Drinking Water Softening/Scale Prevention Technology Assessment and Performance of Template Assisted Crystallization

by

Lin Shen

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

Hard water typically has a hardness concentration over 120 mg/L CaCO$_3$. Hardness is not a regulated drinking water parameter and does not have severe health effects. However, hard water causes more soap and detergent consumption and can cause scaling problems on household heating appliances, distribution pipes, and industrial cooling equipment.

There are various approaches to soften hard water or prevent scale formation at the centralized and the household scale. In order to choose the best treatment for a specific set of conditions, an appropriate technology evaluation is necessary. Prior research have tested single technology or compared two or three technologies with respect to their performance. Not many papers have compared all available technologies using the same assessment criteria.

At the household scale, point-of-entry (POE) devices are commonly used. Among these, ion exchange is the most widely applied POE device in Canada, though it has two major disadvantages: high sodium concentration in softened water and high chloride content in the brine which is often discharged into the sewer. Hence, there is an increasing interest in adopting salt-free treatment technology. Template assisted crystallization (TAC) is a relatively new household scale prevention technology. TAC media transforms free calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions into insoluble microcrystals. TAC technology has the potential to be an alternative to ion exchange, but there is very little published journals about this technology.

Therefore, this study had two objectives: 1) to assess and rank currently available softening and scale prevention technologies at both the centralized and household level, and 2) test the performance of the TAC technology using two source waters.

The multi-criteria assessment (MCA) method was utilized to evaluate centralized technologies (lime softening, pellet softening, nanofiltration, and ion exchange) as well as household technologies (TAC, ion exchange, nanofiltration, electrically induced precipitation, magnetic water treatment, and capacitive deionization). Criteria that were chosen in this assessment were: waste disposal, energy requirement, life-cycle cost, efficiency, subsequent treatment needed for finished water, chemical addition, easy to use, and validated technology. The initial assessment assigned a higher weight to the first four criteria listed. A sensitivity analysis (SA) was done by changing the weight assignment of different criteria. Three cases were selected: more focus on waste disposal and energy requirement; more emphasis on cost;

each criterion shared equal importance. For the centralized technologies assessment, pellet softening had the highest score, followed by ion exchange, lime softening, and nanofiltration. SA results showed that although the total score of each technology varied, the final rank did not change. For the household technologies assessment, TAC had the highest score, followed by ion exchange, magnetic water treatment, electrically induced precipitation, nanofiltration, and capacitive deionization. SA results showed that the total score varied, but the final rank did not change.

The performance of TAC technology was assessed using four tests which compared untreated and treated water samples of two selected source waters. The first test measured the reduction of free Ca^{2+} by a Ca^{2+} selective electrode after being treated by TAC in two source waters and, test results did not show a lot of reduction with percentage reductions ranging from 4.0% to 5.0% for both locations. The reductions were statistically significant but not large enough to be of much practical value. The second test was to measure the change in total Ca^{2+} and Mg^{2+} concentration after TAC. The changes were relatively small in both source waters, with percentage reductions ranging from 2.7% to 4.4% for Ca^{2+} and 4.0% to 6.9% for Mg^{2+}. Again, the reductions were statistically significant but not large enough to be of much practical value. The third test was a sequential ultrafiltration test utilizing membranes (3000 Da, 1000 Da, and 500 Da) to identify the microcrystal size. This test was not able to isolate substantial amounts of microcrystal, nor did it identify the approximate microcrystal size. The last test was developed as a simplified scale test. Results showed that treated water forms somewhat less scale than untreated water for both source waters. Scale formation potential indices: Langelier Saturation Index (LSI) and Calcium Carbonate Precipitation Potential (CCPP) were also calculated, and results showed that there was essentially no change in both indices after the TAC treatment.

Overall, assessment results showed that using this study's criteria, pellet softening and TAC were the two most suitable technologies to be applied at the centralized and household level, respectively. The TAC performance tests did not establish a substantial reduction in free calcium ions, nor were any crystals isolated. The scale test only showed relatively small differences between untreated and treated water. Future research could construct a flow-through system to test the performance of TAC technology and should also conduct some tests on new and used media.

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List of Abbreviations

Abbreviation	Term
AO	Aesthetic Objective
CCPP	Calcium Carbonate Precipitation Potential
CDI	Capacitive Deionization
EIP	Electrically Induced Precipitation
GPM	Gallons Per Minute
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
IX	Ion Exchange
LSI	Langelier Saturation Index
MAC	Maximum Acceptable Concentration
MCA	Multi-criteria Assessment
MDL	Method Detection Limit
MWCO	Molecular Weight Cut-off
ND	Not Detectable
NF	Nanofiltration
O&M	Operation and Maintenance
PES	Polyethersulfone
POE	Point-of-Entry
POU	Point-of-Use
SA	Sensitivity Analysis
TAC	Template Assisted Crystallization
TDS	Total Dissolved Solids

Chapter 1 Introduction

1.1 Problem statement

Canada has access to 20% of the world's surface freshwater and has 7% of the world's renewable freshwater (Statistics Canada, 2011). Not only does Canada possess abundant drinking water resources, but the quality of drinking water is also strictly regulated. However, the shortage of quality source drinking water remains a problem for some areas. In order to protect the health of each member of society, the Canadian Drinking Water Guidelines have been developed and published by Health Canada since 1968. Consequently, provincial regulations are derived from these guidelines.

In Ontario, in addition to surface water, groundwater is also a significant source for drinking water supplies. Groundwater typically has a high water hardness because it is rich in minerals, especially calcium ions (World Health Organization, 2010). Water hardness in groundwater mainly comes from dissolved polyvalent metal ions which are taken up when water flows through sedimentary rock (World Health Organization, 2010). According to Health Canada (2017), calcium and magnesium as main components of water hardness are not regulated because they do not cause severe health effects. Although water hardness is not a regulated drinking water parameter in Canada, hard water does cause significant aesthetic concerns and can affect the functionality of heating devices. Hard water can cause more soap and detergent consumption; can cause scale formation in heating devices as well as in distribution system; can reduce heat exchanger efficiency, and can also cause the costly breakdown of an industrial cooling tower. Therefore, it is essential to reduce water hardness or prevent scale precipitation to minimize those side effects caused by hard water.

