

Evaluation of ChemFree Technology for Scale Prevention

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Summary

The ChemFree Technology was evaluated using a testing protocol to evaluate scale formation and changes in scale forming potential. The protocol was identical to the protocol used in the research project funded by the WaterReuse Foundation (WRF-08-06) entitled “Evaluation of Alternatives to Domestic Ion Exchange Water Softeners”. The protocol is similar to the one that is currently being developed through IAPMO and may be adopted as an ANSI standard after successful validation. The changes in scale forming potential were assessed using an ion selective electrode to measure the free calcium ion concentration. The free calcium ion concentration represents the reactive form of calcium. Langelier saturation index calculations were used to assess scaling potential. The

ChemFree Technology was effective at preventing scale formation and solids formation on the heating element and heating bath was reduced by greater than 50% as compared to the control. The solids formed were not chemically bound to surfaces and were easily removed by brushing. The solids formed were greater than 90% calcium carbonate. The Langelier Index was reduced to a value near zero which is consistent with a water that will not form scale after treatment.

Conclusions

Chemfree technology resulted in a stable water after treatment that was neither scale-forming or corrosive. The reduction in free calcium ion concentration could not be attributed to solids formation in the heating bath and was most likely due to the formation of sub-micron calcium carbonate crystals.

The free calcium ion concentration decreased by 30-60% with Chemfree technology while no decrease was observed with the control. This decrease resulted in a decrease of Langelier Index at room temperature to near zero.

Chemfree technology resulted in a 66% reduction in solids formed on the heating element and heating bath as compared to the control. The solids formed with Chemfree technology were not chemically bound to surfaces and were easily cleaned by physical brushing. The solids formed were greater than 90% calcium carbonate.

Methodology

The testing protocol focused primarily on scale development from the heating of water. Water is continuously contacted with a heating coil and the formation of scale on the heating coil and in the container containing the coil was quantified. For the purpose of this study, the tests were run with intermittent flow to simulate domestic household use and no recirculation through the water conditioning device was done. Tests were completed with ChemFree Technology and compared to a control with no treatment. The method is a simple reliable method for quantifying scale formation where heating at 80°C will reduce the solubility of calcium carbonate.

The experimental system used in this study is presented in Figure 1. The main components are a water supply tank, a pump, treatment lines, the treatment device, a check valve, a water heater, a temperature controller and a 14 liter container. A timer was used to control the flows and periodically turn water on and off during the day. An 8 hour rest period with no flow through the system occurred each evening.

The centrifugal pump was rated to provide a minimum pressure of 30 psi for the flows and head loss in the system. A ball valve was placed after the pump and to control the flowrate at 1 gpm.

Figure 1.

Side View of Actual Experimental Apparatus
A top view of the treatment device is presented in Figure 2. Each treatment train had a by-pass loop to evaluate no treatment as control.

The Chemfree technology was inserted in one of the by-pass loops. This was identical to how the electromagnetic technology was evaluated during the Water Reuse Foundation study.



Figure 2.

Top View of Experimental Apparatus. The Chemfree treatment device is the silver tube that inserted into one of the bypass loops.



The capacity of the water supply tank used was 350 gallons and it was refilled once during the experiment for a total of 700 gallons used for each test. Tempe Tap water was used during the test which was a blend of groundwater and Salt River Water. Testing consisted of water intermittently being pumped through the system at a flowrate of 1 gpm throughout the day to simulate the turning on and off of faucets in a home setting. The timer settings for the flow are listed in Table 1. A total of 700 gallons were pumped through the system over a period of 21 days with an average flow of 34 gallons/day. The centrifugal pump pumps water at a rate of 1 gpm. Piping was installed using PVC pipe with $\frac{3}{4}$ inch nominal inside diameter. The heating bath capacity was 14L and the heating bath temperature was set at 80°C with an inner pump that constantly circulates the water inside to maintain an even temperature. The wattage of the heating element is 1200W and it has a surface area of 738cm² giving it a watt density of 1.6W/cm². The Chemfree technology will be installed in accordance with the recommendations of Chemfree.

