Final Report **September 16, 2015**

Regional Municipality of Waterloo
Nucleation Assisted Crystallization/Template Assisted Crystallization (NAC/TAC) Performance Study – Life Expectancy of NAC/TAC media and Assessment of Testing Method

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Executive Summary

Two different nucleation assisted crystallization/template assisted crystallization (NAC/TAC) treatment systems were selected for study at the William St Pumping Station located in Waterloo. Both systems were rated by the manufacturer to treat 10 gallons per minute (gpm) and both systems were operated at a flowrate of 5 gpm. The two systems were denoted Train 1 and Train 3. In order to simulate extended operation, the systems were operated for 5 hours followed by a 1 hour rest period. This resulted in a daily flow of 6,000 gallons per day which is comparable to 37.8 days of water use for a typical residential customer in Waterloo. Initial testing (Phase 1) was done by operating the systems for a total of 44 days and samples were taken for analysis 3 times a week. Measurement of both total calcium and free calcium using an ion selective electrode was used to assess treatment efficacy. If template assisted crystallization is working effectively, the free calcium ion concentration will decrease while there will be no change in the total calcium ion concentration. The maximum decrease in free calcium ion concentration was predicted to be 34 mg/l. The prediction was based on reducing the Langelier Index from +0.24 to 0 at 10^{o}C which changes the water from scale forming to non-scale forming. Initial results were promising with a reduction in free calcium ion concentration of 33 and 27 mg/l for Trains 1 and 3, respectively. A rapid deterioration in performance occurred in Train 1 and performance also deteriorated in Train 3. Starting on day 17, measurements of free calcium ion concentrations began to exceed the total calcium concentrations, which is not logical. It was discovered that ion selective electrode was not working properly and the electrode was replaced. Measurements after day 36 were logical with free calcium ion concentrations consistent with total calcium concentrations. The criteria for a decrease in performance was set at a 50% decrease in the change in the free calcium ion concentration. Train 3 met this criteria after 44 days (equivalent to 4.5 years of operation) while Train 1 did not meet the criteria. The problems with the ion selective electrode make it difficult to assess exactly when Train 1 failed to meet the criteria. Media samples were removed after 44 days for analysis by scanning electron microscopy and EDX. Both media samples were colored and Train 1 media being

much darker than Train 3 media. Analysis showed the manganese oxide was the major component on the surface of the media with more manganese oxide on Train 1 media as compared to Train 3 media. Samples at the beginning and end of the experiment were analyzed for a complete suite of metals including iron and manganese. Removal of manganese in Train 1 occurred in both samples with an average removal of 0.055 mg/l. The influent manganese concentration of 0.037-0.040 mg/l is less than the manufacturers recommended maximum level of 0.05 mg/l. It is possible that placement of the treatment trains immediately after chlorination at the William St Pumping Station accelerated the fouling of the Train 1 media by manganese oxide. Chlorination will oxidize reduced manganese from the +2 to the +4 oxidation state and if the manganese is still reacting it is very likely to attach to a surface. It is not clear if this phenomena would occur at residences in the distribution system. Activated carbon pre-treatment might be effective at reducing manganese oxide fouling.

Because of the possible problems with the ion selective electrode during initial testing, a second more limited test (Phase 2) was completed using the same treatment train. The media was replaced with fresh virgin media and the treatment trains were operated as they were in the initial testing. Sampling frequency was twice a week and data interpretation was based on the reduction in free calcium ion concentration. A new calcium ion selective electrode was obtained for the second test run. The testing was done during July and August so the temperature ranged from 12.3-14.8^{o}C which was 1-3 degrees higher than the initial testing. Train 3 was operated for 31 days while Train 1 was operated for 47 days. Train 3 met the criteria for a 50% reduction in the change in free calcium ion concentration until day 22 when the flowmeter for Train 3 failed and the test was terminated. It is not certain how much longer Train 3 would have continued to perform. Train 1 met the criteria until day 43 (equivalent to 4.4 years), however, the initial reduction in free calcium ion concentration in Train 1 was lower than Train 3. The second test confirmed the results from the first test regarding the estimated longevity of NAC/TAC media with the water quality tested.

PROJECT GOALS

The primary project goal was to determine the life expectancy of NAC/TAC media, without pre-treatment, using Waterloo's William St. Pumping Station source water

A secondary objective was to demonstrate the use of the calcium ion selective electrode to determine when NAC/TAC media no longer effectively treats water.

METHODOLOGY

The following section was developed by the project team before the project was initiated for the initial testing (Phase 1).

UNITS TO TEST

Watts OneFlow Anti-Scale System, model OF744-10

Pelican Water Systems – Natursoft, model NS3

Both units have maximum flow of 10 U.S. Gallons per minute

METHOD

1.1 Unless otherwise specified, tolerances on indicated test parameters will be +/- 10%.

1.2 Do full metals (inorganic) scan on single-source influent and 2-source effluent waters and also pre-screen source water for solids, chlorine residuals, free calcium ions and total phosphorus. The influent/effluent will be sampled and tested once on the official launch date of the study, once following a month of testing, and once at the completion of the study. If results indicate significant variability in the results between samples, additional tests will be carried out.

1.3 Influent and effluent water will be tested every Monday, Wednesday and Friday during a flow cycle, with one sample taken before and after each NAC/TAC unit, for the following:

- Measured free calcium, using a non-automated calcium ion selective electrode
- Measured pH; alkalinity; free, total and combined chlorine; turbidity; calcium, magnesium and hardness (calculation)

1.4 Target Pressure will be 80 psi.

1.5 Target Flow rate will be five (5) gallons per minute (half the rated max for the unit).

1.6 Test based on daily HH volume of 600 litres (200 L/C/D) or 158.5 GPD (local 3-person household)

1.7 Run flows for five (5) hours on, one (1) hour off and run again for 5 hours, around the clock for total 6,000 gallons in 20 hours of flow (which is equivalent to 37.9 days of target household usage).

1.8 Controls data (loggings flows, volumes, etc., on two trains) will be downloaded once every 7 days via modem (or directly to laptop) and raw data forwarded to Dr. Fox for analysis. Prior to forwarding to Dr. Fox, raw data will be scanned to ensure systems were operating properly during the recorded week.

1.9 SCADA datalog system will record instant flows and pressure every five (5) minutes, while total volumes will be derived from data recording every second. Flow totals for each train will be totalized and logged.

1.10 The test will conclude when the difference between the total calcium concentration and the free calcium ion concentration has decreased in both units by 50%. Template assisted crystallization works by converting dissolved calcium ions in the water into sub-micron calcium carbonate crystals. This reduces the concentration of free calcium ions in the water which effectively conditions the water by reducing the reactivity of the hardness in the water. The sub-micron calcium carbonate crystals also provide the lowest energy surface for crystalline growth which helps prevent scale formation on the surfaces in scale forming environments. Measurement of the free calcium ion concentration is the simplest method to assess the efficacy of NAC/TAC. The difference between the total calcium ion concentration and the free calcium ion concentration provides information on how efficiently the NAC/TAC process is performing. If there is a decay in performance, the difference between the total calcium ion concentration and the free calcium ion concentration will decrease.