Currently, there are several softening and anti-scale technologies applied in drinking water treatment, for example, lime softening, pellet softening, ion exchange, nanofiltration, template

assisted crystallization, etc. Some technologies are used in centralized treatment at the plant level, and some are utilized for household level treatment. Considering different water qualities and treatment demands, each technology has its advantages and disadvantages. Treatment processes that are applied on the centralized scale and the household scale should be evaluated differently. Making an appropriate decision on which technology to use is crucial on both application scales. Many factors/criteria have to be considered in the decision-making process, and multi-criteria assessments (MCAs) is a commonly used approach to do these type of evaluation (Godskesen et al., 2018). MCAs consider different criteria and give each criterion a different weight according to its importance to the decision maker. By applying a higher weight on criteria that are more important, the assessment results could give the most beneficial treatment option. However, there were not many published papers which systematically compare softening and scale prevention technologies at the centralized scale and/or household scale using MCA method. Most assessments were done on centralized softening technologies using life cycle assessment (LCA) which is an assessment method that incorporates environmental impacts with all stages of the equipment (Godskesen et al., 2010; Mohapatra et al., 2002).

In Ontario, a popular installed household water softening technology is ion exchange (Fox et al., 2014). Using the exchange resin, the softened water contains barely any calcium and magnesium ions but has elevated sodium levels. In addition, ion exchange resins need to be regularly regenerated by adding sodium chloride salt (Crittenden et al., 2011). Sodium ions exchange Ca^{2+} and Mg^{2+} that had previously attached to the ion exchange sites on the resin surface, and a concentrated brine which contains Ca^{2+}, $Mg^{2+,}$ and Cl^- is discharged into the sewer or municipal wastewater system (Crittenden et al., 2011). However, two main problems are raising concerns increasingly. The first one is the concentrated brine with high chloride concentration, which is discharged into the sewer system. Chloride is not removed in wastewater treatment plants, therefore, chloride is discharged into receiving water bodies. There is a continuing rising trend of chloride detected in some part of Ontario for past decades in

groundwater and surface water (Government of Ontario, 2015). Increased chloride level can cause problems to the aquatic ecosystem and affect the drinking water quality, if this water is used for drinking water production,. Another concern related to the ion exchange technology is that the softened water has elevated sodium concentrations that might be a problem for some individuals' health. Therefore, salt-free technologies as an alternative to ion exchange softening are currently gaining more attention.

Template assisted crystallization (TAC) is a relatively new technology applied for drinking water scale prevention purposes. TAC units contain polymeric beads with nucleation sites on the bead surface. When water flows through these beads, free Ca and Mg ions nucleate on the nucleation sites and form chemically stable microcrystals, which eventually dislodge. Microcrystals flow with the water and act as further nucleation sites in the distribution system (Fox et al., 2014). The presence of stable microcrystals prevents scale formation on both pipes and heating surfaces (Wiest et al., 2011). TAC has the potential to be an environmentally friendly alternative to ion exchange in households, because TAC does not require salt input to regenerate media, therefore no concentrated brine is discharged into the natural environment. However, there are no peer-reviewed papers in the drinking water literature and only very few reports regarding this technology and its performance. A report by Fox et al. (2011) tested the performance of the TAC technology and also compared it with other available household softening/scale prevention technologies. The report found that the TAC unit tested in the experiment was able to remove more than 88% scale deposit. Another report by C3 Water Inc. (2015) prepared for the City of Guelph mentioned that TAC could be a potential alternative to the ion exchange unit which requires salt input; however, it was also stated that TAC is relatively new applied technology and need further tests.

1.2 Research objectives

The primary objectives of this research were: to identify, assess and rank currently available softening/scale prevention technologies which are best suited for scaling prevention at centralized treatment plants and at the household levels; and to evaluate the performance of template assisted crystallization (TAC) applied at the household level using two different water sources.

Specifically, the main objectives of this research were to:

1) Evaluate and rank selected centralized softening technologies (lime softening, pellet softening, ion exchange, and nanofiltration) using a multi-criteria assessment approach;

2) Evaluate and rank selected household softening/scale prevention technologies (template assisted crystallization, ion exchange, nanofiltration, electrically induced precipitation, capacitive deionization, and magnetic water treatment method) using a multi-criteria assessment approach;

3) Evaluate the performance of TAC by measuring changes in hardness, specifically changes in total Ca, total Mg, free Ca concentrations, and the calcium carbonate precipitation potential;

4) Test the change of metal ion concentration in the water after being treated by the TAC unit;

5) Investigate the performance of TAC in terms of scale prevention by developing and applying a simplified scale testing procedure;

6) Estimate the approximate microcrystal size generated by TAC and quantify these microcrystals after TAC treatment by using a sequential ultrafiltration test procedure.

1.3 Thesis structure

This thesis consists of five chapters, with Chapter 3 and 4 structured in journal article format. Chapter 1 provides research motivations, research objectives, and a brief description of

the thesis structure. Chapter 2 is the literature review chapter which provides an overview and summary of several softening/scale prevention technologies. Information collected includes treatment principles, performance, cost, efficiency, advantages, and disadvantages. Chapter 3 is the first results chapter presenting the assessment results of centralized technologies and household technologies using a multi-criteria assessment approach. This chapter also presents the multi-criteria assessment methodology and includes a summary table of the criteria selected in this evaluation, weight and score assignment as well as the summarized information related to each technology which is based on the literature review done in Chapter 2. The assessment criteria were changeable according to the assessment focus, and weight assignment was varied by doing a sensitivity analysis. Chapter 4 is the second results chapter and is based on experimental results evaluating TAC units using two source waters. Hardness ion measurements, metal ion measurements, simplified scale tests, and ultrafiltration test results analysis are also presented in this chapter. Chapter 5 is a summary of the main findings and conclusions of the entire research. Recommendations for future studies are provided in this chapter as well. Supplementary materials and data are listed in the appendices as supporting information.

