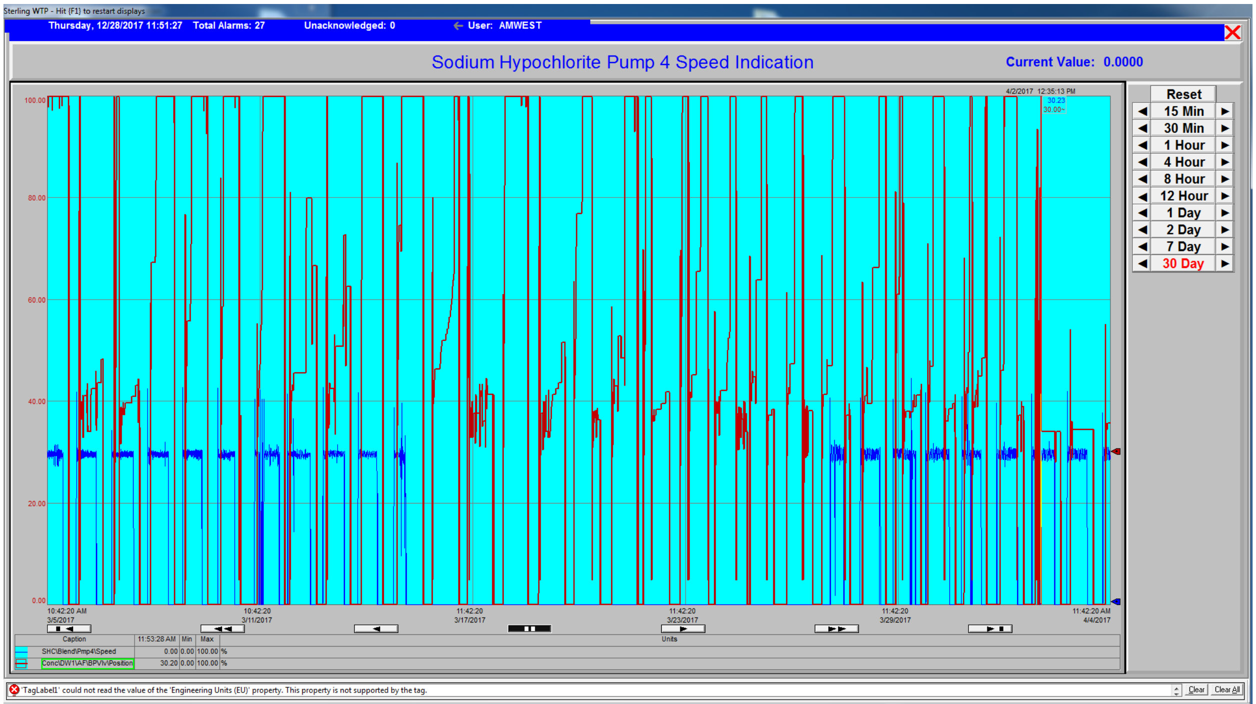


Figure 11. Deep Well 1 backpressure valve position (red) and sodium hypochlorite pump speed (blue) during March 5 – April 4, 2017. One manual filter cleaning on April 2.

Building upon the history of the backpressure monitoring of Deep Well 1, **Figure 12** reveals clearly that in one week of dosing Nutreat™ 1700 exclusively (with no sodium hypochlorite addition), no automatic backwashes or manual filter cleanings were required. **Figure 13** shows that over a one-month period under the same conditions, only 5 total automatic backwashes occurred with no manual cleanings required.