Table 1: Timer Settings

6:00 AM	6:03 AM
7:00 AM	7:03 AM
8:00 AM	8:03 AM
9:00 AM	9:03 AM
10:00 AM	10:03 AM
11:00 AM	11:02 AM
12:00 PM	12:02 PM
1:00 PM	1:02 PM
2:00 PM	2:02 PM
3:00 PM	3:02 PM
4:00 PM	4:02 PM
5:00 PM	5:02 PM
6:00 PM	6:02 PM
7:00 PM	7:02 PM

The 350 gallon storage tanks were cleaned between testing using a 10ppm solution of chlorine and then rinsed with the water to be tested. The tanks were filled with 350 gallons of the water being tested and then refilled after 10.5 days of testing to complete the 700 gallon requirement. Water was sampled every other day to monitor water quality parameters. Water samples were taken from the water tanks and after the heating bath during each sampling event. Sampling events were timed to coincide with periods when the pump was on and post-treatment samples were taken after 1 minute of pumping.

After 21 days of testing, the accumulated scale from the heating elements and containers was removed and quantified. Solid scale was removed from the heating element by scraping and combined with loose scale from the container and weighed. For the control, acid washing of the heating element was necessary to remove the scale. The solids formed during testing with Chemfree technology were easily removed by brushing. A 20 mg sample of the solid scale was dissolved using hydrochloric acid (HCl) and diluted in 100mL of deionized water. The pH was raised to approximately 7 using potassium hydroxide. The solution was then tested for calcium and hardness content using the EDTA titration method and the percentage of calcium carbonate was calculated and also applied to assess the total weight of scale collected. The remaining scale in the container and on the heating element was dissolved using a 1N HCl solution for the control. The solution was also neutralized with potassium hydroxide and then measured for calcium and hardness content using the EDTA method. The total scale formed during each test was determined by summing the total mass of scale collected with the calculated mass of scale that was dissolved in acid. The mass was calculated using the calcium and hardness content of the 10 mg solid sample dissolved in acid. For the Tempe Tap water to be used in the test, the scale was found to be >97% CaCO₃ and approximately 30 g of scale was formed with the control.

In addition, photographs of the elements were taken for visual comparison.

Water samples were also analyzed for free calcium ions using an ion selective electrode. The change in the free calcium ion concentration was used to quantify the conversion of calcium to suspended calcium carbonate crystals. This is a useful tool in understanding the mechanism whereby Chemfree technology can prevent scale formation. Measurements of pH and alkalinity were done to allow for calculation of the Langelier Index and the Adjusted Langelier Index after treatment. The Langelier Index is a standard measure of scaling potential and values near 0 indicate a stable water that will not form scale while positive values are associated with scale formation. Negative values of the Langelier Index represent a water that can be corrosive and dissolve scale. The adjusted Langelier Index was calculated after treatment to account for both the decrease in free calcium ion concentration and the corresponding decrease in bicarbonate ions that must occur if calcium carbonate forms. A mass balance was also done to determine the total formation of solids/scale in comparison to the total quantity of scale-forming minerals that passed through the system.

Results

The experiment was completed over a 21 day period in October and November of 2014. The flowrates were maintained relatively constant throughout the experiment as the centrifugal pump was not affected by changes in the head in the water supply tank. The flowrates are plotted in Figure 3. The daily flowrates varied between 31 and 35 gpd and the target flowrate was 34 gpd.

Figure 3.
Measured flowrates during 21 day test period.