Chapter 2 Literature Review

2.1 Introduction

Hardness in drinking water is defined as the total concentrations of dissolved metallic polyvalent cations. Primarily, hardness is the sum of calcium and magnesium ions. Other ions can also contribute to water hardness such as iron, manganese, strontium, aluminum, and zinc (World Health Organization, 2010). Hardness is expressed as equivalent calcium carbonate concentrations. There are two types of hardness: carbonate hardness refers to the concentration of polyvalent ions that contribute to alkalinity such as carbonate and bicarbonate (Crittenden et al., 2012). In addition, non-carbonate hardness represents the concentration of polyvalent ions associated with non-alkalinity anions such as sulphate and chloride (Crittenden et al., 2012). In water treatment studies, total water hardness is the sum of carbonate and non-carbonate hardness.

There are four drinking water hardness levels characterized: soft water has a concentration level from 0 to 60 mg/L $CaCO_3$; medium soft water has a concentration level from 60 mg/L to 120 mg/L $CaCO_3$; hard water has a concentration level from 120 mg/L to 180 mg/L $CaCO_3$; very hard water has a concentration level of over 180 mg/L (Environmental Canada, 1977).

Surface water, such as lakes and rivers, as well as groundwater, are two major sources of drinking water. In Ontario, the average drinking water hardness supplied by surface water sources is 95 mg/L with the range from 3.7 mg/L to 296 mg/L (Health Canada, 2009). The average drinking water hardness supplied by groundwater sources is 294 mg/L, with the range from 40 mg/L to 1300 mg/L (Health Canada, 2009).

The primary natural source of water hardness is soil and sedimentary rocks that contain calcium and magnesium components. The inorganic chemical industry and mining industry are the two main industrial sources of water hardness (Biesecker & George, 1966). Groundwater generally has a higher hardness level compared to surface water.

Hard water causes problems such as scale deposition in plumbing pipes and heat-transfer appliances, costly breakdown of industry boilers and cooling towers, high consumption of detergents, high consumption of sequestering agents used in cooling water (Greenleaf et al., 2006), membrane fouling (Greenleaf et al., 2006) as well as problems of deterioration of fabrics (Crittenden et al., 2012).

Softening processes which remove calcium, magnesium, as well as other dissolved hardness minerals, are indispensable to domestic and industrial water supply and are also crucial as a pre-treatment of brackish water and seawater desalination (Fang & Wang, 2014). Regarding the drinking water softening processes application, in this chapter, softening technologies will be classified into two categories: centralized softening and household softening.

The objective of this chapter is to review and compare different softening technologies on a centralized scale and household scale.

2.2 Centralized softening technologies

Centralized water softening approaches treat hard water in a "central" location, which is generally a part of the drinking water treatment plant, then softened water is distributed to the community via pipelines and channels. In this section, four centralized water softening technologies are discussed: lime softening, pellet softening, nanofiltration, and ion exchange.

2.2.1 Lime softening

Lime softening is the earliest applied drinking water softening method, which is also a chemical softening method. General treatment procedure includes: raise pH to 11 for Mg precipitation; recarbonate to pH=10 for Ca precipitation; finally, adjust pH to about 8 for distribution.

For calcium carbonate hardness removal, lime is the commonly used chemical. Reaction equations are listed below:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3(s) + H_2O \hspace{3cm} \text{Equation 1}$$

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3(s) + 2H_2O \hspace{2cm} \text{Equation 2}$$

$$Mg^{2+} + 2HCO_3^- + 2Ca(OH)_2 \rightarrow 2CaCO_3(s) + Mg(OH)_2(s) + 2H_2O \hspace{1cm} \text{Equation 3}$$

$$Mg^{2+} + SO_4^{2-} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{2+} + SO_4^{2-} \hspace{2cm} \text{Equation 4}$$
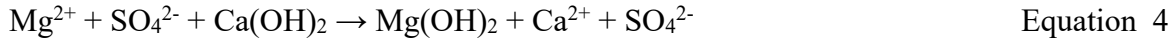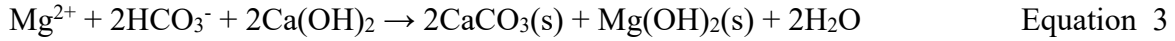
When lime ($Ca(OH)_2$) is added to water, it reacts with CO_2 first and forms the calcium carbonate ($CaCO_3$) precipitate (Equation 1). This step does not remove hardness (from water). The second stage is the conversion of bicarbonate species to carbonate species (Equation 2), which requires a pH around 9.3 (Crittenden et al., 2012). For magnesium hardness removal, a pH of at least 10.5 is required for an effective $Mg(OH)_2$ precipitation according to practical experience (Equation 3) (Crittenden et al., 2012). Equation 4 represents that non-carbonate hardness is also removed in this process.

Lime-soda softening is an alternative to use lime exclusively during the softening process. Soda ash (Na_2CO_3) is added when the source water does not have enough carbonate alkalinity (HCO_3^-) to react with lime. This method can remove both carbonate and noncarbonate hardness (Crittenden et al., 2012).

$$Ca^{2+} + SO_4^{2-} + Na_2CO_3 \rightarrow CaCO_3(s) + 2Na^+ + SO_4^{2-} \hspace{2cm} \text{Equation 5}$$
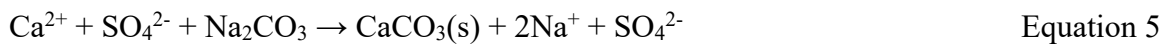
Caustic Soda softening is another alternative to lime softening. Caustic soda ($NaOH$) is added when the source water does not have enough carbonate hardness to react with lime.