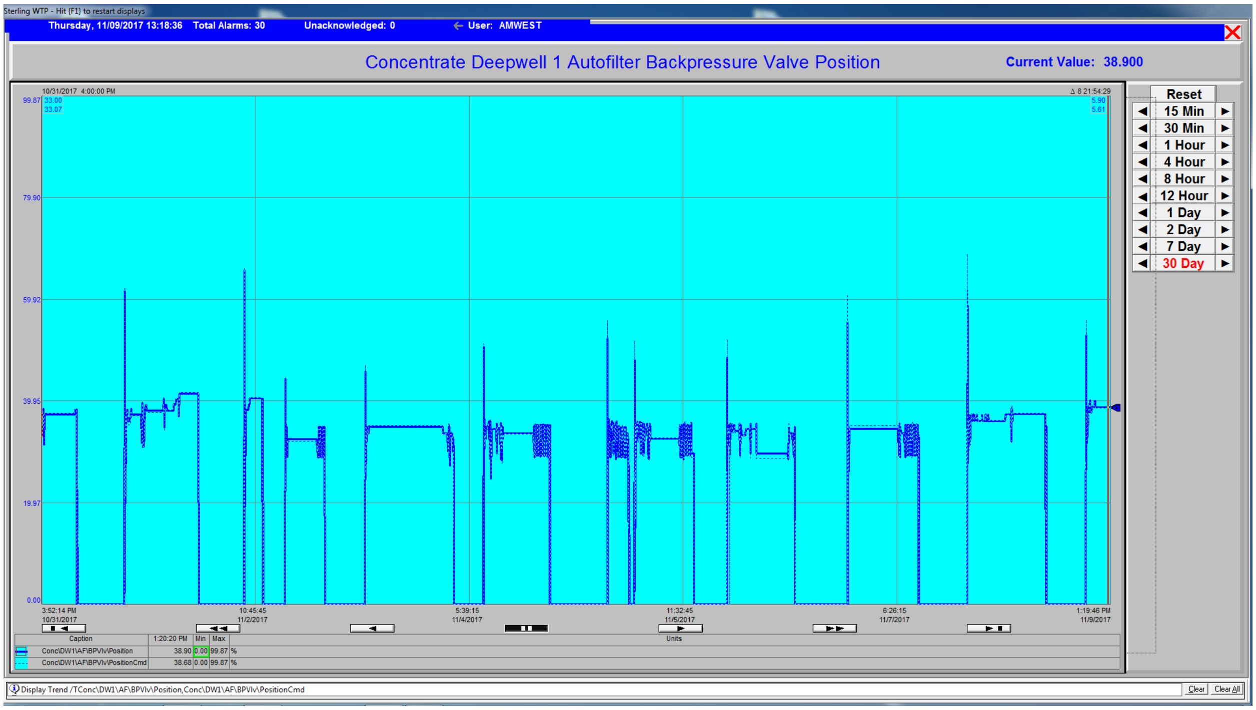


Figure 12. Deep Well 1 backpressure valve position during exclusive dosing of Nutreat™ 1700 for an approximate one-week period. No automatic backwashes or manual cleanings required.

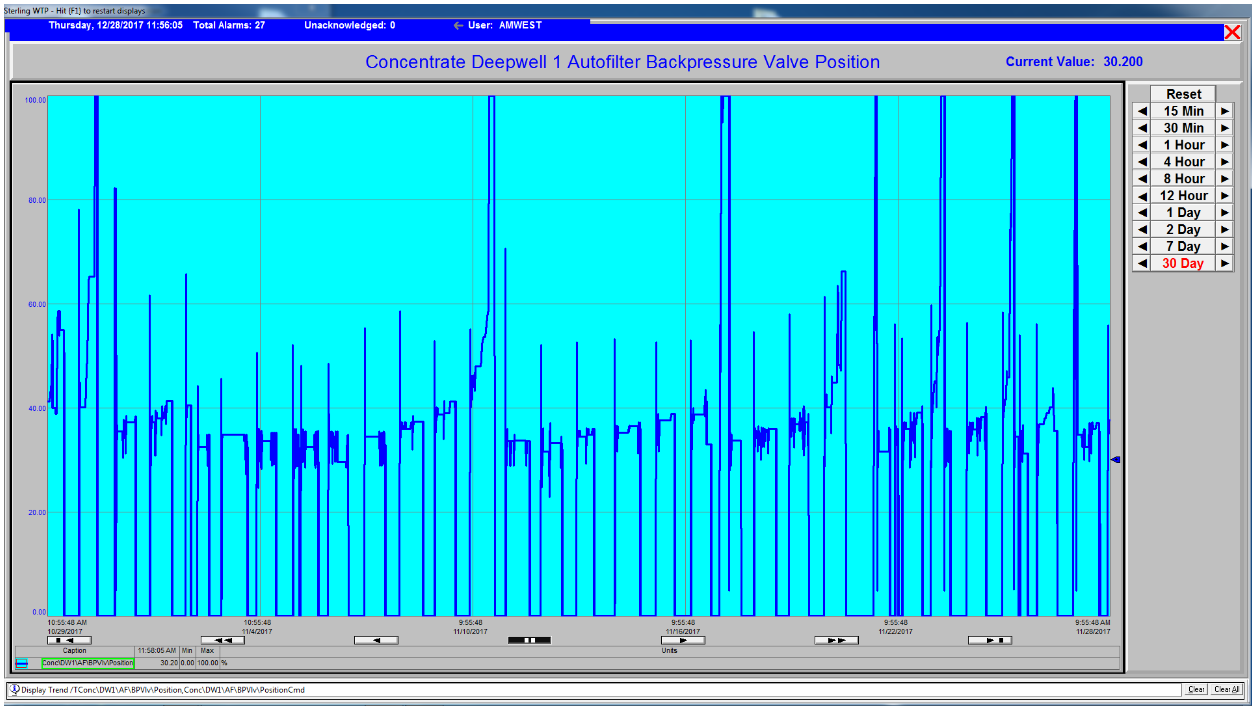


Figure 13. Deep Well 1 backpressure valve position during exclusive dosing of Nutreat™ 1700 for one month. Five automatic backwashes with no required manual cleanings.