Modifications to the methodology for the Phase 2 testing included a reduction in the number of analyses and the frequency of analyses. The number of analyses was reduced primarily to the parameters necessary to estimate the Langelier Index. The frequency of sampling was reduced to twice a week. In this manner the testing could be completed with the remaining funds and the information obtained would be complete enough to evaluate the NAC/TAC performance. The performance evaluation was based primarily on the reduction in the free calcium ion concentration by the treatment trains.

RESULTS

Phase 1

Langelier Index calculations were done to determine the potential reduction in free calcium ion concentration with the source water. The source water had a calcium ion concentration of 140 mg/l and an alkalinity of 345 mg as $CaCO_3$/l which resulted in Langelier Index of +0.24 which is scale forming. An adjusted Langelier Index was calculated based on a decrease in free calcium ion concentration and assuming that a corresponding decrease in alkalinity occurs as $CaCO_3$ crystal form. The results for 10^oC and 25^oC are presented in Table 1. The decrease in the free calcium ion concentration of 34 mg/l will result in a Langelier Index of 0 which is not scale forming. The actual water temperature during the study was 11^oC and the predicted decrease of 34 mg/l was consistent with the maximum decreases (33-37 mg/l) observed during the study. Table 1 also includes Langelier Index calculations at 25^oC and it can be seen that the Langelier Index increases and much larger decreases in free calcium ion concentration would be possible if treatment were to occur at higher temperatures.

Table 1. Change in Langelier Index with Decrease in Free Calcium Ion Concentration

Decrease in Free Ca^{2+} (mg/l)	Langelier Index (10^{o}C)	Langelier Index (25^{o}C)
0	+0.24	+0.55
20 mg/l	+0.11	+0.41
30 mg/l	+0.05	+0.35
34 mg/l	0.00	+0.30
40 mg/l	-0.06	+0.24

The free calcium ion concentration results were analyzed to assess performance by two methods. The first method assessed performance by taking the difference between the total calcium concentration and free calcium ion concentration in the influent and subtracting the difference between the total calcium ion concentration and the free calcium ion concentration after treatment (Equation 1).

1. Difference = (Influent Total Ca – Influent Free Ca) – (Treated Total Ca – Treated Free Ca)

Equation 1 was the original method proposed to assess performance as it takes into account any Ca that is combined prior to treatment. Analytical issues that resulted in free calcium ion concentrations greater than total calcium made a simpler method to assess performance more logical. The second method used to assess performance is simply the difference between the influent free calcium ion concentration and the treated free calcium ion concentration.

2. Difference = Influent Free Ca – Treated Free Ca

The criteria used to assess deterioration of performance was a 50% reduction in the difference for both 1 and 2.

The results for performance measure 1 are presented in Figures 1 and 2 for Trains 1 and 3, respectively. A clear decline in performance is observed with Train 1 while Train 3 appears to be performing at the end of 44 days of operation. On day 17, the results from the free calcium ion electrode were not logical as the free calcium ion concentration exceeded the total calcium ion concentration and the performance measure declined to near 0 in both treatment trains. Data collected until day 38 remains scattered, however Train 3 was clearly performing better than Train 1. On day 38, the analytical method was adjusted to measure the free calcium ion concentration after 15 minutes to allow for complete reaction after treatment. The data from Train 3 meets the performance criteria of less than a 50% reduction while Train 1 did not meet the performance criteria.

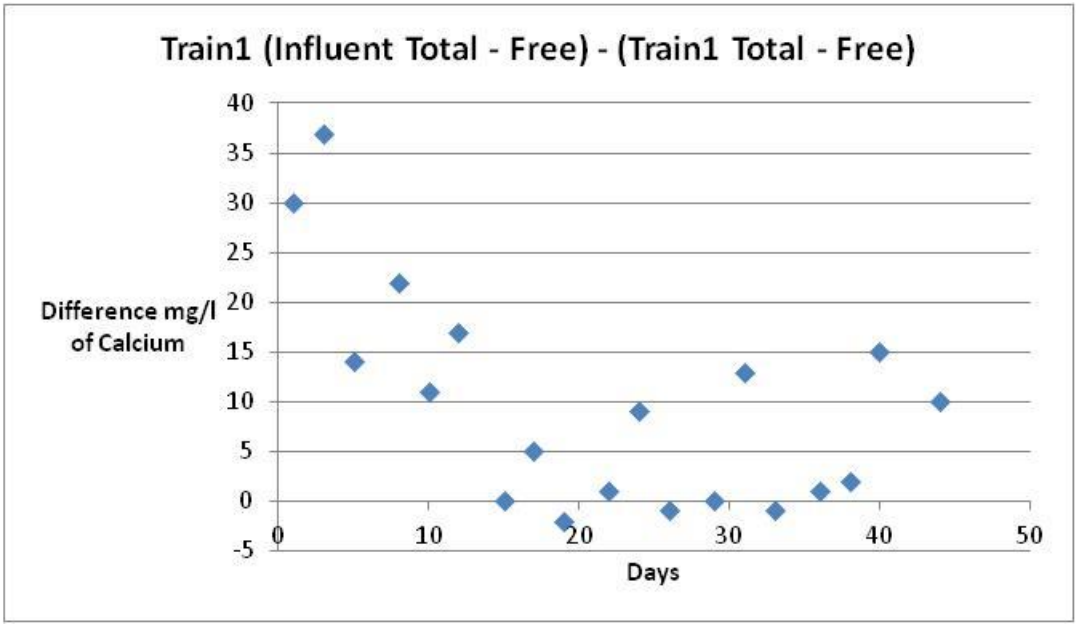

Figure 1. Difference between influent total Ca –influent free Ca and Train 1 treated total Ca-Train 1 treated free Ca.

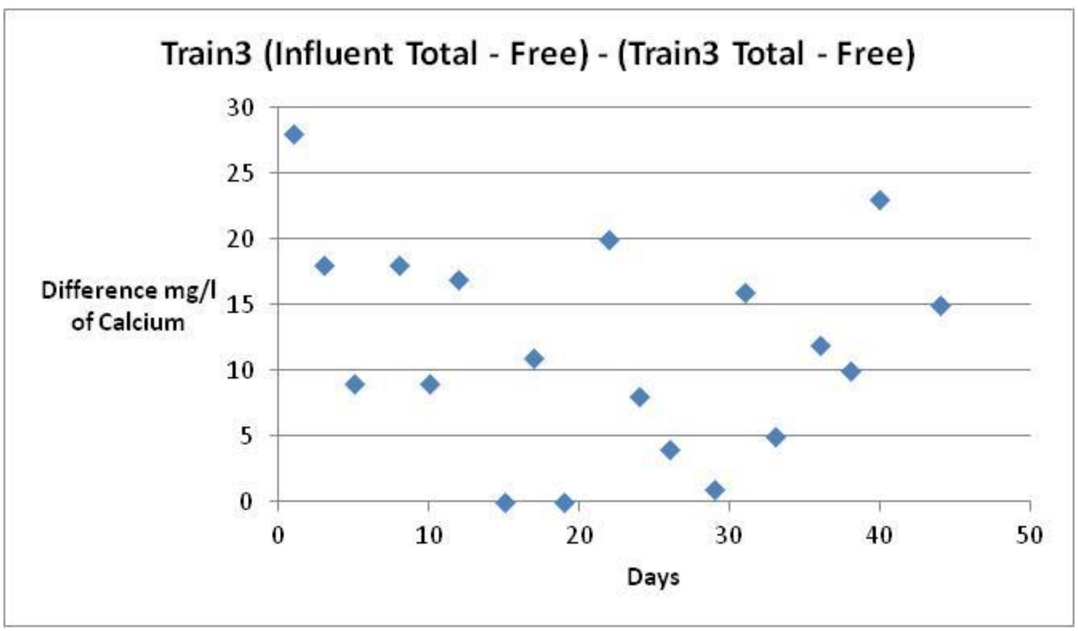

Figure 2. Difference between influent total Ca – influent free Ca and Train 3 treated total Ca-Train 3 treated free Ca.