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \hspace{3cm} \text{Equation 6}$$

$$Ca^{2+} + 2HCO_3^- + 2NaOH \rightarrow CaCO_3(s) + 2Na^+ + CO_3^{2-} + 2H_2O \hspace{1cm} \text{Equation 7}$$

$$Mg^{2+} + 2HCO_3^- + 4NaOH \rightarrow Mg(OH)_2 + 4Na^+ + 2CO_3^{2-} + 2H_2O \hspace{1cm} \text{Equation 8}$$

$$Mg^{2+} + SO_4^{2-} + 2NaOH \rightarrow Mg(OH)_2 + 2Na^+ + SO_4^{2-} \hspace{2cm} \text{Equation 9}$$

$$Ca^{2+} + SO_4^{2-} + Na_2CO_3 \rightarrow CaCO_3(s) + 2Na^+ + SO_4^{2-} \hspace{2cm} \text{Equation 10}$$
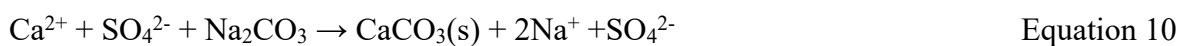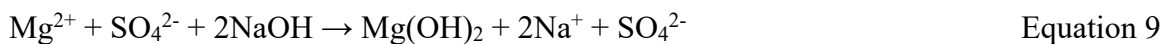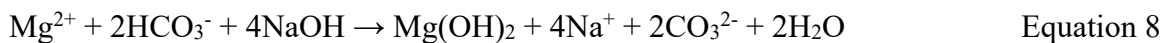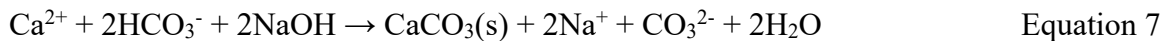
Recarbonation is a common final step for all kinds of lime softening approaches. The main purpose of this step is to adjust the pH of the finished water and to prevent the precipitation of carbon scale on the filter sand or piping of the distribution system (Wang et al., 2005). Carbon dioxide addition also converts carbonate to bicarbonate ions to stabilize the finished water.

Conventional lime softening process can reduce the water hardness level. Therefore, it can decrease the scale forming tendency and reduce the consumption of cleaning agents. The efficiency of lime softening in water hardness removal is relatively high, and the softened water has the residue hardness level around 40 mg/L $CaCO_3$ (Wang et al., 2005). Lime softening also aids to remove radium 226/228, arsenic, uranium, and heavy metals (McNeill & Edwards, 1997; Clifford, 1990; Sorg, 1990). Also, lime softening removes some organics and reduces the total organic carbon level. Fulvic acid, humic acid, organophosphate, phosphonate can be effectively removed by lime softening as well (Liao & Randtke, 1986). In addition, lime softening process assists in iron, manganese, and some heavy metals removal as well (Crittenden et al., 2012). Besides, some carboxylic acids and phenols can be removed by absorbing onto $CaCO_3$ precipitate (Liao & Randtke, 1986). Chemicals used in lime softening are relatively easy to purchase and safe to use.

With the high efficiency, lime softening is a popular centralized softening technology used in the United States and other countries. However, there are disadvantages and concerns associated with lime softening. First of all, it produces a large quantity of wet sludge which has a very high concentration of $CaCO_3$ and $Mg(OH)_2$ mixture, and usually with a relatively high pH. A large city in Iowa state, which relies mainly on lime softening to treat hard water produces about 32,000 tons (dry weight) of lime sludge annually (Jones, 2011). Wet sludge is difficult and costly to dispose. The lime sludge is generally disposed into a municipal solid waste landfill or use lagoons to store the wet sludge from the water plant. However, the transportation, dewatering processes, landfill leachate control is expensive. The sludge disposal cost for a city can be as high as US $600,000 per year (Jones, 2011). Sludge might also contain colloidal coagulation

residues as well as some unreacted lime (American Water Works Association, 1981). Wet sludge can be stored and dewatered in lagoons, can be treated via gravity thickening or sludge palletization, and can go through landfill (American Water Works Association, 1981). In order to make the sludge residual treatment more cost-effective, possible usage of dry sludge is worthwhile to be considered. Lime sludge can potentially be used to apply in agriculture, to control SO_x generated in power plant, to neutralize wastewater and also can be used as road construction materials (Jones, 2011; Shannon et al., 1997; Watt & Angelbeck, 1977).

Another disadvantage is that the pH adjustment process as a post-treatment is needed for softened water because of the high pH after being treated by the softening process. As discussed previously, this step is to add CO_2 to stabilize the finished water and prevent further precipitation in the distribution system.

The third drawback is that the lime softening process requires extensive land use (Bergman, 1995), and its initial installation cost is relatively high as well. The construction of lime softening treatment needs a separate land space for lagoon, which is used to store wet sludge generated. Because of the continuously high demand of chemical input as well as the further sludge treatment, the maintenance cost is relatively high as well.

The last concern is that when soda is added in lime soda or caustic soda softening as presented in Equations 5-10, it might increase sodium levels in the finished water as well.

Generally, lime softening is a well-developed centralized technology and is commonly applied currently. The knowledge gap is not significant for this treatment approach; the next step would be the optimization of sludge treatment and cost reduction.