After more than three months of operation with Nutreat™ 1700, routine maintenance of the tank includes periodic disinfection, though at a much lower frequency. Monthly disinfection is currently implemented over 2-3 days, compared to the previous 2-week intervals.

Verifying Optimized Scale Control: Sustained Vacuum Flow

The periods of varying demand on the deep well injection system can be seen in the previous figures by differences in peak valve positions. Periods of time when the valve position is at 100% (**Figures 9-11**), higher demand, and therefore higher flow, is implied. Periods when the valve position is lower (**Figures 12-13**), less flow through the Deep Well 1 line occurs. To address the influence that demand may have on scale formation, an additional marker Sterling uses to measure an improvement in scale control during the concentrate discharge process is the sustained flowrate to the Deep Well achieved under vacuum.

Application of Nutreat™ 1700 began on September 15, 2017. By September 19, Sterling saw an increase of greater than 10% in the Deep Well 2 sustained flowrate under vacuum, as shown in **Figure 14**.

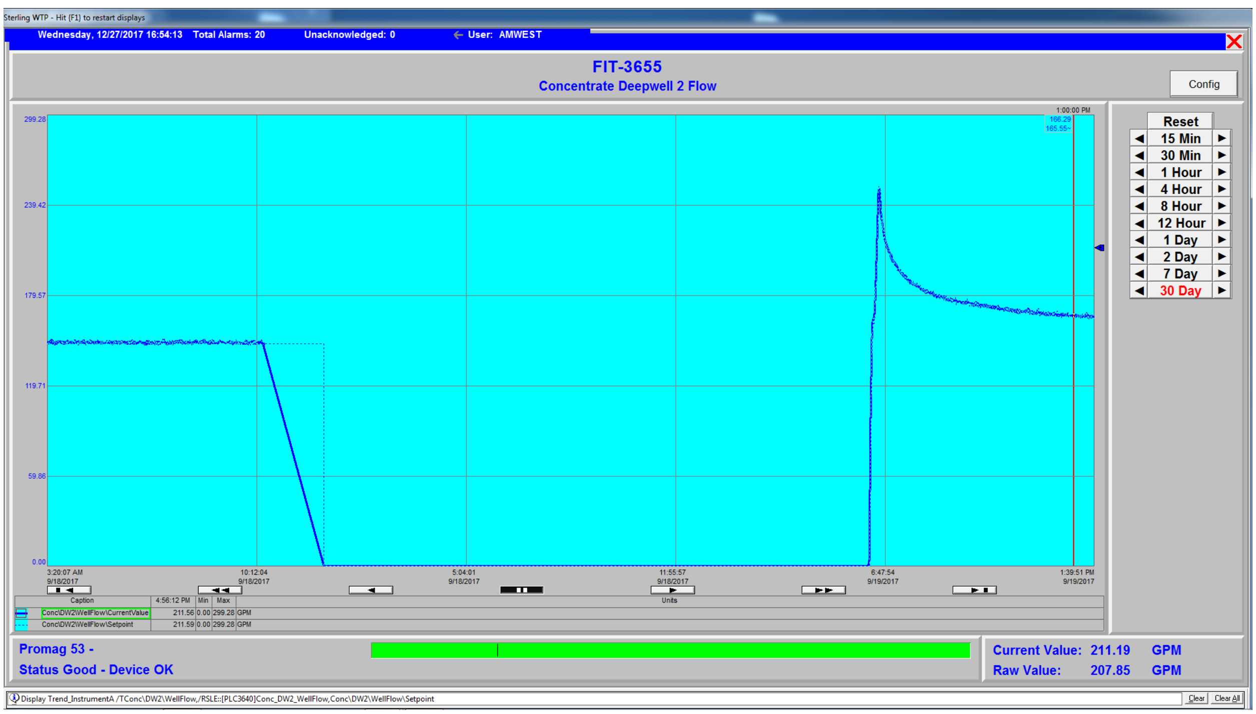


Figure 14. Deep Well 2 sustained flowrate under vacuum increased from 148 gpm to 166 gpm with the conversion from Pretreat Plus® 2000 to Nutreat™ 1700.

Figure 15 reveals that as of December 2017, the increase in the sustained flowrate under vacuum for Deep Well 2, as represented by the black line, is being maintained. It also displays a telling comparison between two timeframes during which the well capacity should be similar, as the flow and vacuum pressure of an injection well can be affected by the capacity of the reservoir. The blue line represents the same month from the previous year. The sustained flowrate in December 2017 was at least 10% greater than that in December 2016. This is an indicator that the difference in flow is due to a reduction in the presence of scale, as opposed to a change in demand. A comparison between November of 2016 and 2017 showed an almost identical trend.