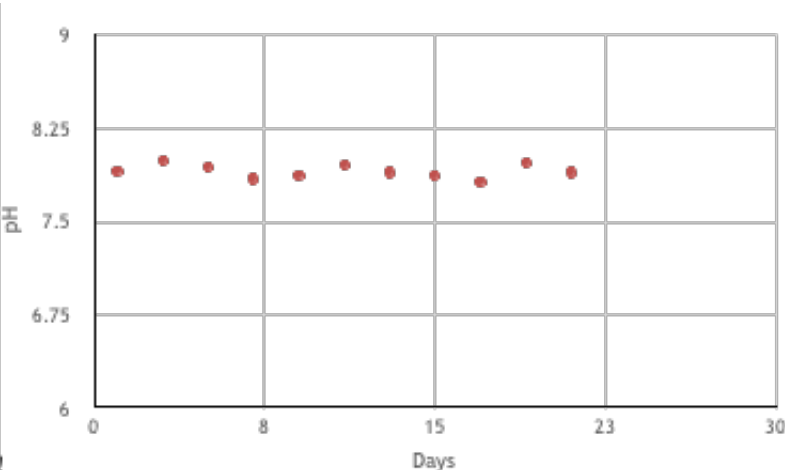
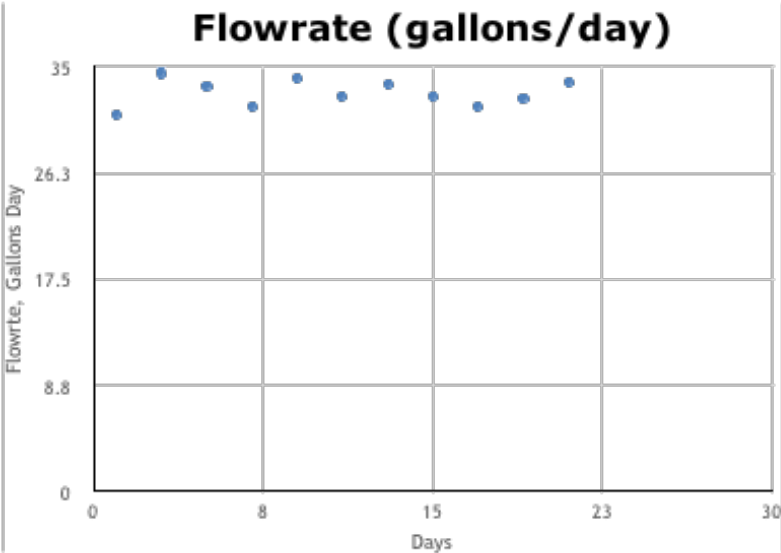


Figure 4.
Measured pH during 21 day test period (no change between input and output water)

The water quality was stable during the experiment and there was very little change in pH, alkalinity and total calcium ion concentration. The pH, alkalinity and total calcium ion concentration (measured using EDTA titration) are presented in Figures 4, 5 and 6, respectively.