2.2.2 Pellet softening

As a centralized softening method, pellet softening is commonly used in European countries, especially in the Netherlands where it has been used for decades. Pellet softening

utilizes an up-flow reactor with a fluidized bed inside as presented in Figure 2.1. Water flows in from the bottom of the treatment unit and then up through seeding materials which transform into pellets. Pellets act as seeding materials which are usually sand grains can facilitate the precipitation of calcium carbonate by providing a surface area for precipitation. Caustic soda (NaOH) or lime ($Ca(OH)_2$) is injected from the bottom as well to raise the pH so that it can facilitate Ca in the water to better precipitate onto pellets as $CaCO_3$. The chemical reactions are described as follows:

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3(s) + 2H_2O \hspace{3cm} \text{Equation 11}$$

$$Ca^{2+} + HCO_3^- + NaOH \rightarrow CaCO_3(s) + Na^+ + H_2O \hspace{3cm} \text{Equation 12}$$
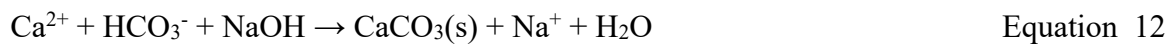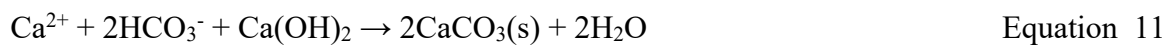
As hardness precipitates, pellets grow larger and settle down due to gravity and finally are removed from the bottom. Removal of enlarged pellets does not affect the operation of the pellet reactor, which means pellet softening can perform continuously. Treated soft water is discharged from the top of the treatment unit. Also, because of the relatively high pH, the treated water pH needs to be adjusted in order to be safely distributed. pH adjustment is commonly done using CO_2. Pellet softening shows high hardness removal efficiency to meet the softening target (Hofman et al., 2006).
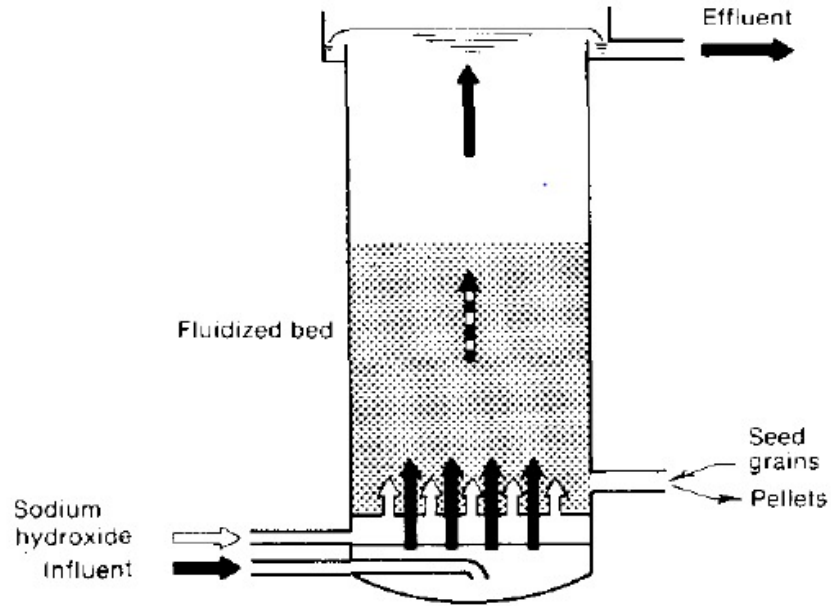
**Figure 2.1 Schematic of the pellet reactor (Graveland et al., 1983). Used with permission, ©
John Wiley and Sons.**

The difference between using two chemicals ($Ca(OH)_2$ and NaOH) is the amount of coated
pellets generated. Using $Ca(OH)_2$, the amount of $CaCO_3$ that precipitates as dry solid waste is
2.3-2.6 times higher than when using NaOH (Graveland et al., 1983). Compared to lime
softening, pellet softening does not generate a large amount of wet sludge which is difficult to
handle. In contrast, removed pellets are easily dewatered and can be reused as agricultural lime,
wastewater neutralizer, and animal feed additive (Hofman et al., 2006). Pellet softening has a
relatively smaller footprint and lower installation cost (Hofman et al., 2006). In addition to
efficiently removing calcium hardness and TDS, it also precipitates iron (Fe) and manganese
(Mn) as $FeCO_3$ and $MnCO_3$ (Graveland et al., 1983). Pellet softening also decreases the release
of copper and lead (Groenendijk et al., 2008); thus, treated water minimizes environmental and
health effects. It was reported that copper emission was reduced by 30% after introducing pellet
softening in the treatment plant of Nuland in 2005 (Groenendijk et al., 2008).

There are also some disadvantages related to pellet softening. First of all, pellet softening is
not particularly efficient in Mg removal, with less than 10% of Mg in the water incorporates into

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CaCO$_3$ precipitate (Hofman et al., 2006). Another concern is that if the process adds caustic soda, the sodium concentration in the finished water will be higher. In addition, an extra pH adjustment process as a post-treatment is required because the finished water has a higher pH value than the distribution guideline. Besides, the performance of pellet softening is affected by pre-treatment as well as raw water quality. For example, if non-aerated groundwater with a high phosphate (PO$_4^{3-}$) concentration is treated, pellets will contain some water, and excessive bed growth might occur (Moel et al., 2006). Another concern is that a large number of seeding materials is needed for replacement. Because as the precipitation process proceeding, reaction sites will decrease due to the precipitate formation, and this leads the reaction to slow down.

Pellet softening is also a well-developed centralized technology with high water hardness removal efficiency. There is not a lot of knowledge gap related to this technology. However, studies on pellet reuse still have high research values.