The results for performance measure 2 are presented in Figures 3 and 4 for Trains 1 and 3, respectively. A clear decline in performance is again observed with Train 1 while Train 3 appears to be performing at the end of 44 days of operation. On day 17, the data becomes more scattered and this is most likely due to analytical problems. However, the data from performance measure 2 is not as variable as performance measure 1. Data collected until day 38 remains scattered, however Train 3 was clearly performing better than Train 1. On day 38, the analytical method was adjusted to measure the free calcium ion concentration after 15 minutes to allow for complete reaction after treatment. The data from Train 3 meets the performance criteria of less than a 50% reduction while Train 1 did not meet the performance criteria. Thus both performance measures provide the same results and simply measuring the free calcium ion concentration is likely sufficient to assess performance.

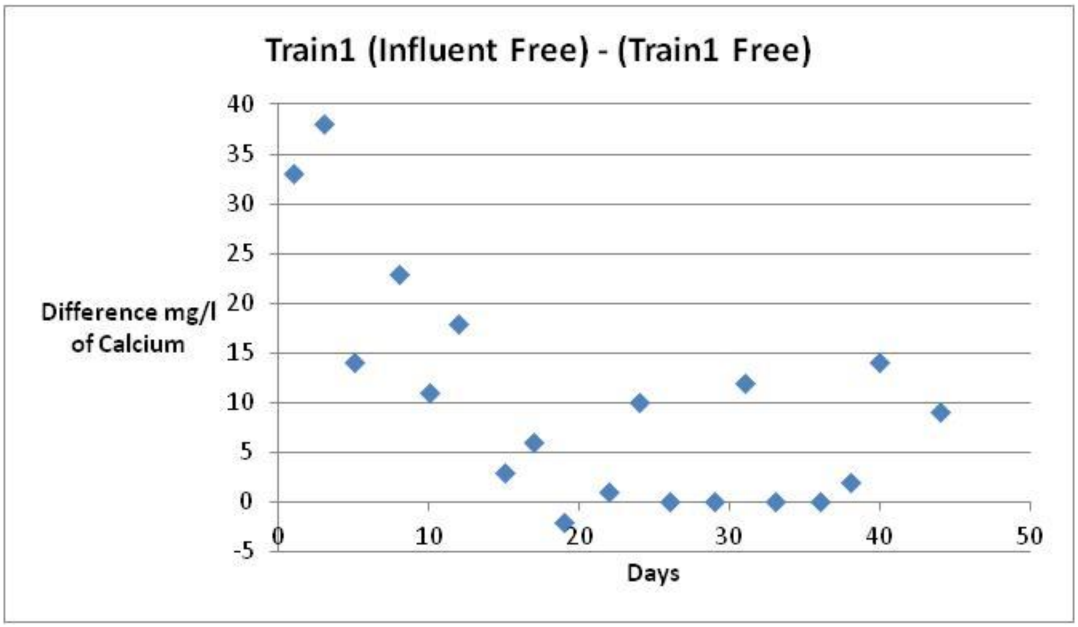

Figure 3. Difference between influent free Ca and Train 1 treated free Ca.

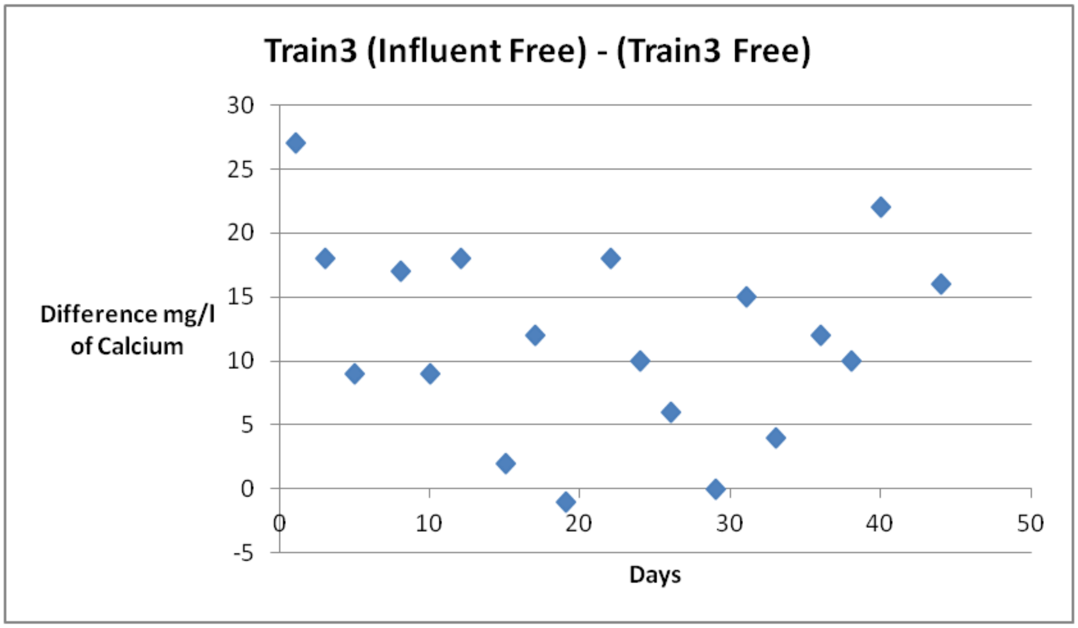

Figure 4. Difference between influent free Ca and Train 3 treated free Ca.

Media samples were taken from both Train 1 and Train 3 after the 44 days of operation. The samples were dried and sent to Arizona State University for analysis by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). A picture of media from Train 1 and Train 3 along with virgin media is presented in Figure 5. The virgin media was obtained from the Environmental Engineering Laboratory at Arizona State University and was not obtained from Train 1 and Train 3. The used Train 1 media has a dark brown/black discoloration while the virgin media is almost white. The used Train 3 media has tan discoloration while the virgin media is also almost white. The average size of the media is approximately 1 mm in diameter. The media from Train 3 also contained clear plastic beads approximately 3-4 millimeters in diameter. The beads might increase agitation and help prevent the attachment of agents that foul the media. The visual evidence is clear that both media had been coated and the Train 1 media had the darker coating.