Figure 5.
Measured alkalinity
during 21 day test
period

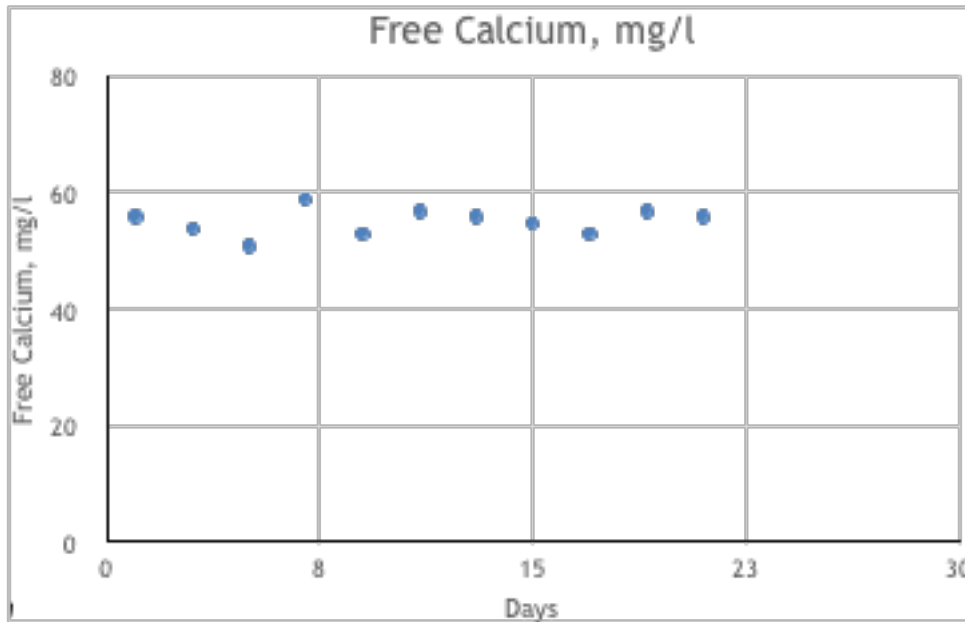
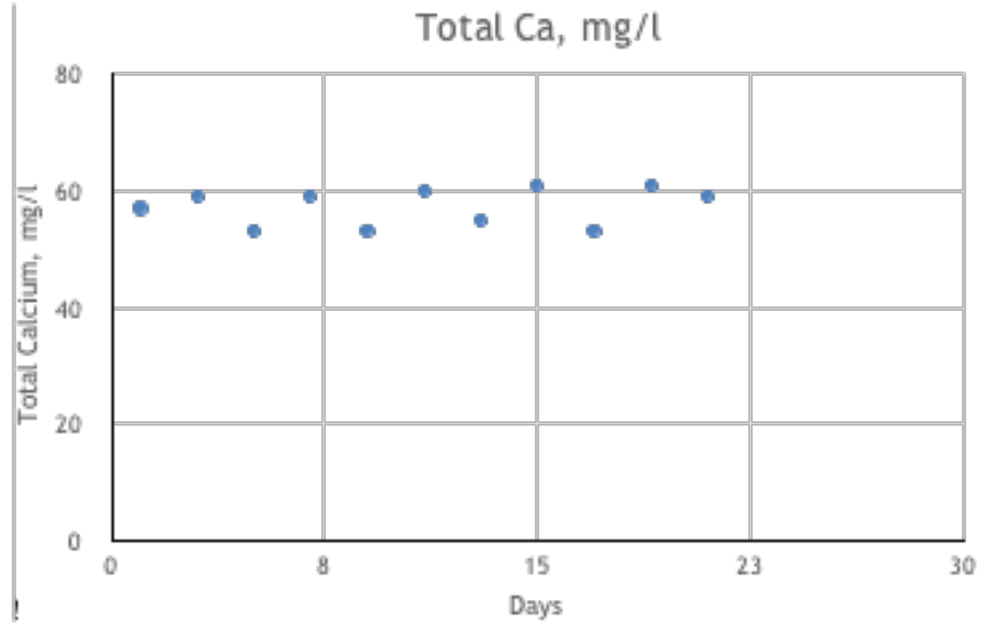
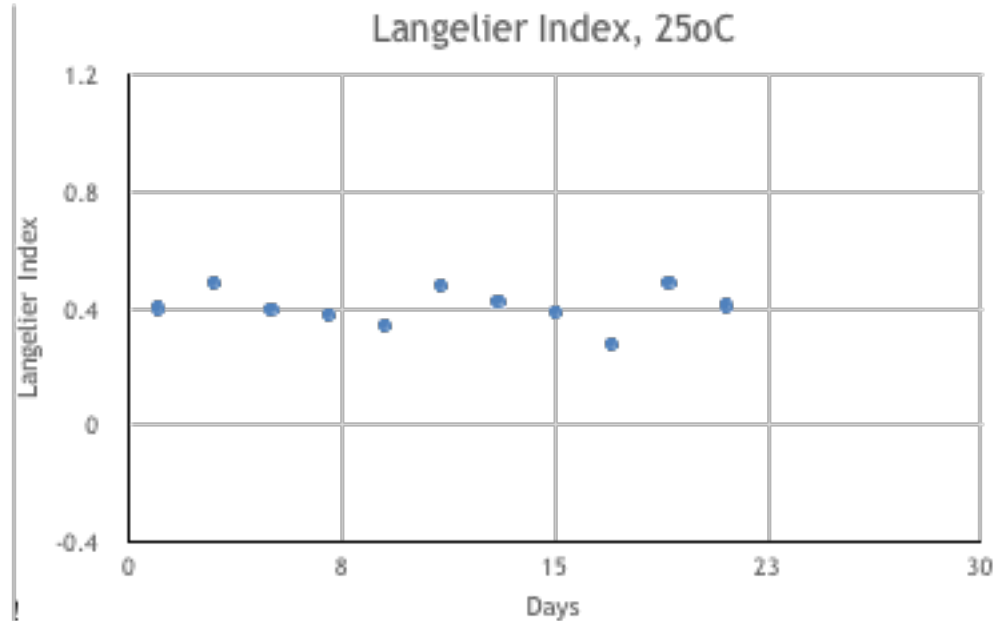


Figure 6.
Total calcium
concentration during
21 day test period.

The free calcium ion concentration measurements are presented in Figure 7. The free calcium ion concentrations were within five percent of the total calcium concentrations in the Tempe Tap Water. The similarity in concentrations implies that the majority of calcium was present as free calcium ions and it was not suspended calcium carbonate or other colloidal forms of calcium.

Figure 7.

Free calcium ion concentrations during 21 day test period.