2.2.3 Nanofiltration and reverse osmosis

Membrane filtration technology is also commonly used in drinking water treatment processes, and it is preferred over other technologies in disinfection, distillation, and media filtration (Pendergast & Hoek, 2011). There are four major membrane treatment processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The hierarchy of these processes is presented in Figure 2.2. The most popular membrane technologies used for water softening purpose are RO and NF, although RO removes more than just hardness. Both treatment technologies are operated under pressure and require some pretreatment to facilitate membrane performance (American Water Works Association, 2007).
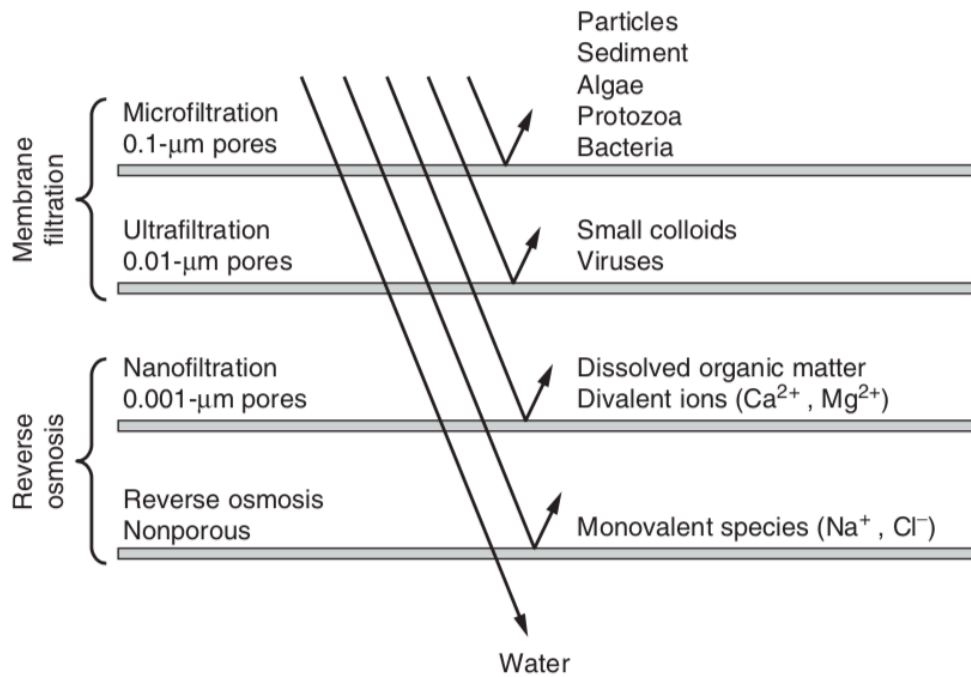
Figure 2.2 Hierarchy of membrane treatment processes with pore size and rejection components (Crittenden et al., 2012). Used with permission, © John Wiley and Sons.

Reverse osmosis is commonly applied for ultrapure water generation and water reuse process (Pendergast & Hoek, 2011). RO membrane is nonporous (Crittenden et al., 2012), while the nanofiltration membrane has the pore size of less than 2 nm (Ulbricht, 2006). Because reverse osmosis membrane has a smaller pore size, it requires higher pressure input and can remove more small ions and molecules as presented in Figure 2.2. Therefore, RO does not only removal hardness ions (divalent ions) but also removes some monovalent components, inorganic contaminants, total dissolved solids (TDS) and other components as well (American Water Works Association, 2007). RO treated water contains almost no dissolved species. Reverse osmosis is not only used for water impurity removal purposes but also for potable water production from the ocean and brackish water (Crittenden et al., 2012).

NF is successfully applied in hardness, organic matters, and heavy metal removal (Pendergast & Hoek, 2011). As well as removing dissolved divalent ions such as Ca^{2+} and Mg^{2+} in water, the nanofiltration unit also removes other contaminants such as arsenic and nitrate

(Crittenden et al., 2012). Nanofiltration membranes can remove 80% to 95% of divalent ions. Nanofiltration is a pressure driven process as well using a semi-permeable membrane. Only certain kinds of ions can pass through (dissolved monovalent ions such as Na^+ and Cl^-). Thus, the filtered water contains almost no hardness (Ca^{2+} and Mg^{2+}).

Nanofiltration softens water without producing a large amount of wet sludge compared with conventional lime and pellet softening processes. The most advantageous fact for nanofiltration is that the permeate contains almost no hardness ions. The typical rejection rates are 70-90% (Van Der Bruggen & Vandecasteele, 2003). Nanofiltration also effectively removes NOM which makes it an excellent option for color removal, TDS removal, and disinfection by-product (DBP) formation control (Crittenden et al., 2012; American Water Works Association, 2007). Another advantage of using nanofiltration is that the treatment unit requires less land; therefore, the process is flexible to apply (Van Der Bruggen & Vandecasteele, 2003). Compared with the reverse osmosis process that requires high-pressure input over 250 psi ($1.72{\times}10^6$ Pa), nanofiltration only requires pressure as low as 70 psi ($4.8{\times}10^5$ Pa), which saves much more energy consumed (Wilson Engineering LLC, 2013). In addition to the high hardness removal rate, nanofiltration can also effectively remove other dissolved substances: arsenic, bicarbonate, chloride, fluoride, iron, manganese, nitrite, sulfate, total organic carbon (Wilson Engineering LLC, 2013; American Water Works Association, 2007). Nanofiltration does not need extra salt or chemical addition like ion exchange and chemical softening processes.

Although nanofiltration is an effective softening technology, it has some drawbacks as well. As with other membrane processes, membrane fouling is the first problem that needs to be considered which requires regular cleaning and ultimately replacement of membrane modules. Another aspect of nanofiltration is that typical nanofiltration treatment recovers around 75% feed water, 25% is rejected by the membrane as stated in Wilson Engineering LLC (2013) report and is disposed as wastewater. However, the recovery and rejection percentages depend on specific

set-up. If several stages are used, the rejection would be much lower. As for centralized treatment, 25% water loss is a huge amount.

Moreover, the rejection stream could have a concentration four times (changes according to set-up) as high as the raw water (Wilson Engineering LLC, 2013). The disposal of concentrated waste composes a significant portion of the overall cost (Squire et al., 1997). Another concern is that nanofiltration generally requires pressure input. Thus, the energy consumption is also higher than conventional chemical softening methods (Du et al., 2018). Besides, nanofiltration needs posttreatment such as aeration, disinfectant addition, pH adjustment, and corrosion inhibitor chemicals addition on finished water (American Water Works Association, 2007).