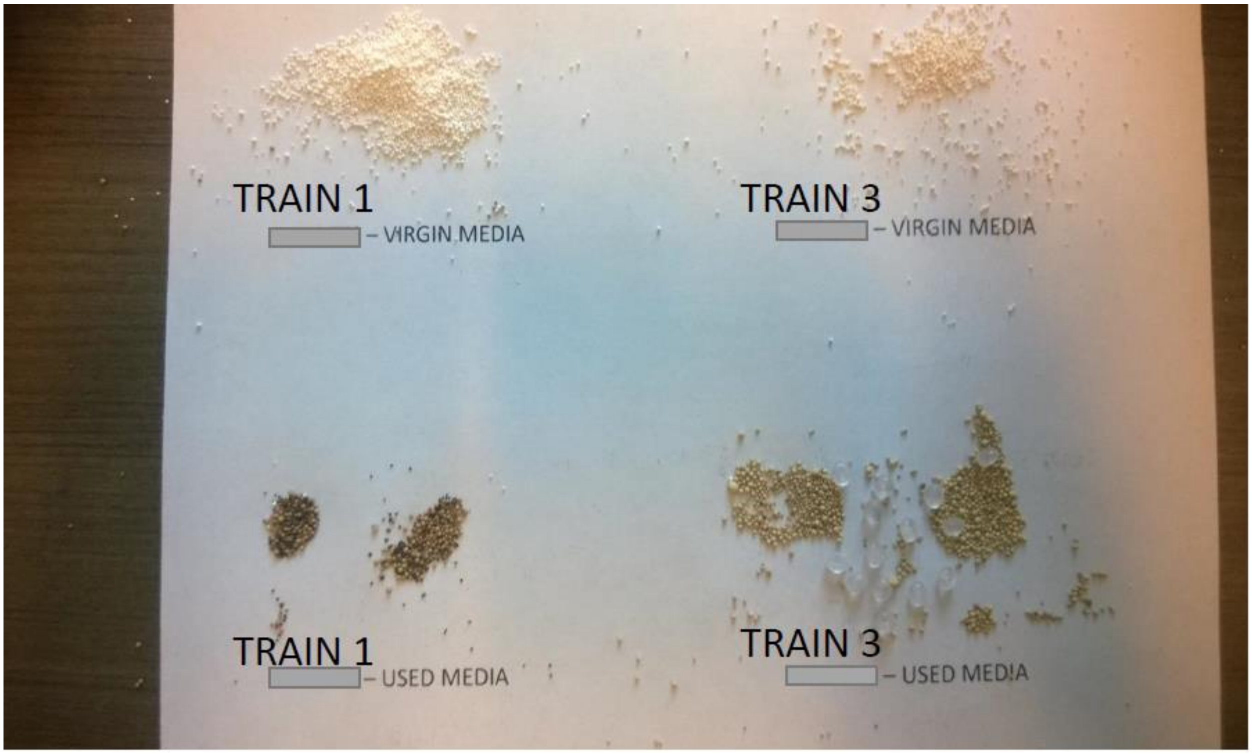

Figure 5. Picture of media after 44 days of operation and virgin media. Note virgin media were obtained independently and were not obtained from Train 1 and Train 3 prior.

Scanning electron micrographs were obtained at the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University. Electron micrographs of Watts and Pelican Media are presented in Figures 6-9. Both media appear to be similar in terms of the template pattern. Debris on the media surface is also similar (Figures 7 and 9) and appears to be calcite (calcium carbonate crystals) that is consistent with residual calcium carbonate after manufacturing. The media was not washed prior to analysis in the scanning electron microscope. The EDX patterns were similar with both media and the major elements identified were C, O, and Ca which is consistent with the elements in polysterene (C,H and O) and calcium carbonate (C, O and Ca).

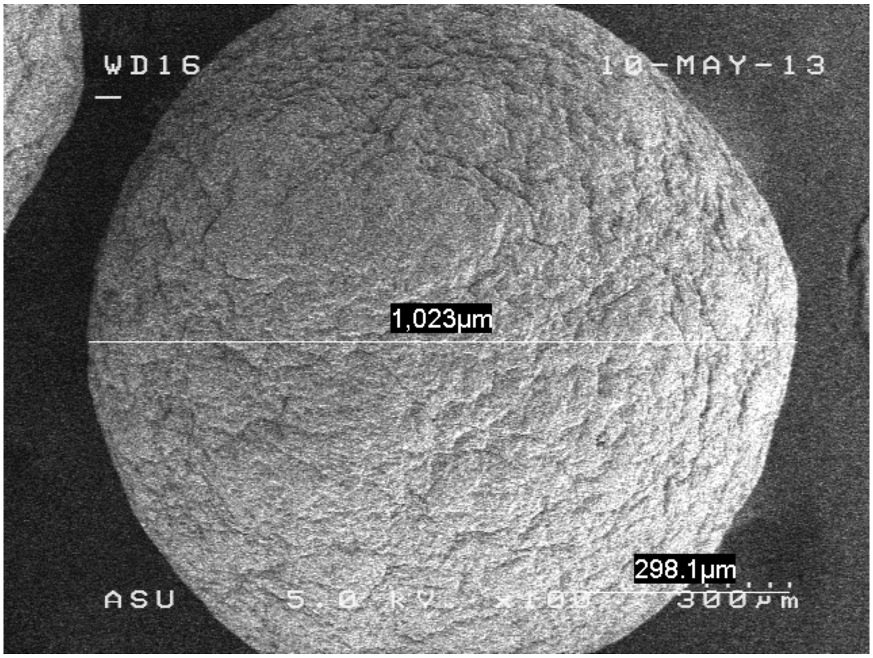

Figure 6. Train 1 Virgin Media at 100X magnification.