The scaling potential of the water used during the study was calculated using the Langelier Index which is a function of the pH, temperature, calcium ion concentration and alkalinity. The Langelier Index for Tempe Tap Water at 25oC is presented in Figure 8. The average value is approximately 0.4 which represents moderate scaling potential. The Langelier Index for Tempe Tap Water at 80oC is presented in Figure 9. The average value of the Langelier Index increases to approximately 1.0 at the higher temperature which represents a strong scaling potential.

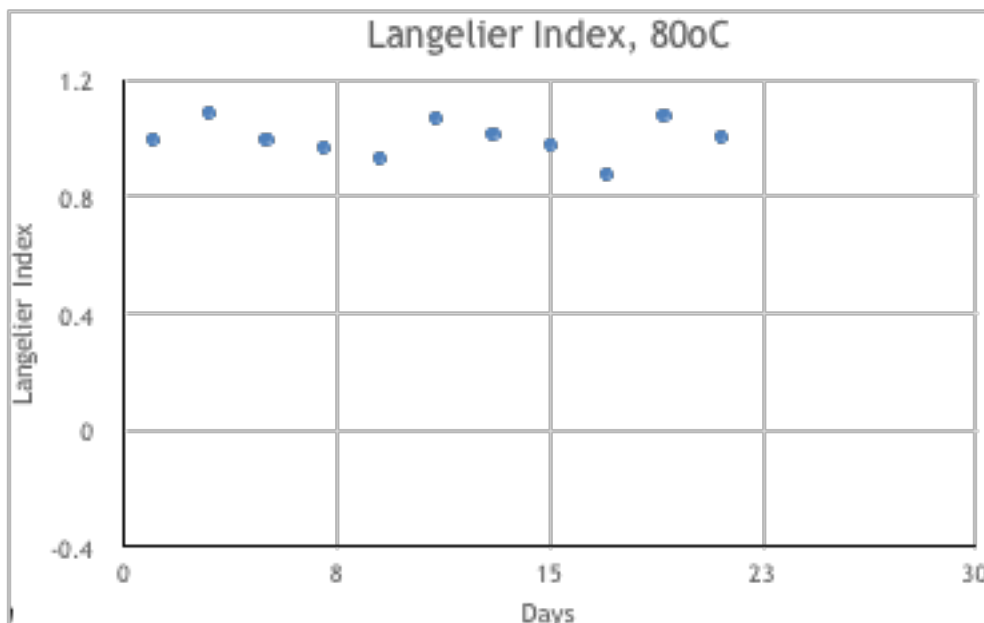
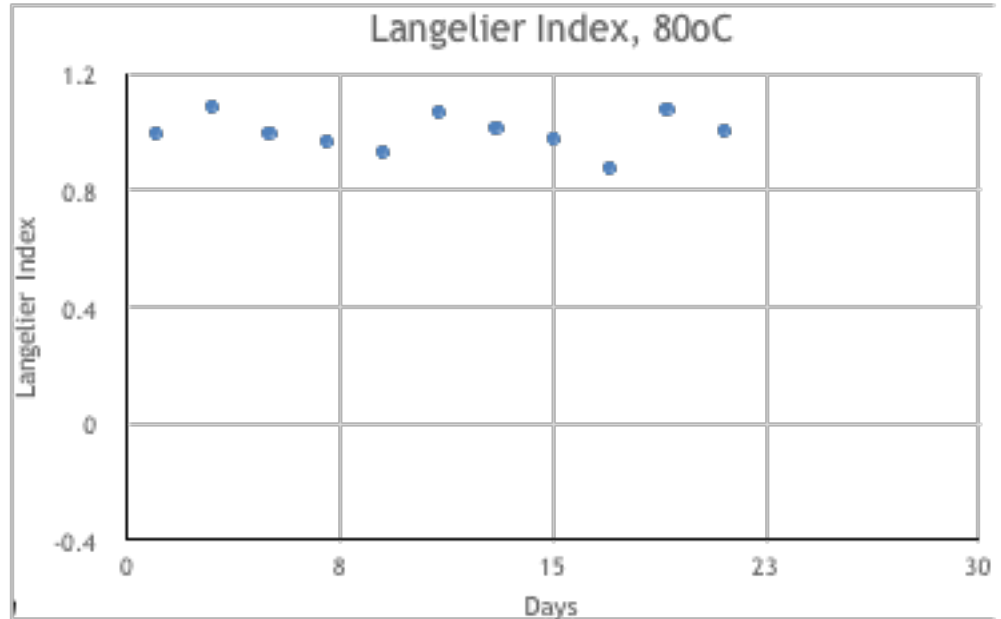


Figure 8.