In conclusion, membrane treatment is effective in drinking water hardness removal. However, advantages and disadvantages exist as described in previous paragraphs. Current research still works on optimizing membrane treatment performance and reducing membrane fouling.

2.2.4 Ion exchange

In drinking water treatment, ion exchange is used for water softening and demineralization (Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, NO_3^-), and TOC reduction (the MIEX® process) (Singer & Bilyk, 2002). It is also implemented for the production of process water. In North America, ion exchange is widely used for small, point-of-use devices which aim to soften the hard water (Crittenden et al., 2012). Ion exchange can be used in industry and municipal water treatment as well, but the application is limited (Crittenden et al., 2012). Full-scale systems that are applied in the industry are primarily designed to prevent scale formation in industrial settings such as power plant boilers. In municipal drinking water treatment plants, ion exchange is generally applied at the end of the whole treatment procedure to remove hardness in drinking water, and it may also be used to create ultrapure water (Crittenden et al., 2012). Unlike the pellet treatment unit using the fluidized bed for reaction, the ion exchange resin is applied in a fixed bed (Apell & Boyer,

2010). Cation exchange also facilitates reducing the membrane enhanced fouling which is caused by dissolved organic matter (Li & Elimelech, 2004).

The critical part of ion exchange is the ion exchange resin. There are cation exchange resin and anion exchange resin. Cation exchange resin that saturated by Na^+ is used in the water softening process. There are three primary constituent groups of a resin bead: solid structure R, active group G, and exchangeable group X (in this chapter, Na^+ is used) (Alsentzer, 1963). The basic process of ion exchange treatment is: hard water passes resin beads, and hardness ions (Ca^{2+} and Mg^{2+}) bind to resin beads. Two Na^+ will be exchanged and released into the water for each hardness ion attachment, as presented in Equation 13 and Figure 2.3 (a). As the process goes through, resin beads will get exhausted. Therefore, when the resin cannot efficiently remove a certain amount of hardness ions, regeneration and cleaning sequence is needed.

$$\begin{Bmatrix} Ca \\ Mg \\ Fe \end{Bmatrix} \begin{Bmatrix} 2(HCO_3) \\ SO_4 \\ 2Cl \end{Bmatrix} + RG(Na)_2 \rightarrow (RG) \begin{Bmatrix} Ca \\ Mg \\ Fe \end{Bmatrix} + Na_2 \begin{Bmatrix} (HCO_3)_2 \\ SO_4 \\ Cl_2 \end{Bmatrix} \text{(Alsentzer, 1963) \quad Equation 13}$$
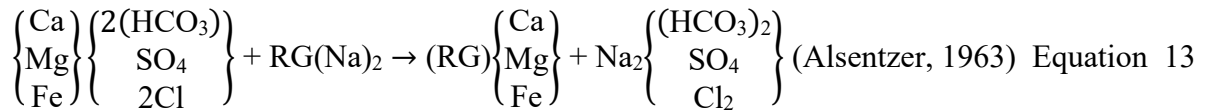
Exhausted resin beads are treated by standard salt solution (NaCl), usually 8-10% by weight (Flodman & Dvorak, 2012). The free Na^+ in the salt solution will exchange Ca, Mg, Fe that bind to the resin surface, as explained in Equation 14 and Figure 2.3 (b). This could simultaneously restore resins to sodium saturated conditions. Regenerated beads are then rinsed by a solution that free of hardness ions, then can be returned to the system (Alsentzer, 1963). After the regeneration process, the excess concentrated brine that contains chloride and hardness ions is discharged directly into the sewer system (Clifford et al., 2011).

$$(RG) \begin{Bmatrix} Ca \\ Mg \\ Fe \end{Bmatrix} + 2NaCl \rightarrow \begin{Bmatrix} Ca \\ Mg \\ Fe \end{Bmatrix} Cl_2 + (RG)\text{-}Na_2 \text{(Alsentzer, 1963)} \qquad \text{Equation 14}$$
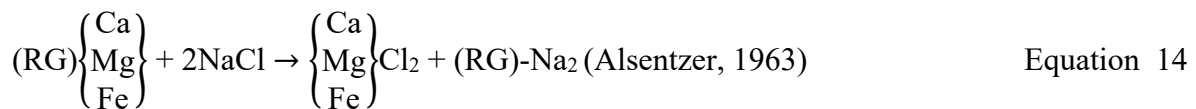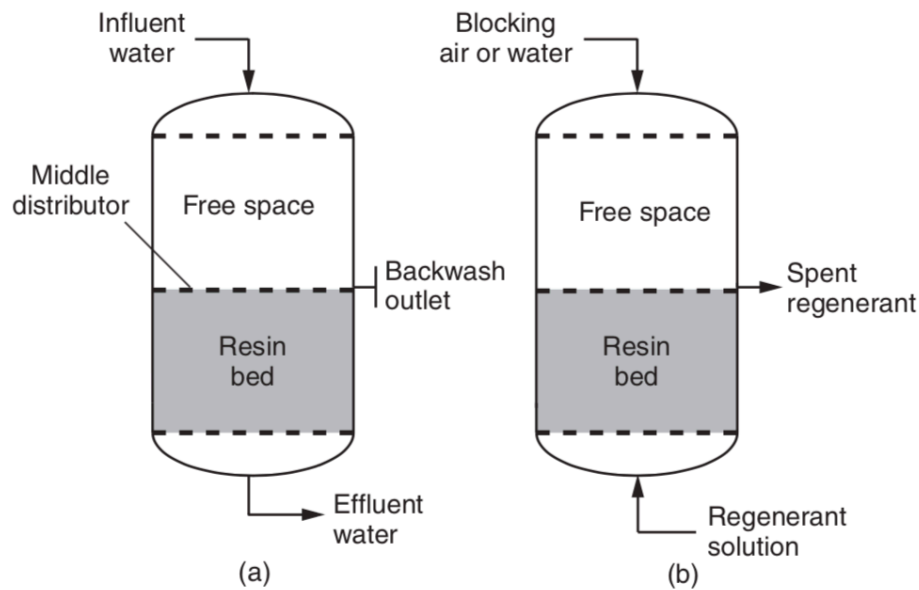
Figure 2.3 Schematic of a fixed bed ion exchange unit. (a) working diagram (b) regeneration diagram (Crittenden et al., 2012). Used with permission, © John Wiley and Sons.