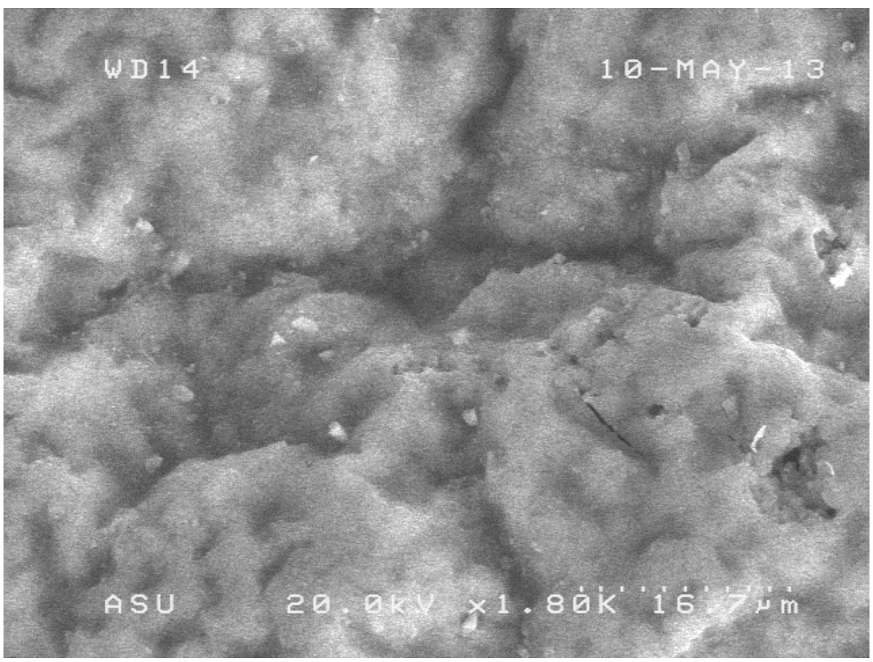

Figure 7, Train 1 Virgin Media at 1800X magnification

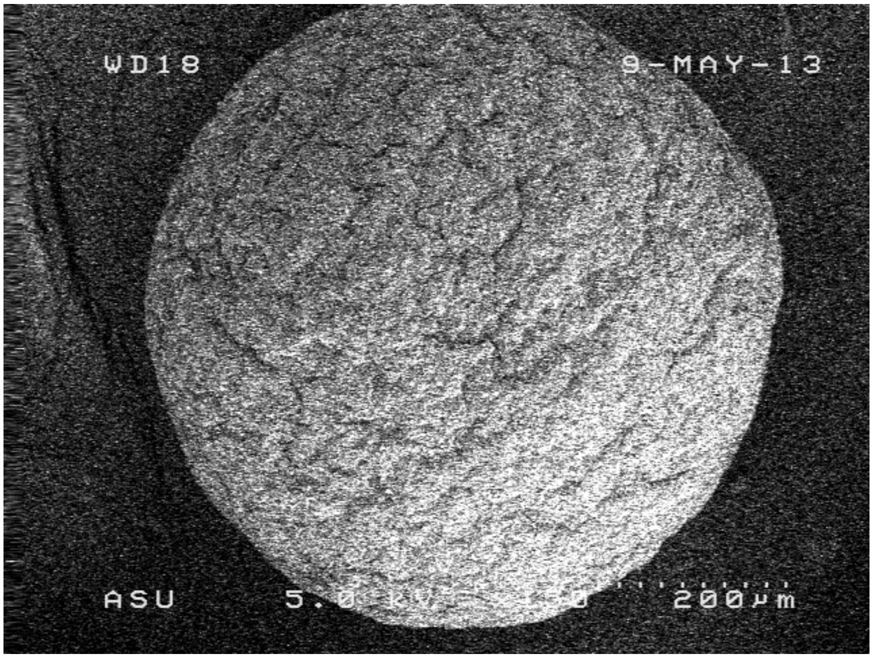

Figure 8. Train 3 Media at 150X magnification.

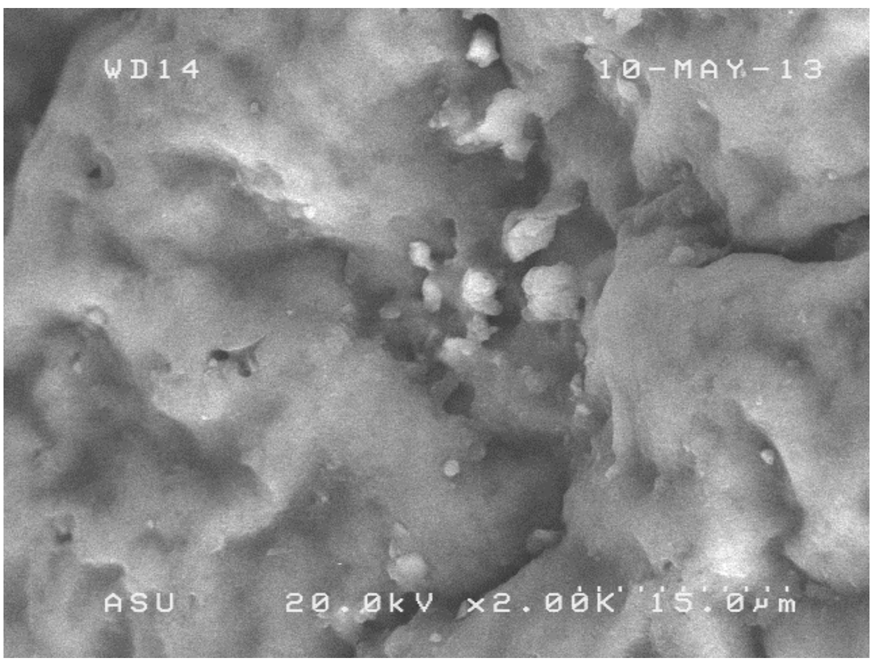

Figure 9. Train 3 Media at 2000X magnification.

Scanning electron micrographs of media used during the Waterloo study are presented in Figures 10-13. The template of both media appears to have been partially filled in based on the lower resolution micrographs (Figures 10 and 12). The Train 1 Media has more debris on the surface as compared to Train 3 media. EDX analysis of the debris on Train 1 Media exhibited a high percentage of Mn (30.5%) and O (37.7%) consistent with manganese oxide with a smaller percentage of Fe (5.1%). EDX analysis of the Train 1 Media overall surface has approximately 3% Mn while the Train 3 Media had approximately 1% Mn. Based on these results, it appears that manganese oxide is responsible for the color on the media and is likely responsible for any deterioration in performance.