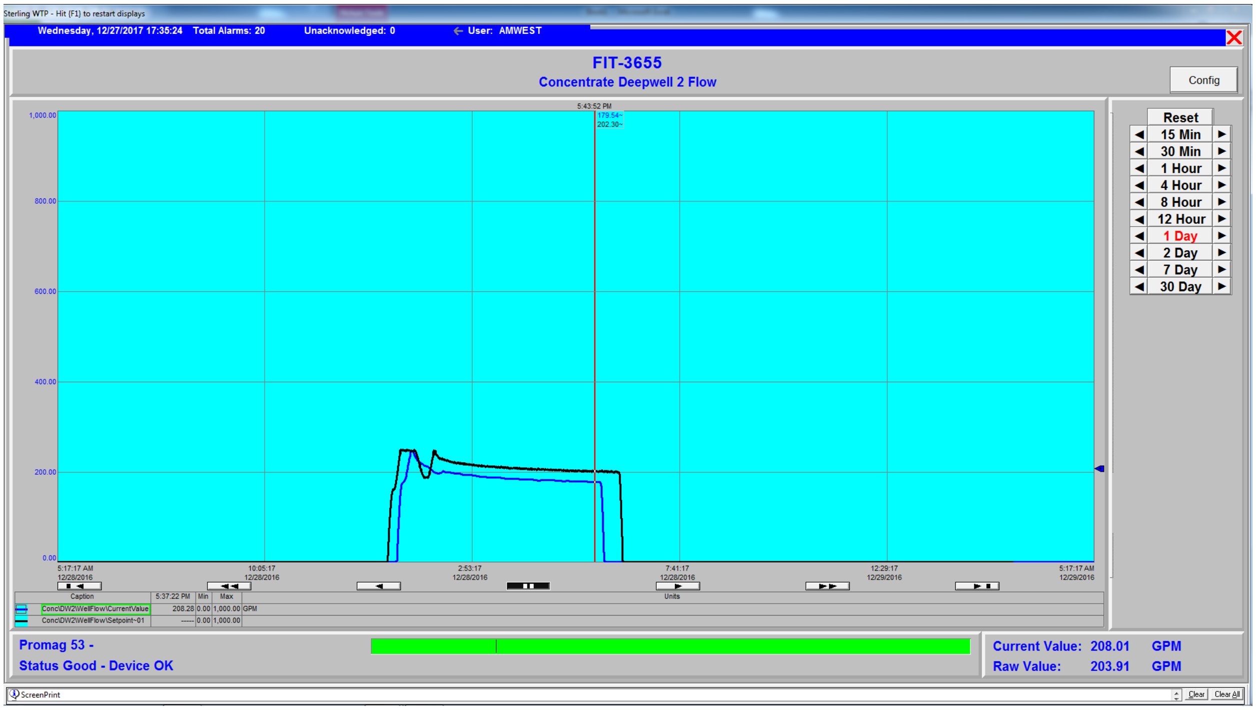


Figure 15. Deep Well 2 sustained flowrate under vacuum increased from 2016 to 2017 during periods of similar demand due to the conversion from Pretreat Plus® 2000 to Nutreat™ 1700.

Conclusions

Lab test studies on both brines from two different sites and two different applications indicated that Nutreat™ 1700 is an effective antiscalant specifically formulated for control of precipitation in high TDS waters, in this case specifically RO/NF brine or concentrate streams. Lab tests also indicated that it is compatible with the currently used phosphonate-based pretreatment chemicals.

During its application at the Sterling Water Treatment Facility, automatic backwashes for the concentrate tank filter decreased, and an increased flow rate under vacuum for both deep wells was observed due to the decrease in scale. The team at the Sterling Water Treatment Plant will continue to monitor this significant progress and work alongside King Lee Technologies if any optimization is necessary. These results show a promising future for RO systems struggling with brine disposal and resulting scale issues while also being concerned about staying within disposal limits.

References

Operational data for this study was provided from the SCADA records of the Sterling Water Treatment Plant.

1. Yallaly, Brandon C.; Labreque, Thomas (2017) RO Concentrate Treatment and Minimization: State of the Technology in Real World Applications. AMTA: Solutions, Fall, pp. 11-17
2. Witham, Trudy (2016) "Moving up to Membranes" http://www.tpomag.com/editorial/2016/08/making_the_shift_from_water_chlorination_to_reverse_osmosis August
3. Stillwell, Christopher J.; et al. (2016) The Pressure Is Still On: Deep Well Injection Performance for RO Concentrate Disposal. AMTA: Solutions, Winter, pp. 14-18