Calculated Langelier Index at 25oC during 21 day test period.

Figure 9.

Calculated Langelier Index at 80oC during 21 day test period.



During testing with Chemfree technology, pictures of the heating element with water in the heating bath were taken on Day 1, Day 11 and Day 21. The pictures are presented in Figures 10a, b and c. One can note a lack of clarity on Day 21 indicating the presence of some solids on the heating element, however, the element still has a shiny stainless steel appearance.



Figure 10a. Heating element in heating bath with water on Day 1.



Figure 10b. Heating element in heating bath with water on Day 11.



Figure 10c. Heating element in heating bath water on Day 21.

After day 21, the heating element was removed from the heating bath and allowed to dry. Water in the heating bath was also eluted and the heating bath was dried to recover any solids in the heating bath. The appearance of solids on the heating bath became apparent when drying was almost complete. The solids were opaque when wet and did not become colored until they were dry. There were also clear spots on the heating element where it was solids had not attached or they had fallen off (Figures 11 a and b). The bottom of the heating element was relatively clean indicating that solids had deposited on the element and true scale had not formed which would have been chemically bound to the heating element. The heating element was easily cleaned with a brush and did not require acid washing for cleaning.



Figure 11a. Heating element with deposited solids after test run with Chemfree technology. Clear spots on the stainless steel element are present and the solids were not chemically bound to the element.



Figure 11b. The bottom of the heating element after testing with Chemfree technology. The bottom of the element has many clear spots which is consistent with deposition of solids as compared to scale formation directly on the element. The element was easily cleaned with physical brushing and did not require acid washing.

The total mass of solids removed from the heating element and heating bath after testing with Chemfree technology was 10.2 grams. With the control test, the total mass of solids was 30.3 grams. Therefore, Chemfree technology reduced the accumulation of solids by 66%. More importantly, the solids formed during testing with Chemfree technology were not chemically bound to the heating element and acid washing was not necessary to clean the element. The solids formed during control testing were chemically bound to the heating element and required acid washing as would be expected with scale. The solids formed during testing with Chemfree technology and the control test were both > 90% calcium carbonate. This was verified by dissolving the solids in acid and measuring the remaining calcium hardness content and was also verified by X-ray diffraction.

A mass balance analysis was done to calculate the total scale forming minerals that passed through the treatment system during testing. The results were used to calculate the percentage of scale forming minerals that reacted to form solids or scale during testing. During control testing, 7.5% of the scale forming minerals were converted to scale. During Chemfree testing, 2.5% of the scale forming minerals were converted into solids.

The Chemfree technology was effective at reducing the free calcium ion concentration during testing and this is one of the reasons that the Chemfree technology was effective. The free calcium ion concentrations after treatment are shown in Figure 12. Prior to treatment the concentrations were between 53 and 60 mg/l and there was a significant decrease that range from approximately 30-60%. This decrease is much too large to be attributed to solids formation in the heating bath and it is most likely due to the formation of sub-micron calcium carbonate crystals formed both during treatment and in the heating bath. The decrease in free calcium ion concentration is shown in Figure 13 and the average decrease in concentration was greater than 20 mg/l. No significant decrease was observed during control testing.

Figure 12.

Free calcium ion concentration after treatment and the heating bath.