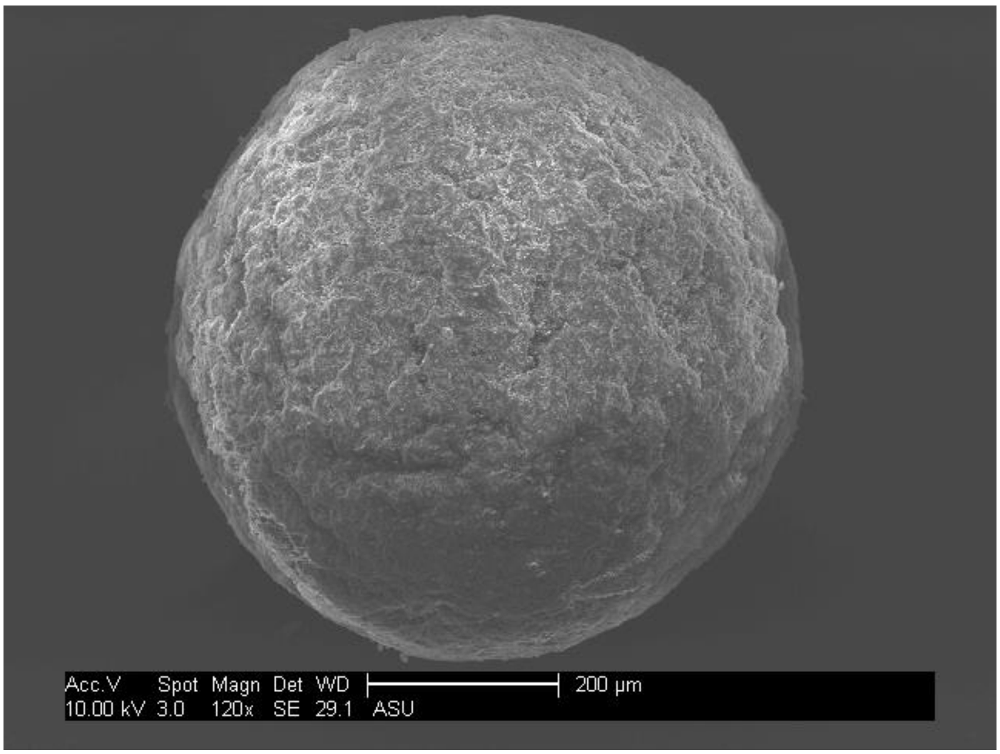

Figure 10. Train 1 Media at 120X magnification

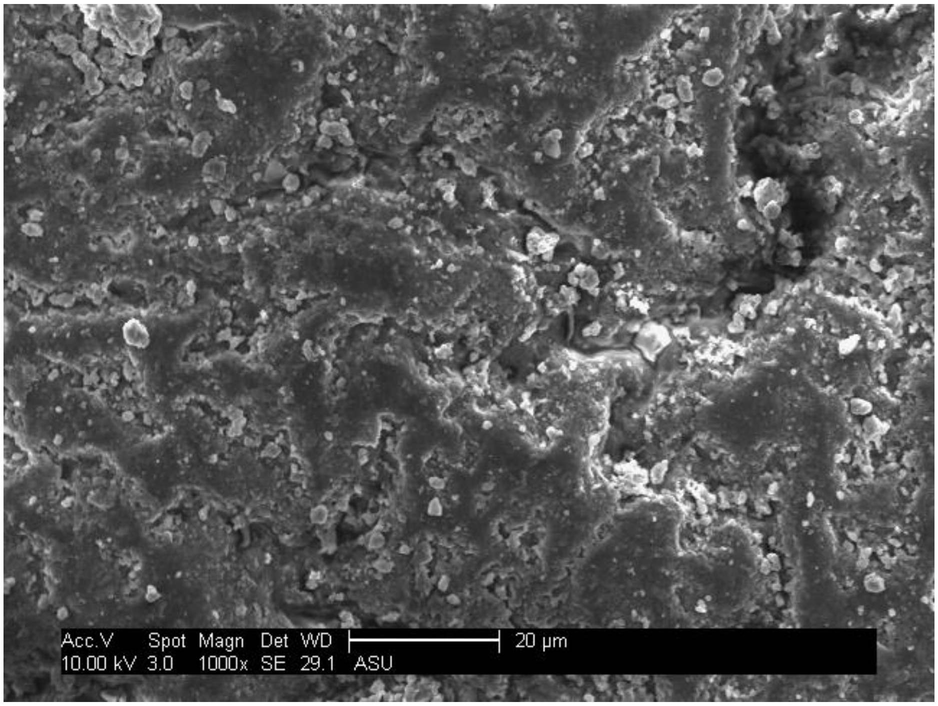

Figure 11. Train 1 Media at 1000X magnification

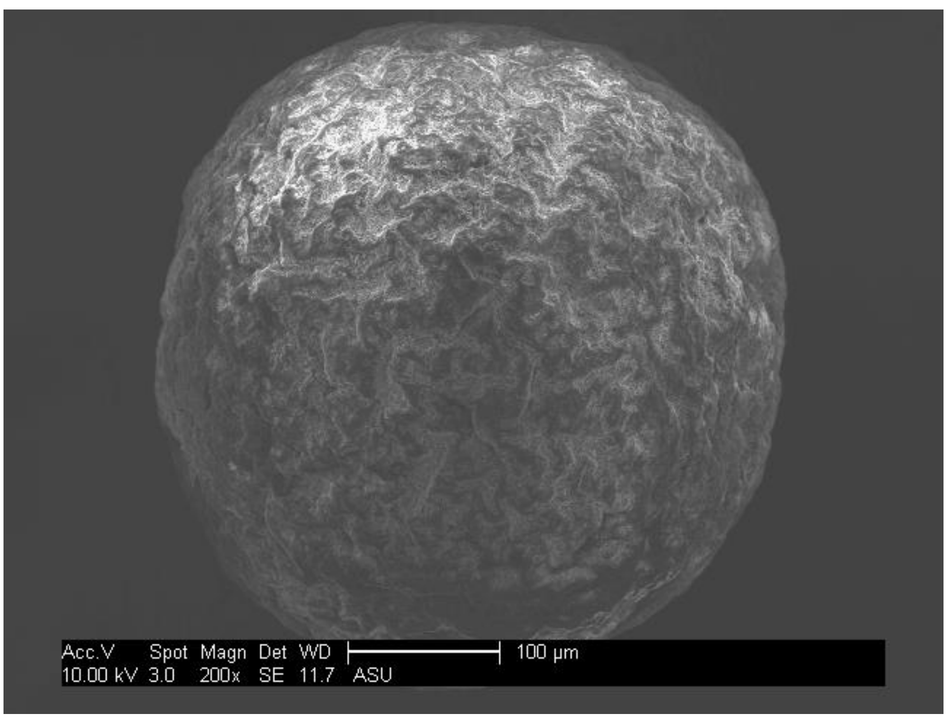

Figure 12. Train 3 Media at 200x magnification

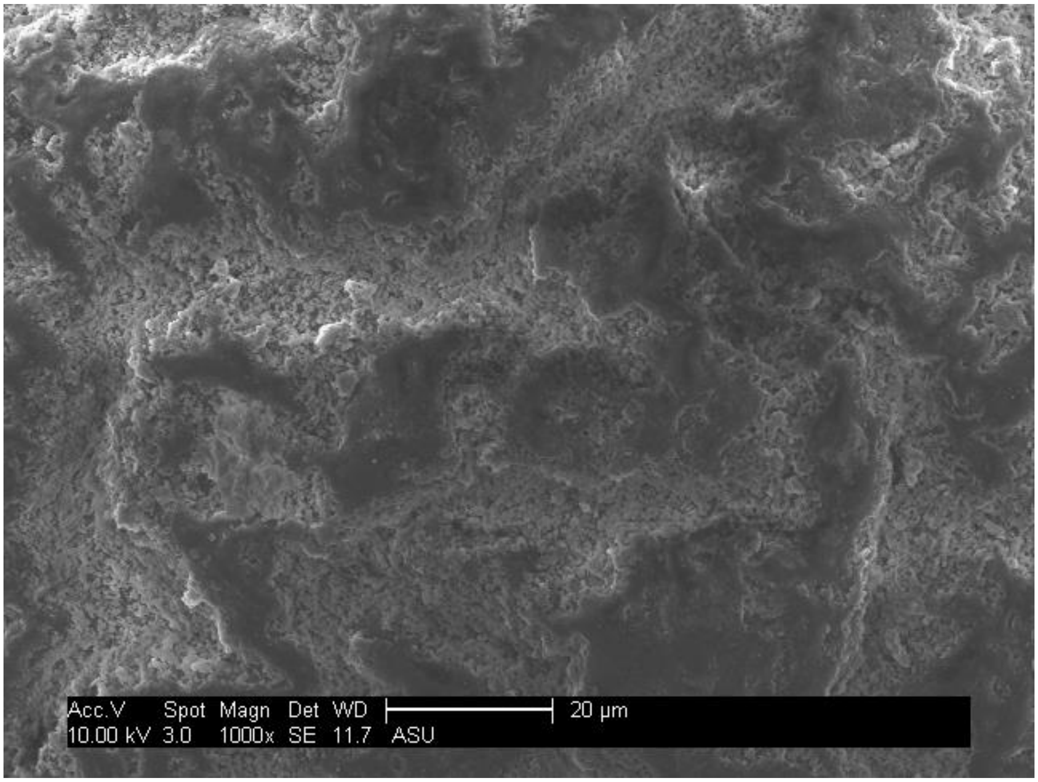

Figure 13. Train 3 Media at 1000x magnification

Water samples obtained on Day 0 and Day 44 were analyzed for a complete suite of inorganic constituents including iron and manganese. The influent iron and manganese concentrations were approximately 0.1 mg/l and 0.04 mg/l, respectively. These values are lower than the maximum concentrations recommended by the manufacturer of Train 1 media which are 0.2 mg/l for iron and 0.05 mg/l for manganese. The iron concentrations for the influent and after the treatment trains are presented in Figure 14. On Day 0, there was some removal of Fe in both treatment trains and on Day 44 there was actually more Fe in the treatment train effluents. The manganese concentration for the influent and after the treatment trains are presented in Figure 15. Train 1 removed 0.06 and 0.05 mg/l on Day 0 and Day 44, respectively. Train 3 removed 0.03 mg/l on Day 0 and the Train 3 effluent was 0.01 mg/l greater than the influent on Day 44. If the removal of Mn in Train 1 was consistent throughout the study, approximately 5.5 grams of Mn could have accumulated on the Train 1 Media. These results are consistent with the Mn observed on the surface of the Train 1 Media using SEM and EDX.