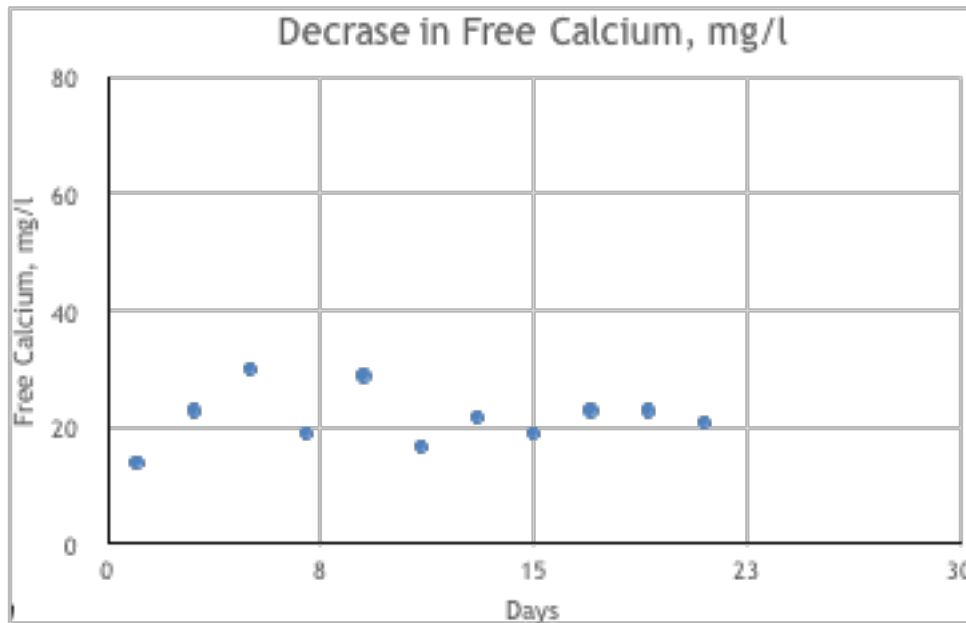
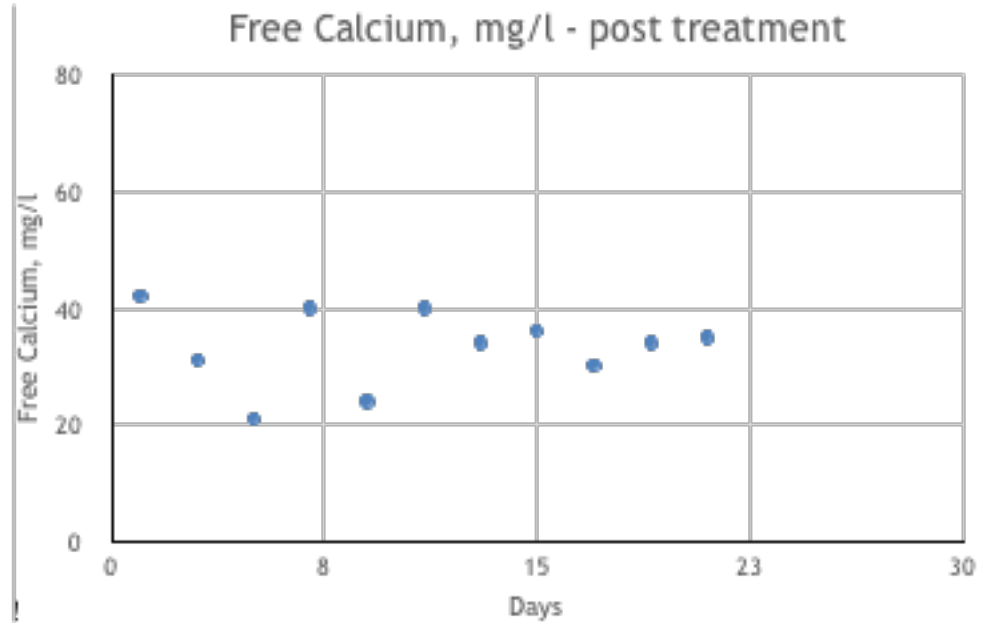


Figure 12.

Decrease in free calcium ion concentration during testing with Chemfree technology

It is important to note that the decrease in calcium ion concentration will decrease the scaling potential of the water after treatment. The Langelier Index was therefore calculate after treatment to assess the change in scaling potential. If the water returns to room temperature (25oC), the scaling potential of the water becomes negligible and can actually dissolve scale when the Langelier Index is negative (Figure 13.). The average value of the Langelier Index after testing with Chemfree technology at room temperature is near zero which represents a stable water that will not form scale and will not cause corrosion. If the water remains at 80oC, the scaling potential is still greatly reduced (Figure 14) as compared to the original scaling potential of the water.

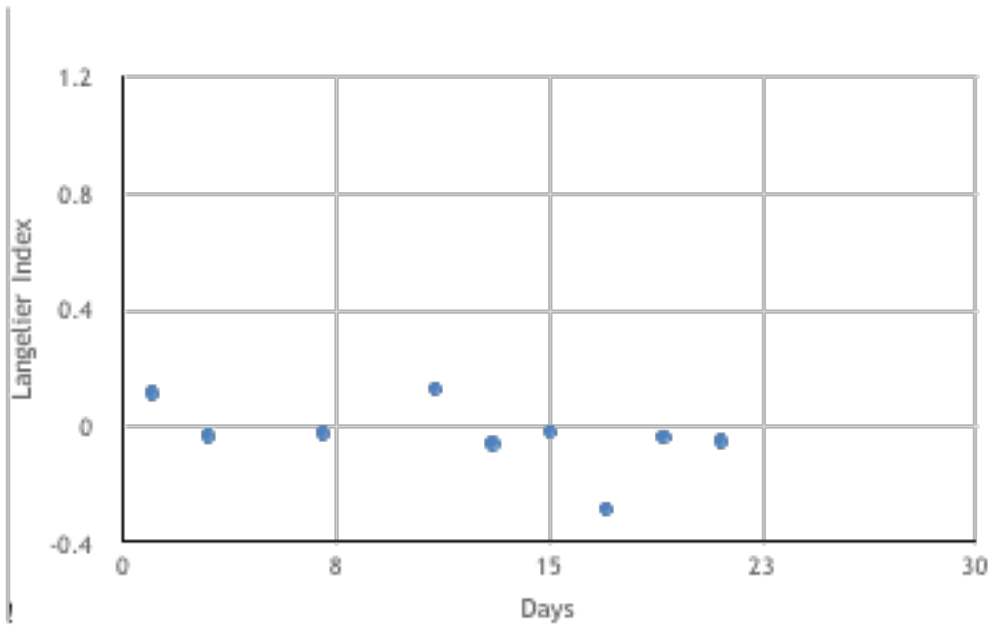


Figure 13.
Langelier Index after treatment with Chemfree technology at room temperature

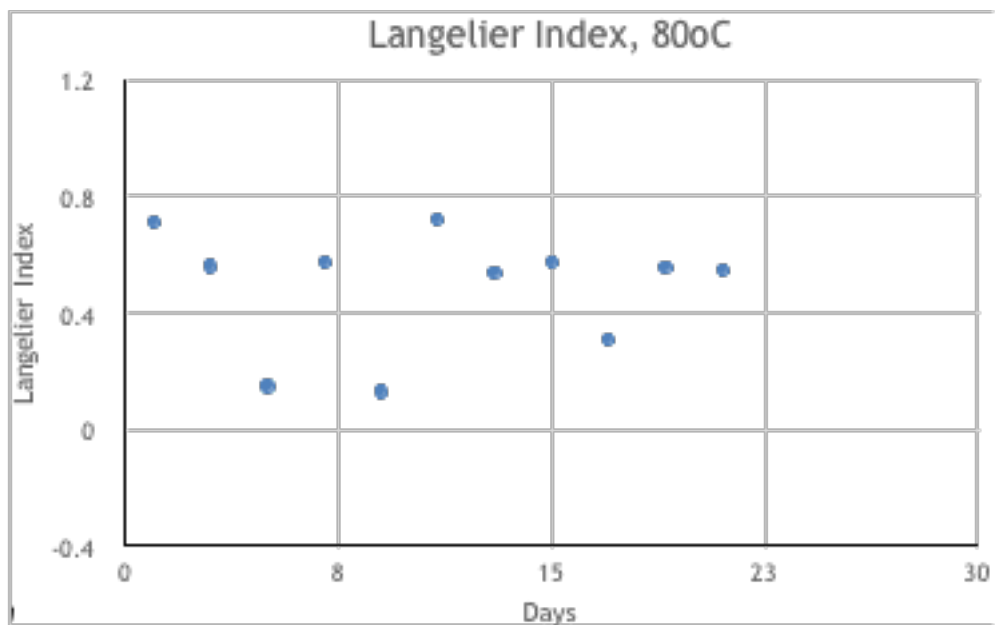


Figure 14.
Langelier Index after treatment with Chemfree technology at 80oC.

Conclusions

Chemfree technology resulted in a stable water after treatment that was neither scale-forming or corrosive. The reduction in free calcium ion concentration could not be attributed to solids formation in the heating bath and was most likely due to the formation of sub-micron calcium carbonate crystals.

The free calcium ion concentration decreased by 30-60% with Chemfree technology while no decrease was observed with the control. This decrease resulted in a decrease of Langelier Index at room temperature to near zero.

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