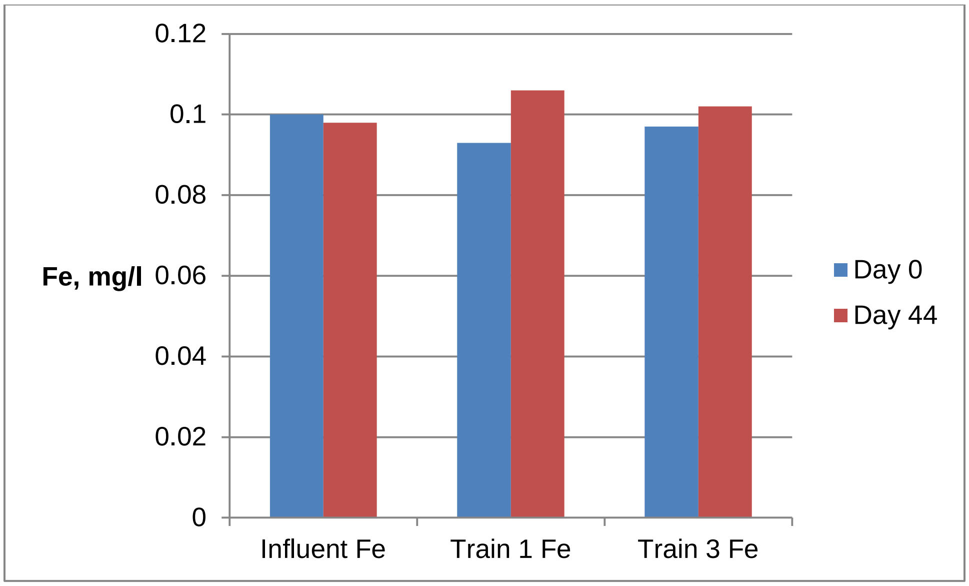

Figure 14. Iron concentrations on Day 0 and Day 44

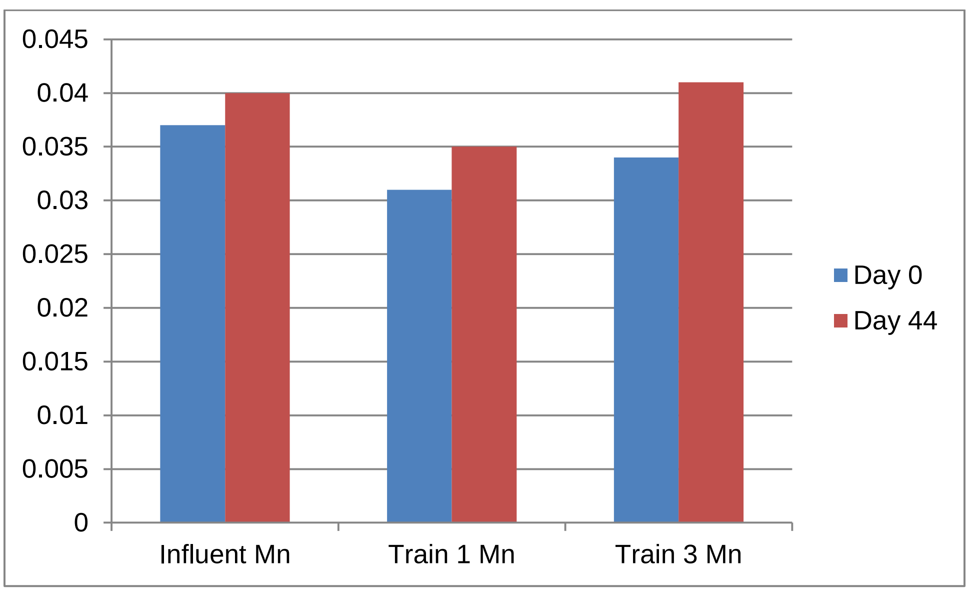

Figure 15. Manganese Concentrations on Day 0 and Day 44

Phase 2

The results for performance measure 2 are presented in Figures 16 and 17 for Trains 1 and 3, respectively. Train 1 had an initial reduction in free calcium concentration of 11 mg/l and the performance was consistent for the first 15 days followed by a period of variable performance where the reduction in free calcium ion concentration ranged from 3 to 60 mg/l. The average reduction in free calcium concentration exceeded the criteria of a 50% decrease in the reduction of free calcium concentration. Therefore, the system is deemed to have been operating successfully until day 43 which is similar to the performance of Train 3 during Phase 1 testing. Train 3 had an initial reduction in free calcium ion concentration of 38 mg/l which was similar to Phase 1 and consistent with a reduction of the Langelier Index value to 0. The performance decreased during the first 5 days but then improved until day 22 and the average reduction in free calcium ion concentration exceeded the 50% reduction criteria during this period. It is not certain how much longer Train 3 would have continued to perform, due to the flow meter malfunction. Temperatures were 1-3 degrees higher during Phase 2 as compared to Phase 1 which can increase the reduction in free calcium ion concentration but might also increase the fouling rate of the media. Train 3 performance was deemed to have the 50% reduction criteria for 44 days during Phase 1. During Phase 2 Train 3 met the performance criteria for 22 days which was the total duration of testing because of flowmeter issues.

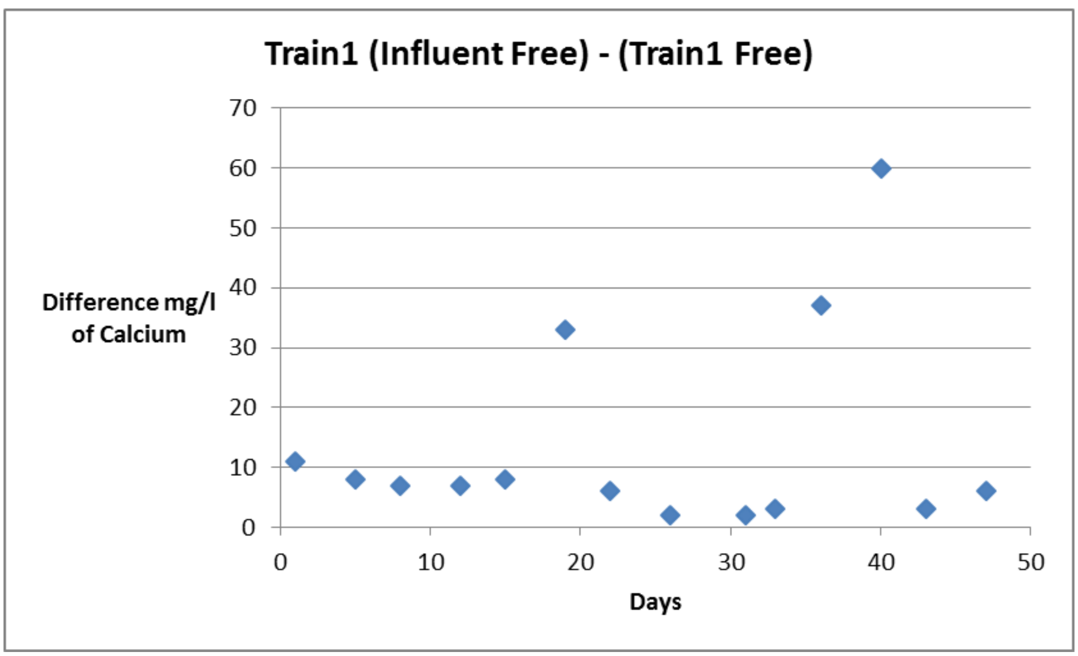

Figure 16. Difference between influent free Ca and Train 1 treated free Ca – Phase 2

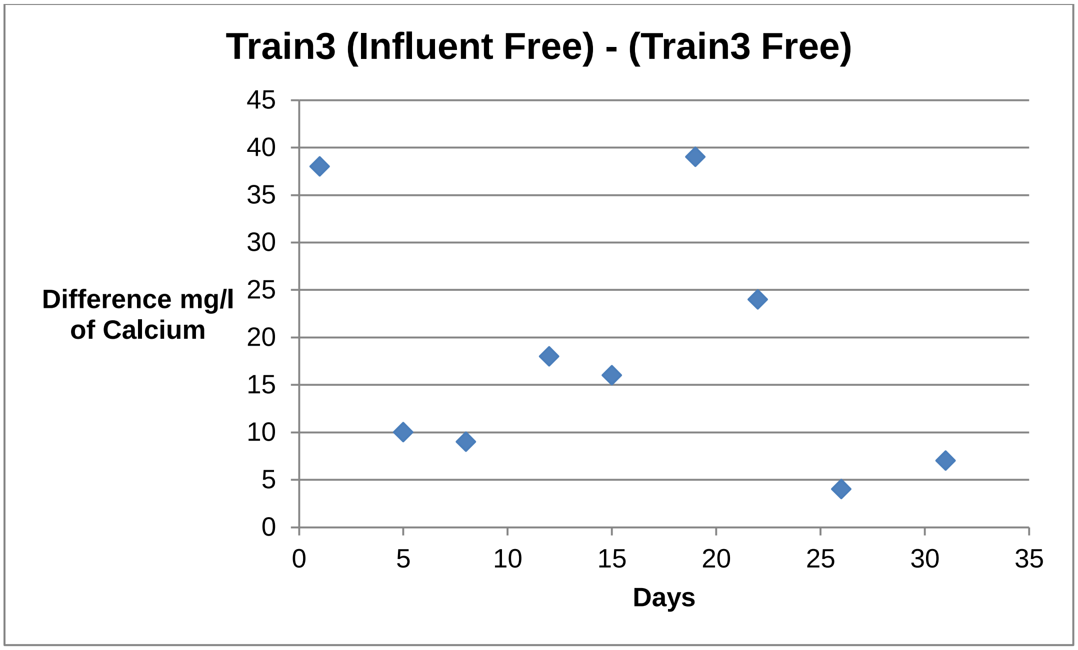

Figure 17. Difference between influent free Ca and Train 3 treated free Ca – Phase 2

CONCLUSIONS

During Phase 1, initial performance of both Train 1 and Train 3 was consistent with expectations based on Langelier Index calculations. Train 1 performance deteriorated during the first 10 days which was equivalent to approximately one year of operation in a typical residence. After 44 days of operation, Train 3 was still meeting the performance criteria of less than a 50% decrease in the performance measure based on the decrease in free calcium ion concentration. Data collected between day 17 and day 36 was difficult interpret as the free calcium ion concentration was sometimes greater than the total calcium concentration. An adjustment to the analytical method was done that helped alleviate the problem for the last several data points collected.

During Phase 2, the initial performance of Train 3 was consistent with expectation based on Langelier Index calculations.   Train 1 met the performance criteria of less than a 50% decrease in performance measured based on the decrease in free calcium ion concentration until day 43 while Train 3 met the performance criteria until at least day 22 (when flow meter failed). While the performance of Train 1 was much more consistent during Phase 2 as compared to Phase 1, the initial reduction in free calcium ion concentration was lower during Phase 2 as compared to Phase 1.

The accumulation of manganese oxide on Train 1 Media during Phase 1 was clearly evident from SEM/EDX analysis and manganese was removed by Train 1 on Day 0 and

Day 44. The influent concentration of manganese of 0.04 mg/l was less than the concentration recommended by the manufacturer of 0.05 mg/l. The placement of the Trains immediately after the chlorination facility at the William Street Pumping Station could have accelerated the fouling of the media by manganese oxide. It is well known that an oxidant such as chlorine can be used to remove manganese from water by coating a surface with manganese oxide. An activated carbon pre-filter could be effective at preventing fouling as manganese oxide could accumulate on the carbon. The carbon would also remove the chlorine, but the primary problem that was observed was manganese oxide accumulation.

RECOMMENDATIONS

A treatment train with an activated carbon or analogous media pre-treatment would be useful to assess the potential impact on manganese accumulation.

Media samples from residences could be obtained after several years of operation and analyzed by SEM/EDX to determine if manganese oxide is accumulating. The residences should receive water from the William St Pumping Station and they should be using the same media as used in this study.

Appendix I

Table A.1 - TAC Study Lab Sampling and Analysis – Phase I

Parameter	**Day one**, Sampling one non treated source and treated after each unit	**Mon, Wed, Fri** Except day one and last day Sampling one non treated source and treated after each unit	**Last day** Sampling one non treated source and treated after each unit
pH	x	x	x
Alk	x	x	x
Free, Total & Combined Cl	x	x	x
Free Ca	x	x	x
TDS	x		x
Turbidity	x	x	x
Hardness (calculation)	x	x	x
Aluminum	x		x
Antimony	x		x
Arsenic	x		x
Barium	x		x
Beryllium	x		x

Parameter	**Day one**, Sampling one non treated source and treated after each unit	**Mon, Wed, Fri** Except day one and last day Sampling one non treated source and treated after each unit	**Last day** Sampling one non treated source and treated after each unit
Boron	x		x
Cadmium	x		x
Calcium	x	x	x
Chromium	x		x
Cobalt	x		x
Copper	x		x
Iron	x		x
Lead	x		x
Magnesium	x	x	x
Manganese	x		x
Molybdenum	x		x
Nickel	x		x
Phosphorus	x		x
Potassium	x		x
Selenium	x		x

Parameter	**Day one**, Sampling one non treated source and treated after each unit	**Mon, Wed, Fri** Except day one and last day Sampling one non treated source and treated after each unit	**Last day** Sampling one non treated source and treated after each unit
Sodium	x		x
Silicon	x		x
Strontium	x		x
Tin	x		x
Titanium	x		x
Uranium	x		x
Vanadium	x		x
Zinc	x		x

Appendix II – NAC/TAC Study Lab Sampling and Analysis

Phase II, July-August 2015

Parameter	**Twice a week** Sampling only on treated after each unit, 2 samples	**Twice a week** Sampling one non treated source, 1 sample
pH		x
Temperature		x
Alk		x
Free, Total & Combined Cl		x
Free Ca	X	x
Hardness (calculation)		x
Calcium		x
Magnesium		x
Manganese		x