Ion exchange softeners have the ability to treat a wide range of hardness concentrations, and they are able to remove almost all hardness ions from influent water (Flodman & Dvorak, 2012). Ion exchange has high hardness removal efficiency of around 95% to 100% (Wilson Engineering LLC, 2013). Ion exchange also does not create any wet sludge. The primary softening process does not require any chemical additives, and the chemical (NaCl salt) used for the regeneration stage only is common and safe. Softened water does not require any post-treatment. The footprint is also smaller, which lowers the capital cost. The ion exchange process is efficient in removing iron and manganese as well (Alsentzer, 1963). Operational cost for ion exchange is particularly cheap when the raw water is relatively low in hardness and has an iron concentration between 2-10 ppm (Alsentzer, 1963), The resin lifespan can be as long as ten years (Wilson Engineering LLC, 2013), which also makes the maintenance cost not that high. Moreover, with the change of water hardness level, the number of operation units or the amount of exchange resins can be easily added or reduced.

There are also some disadvantages of the ion exchange process. The first problem is that softened water contains high sodium concentrations. It also requires a significant amount of salt (generally NaCl) to regenerate the exhausted resins beads. Regeneration process generates a vast amount of concentrated brine which has a high concentration of chloride and mineral ions (Ca^{2+}, Mg^{2+}) (Greenleaf et al., 2006). The concentrated brine with a high chloride level is then discharged into the sewer system and finally discharged in the natural water system. Ion exchange can remove manganese and iron, but resin beads can get fouled, especially when the process is exposed to air because of the precipitation of oxidized iron onto beads surface (Alsentzer, 1963).

Although it is not commonly applied in centralized scale, ion exchange has high softening efficiency and relatively low cost. The main disadvantages related to ion exchange is the high level of chloride salt in the concentrated brine generated and discharge after the resin regeneration process, and the high sodium salt in softened water. This technology is well studied, and recent research also works on analyzing the performance of some integrated approaches on drinking water treatment, minimizing environmental effects related to ion exchange, and upgrading the resin material.

2.3 Household softening/scale prevention technologies

Unlike centralized technologies, household treatment units are applied in individual households and are small scale applications to treat hard water. Most household softening units are point-of-entry (POE) devices, and only rarely would these units be point-of-use (POU) devices which are installed directly at the tap. In this section, six household softening/scale prevention technologies are discussed: template assisted crystallization, ion exchange, nanofiltration, electrically induced precipitation, magnetic water treatment method, and capacitive deionization.

2.3.1 Template assisted crystallization

Template assisted crystallization (TAC) is certified by NSF 61. TAC is a relatively new technology applied in drinking water scale prevention and is available commercially; however, little refereed papers are available describing the operation and the performance of the TAC treatment system. Therefore, some of the descriptions of the TAC technology in this section are based on the manufacturer information. The basic theory for template assisted crystallization (TAC) technology is nucleation, which is facilitated by TAC media. As illustrated in Figure 2.4, the TAC unit uses polymeric beads with nucleation sites on its surface.
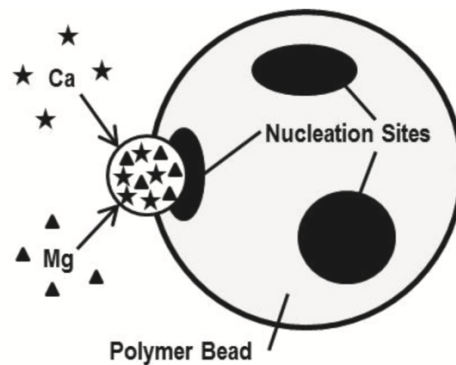
Figure 2.4 Demonstration of the TAC unit media (Fox et al., 2014). Reprinted with permission. © WateReuse Research Foundation.
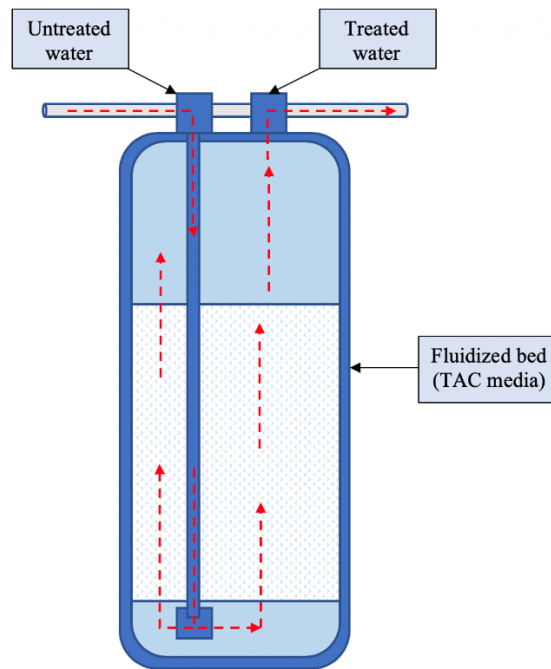
Figure 2.5 Schematic of the up-flow TAC treatment unit

When water flows through the treatment tank, the TAC media is dispersed in a fluidized bed as presented in Figure 2.5, which increases the contact opportunity of hardness ions (Ca^{2+}, Mg^{2+}) and bicarbonate ions (HCO_3^-) in the water. Nucleation sites on the surface of the TAC media attract Ca^{2+}, Mg^{2+}, and HCO_3^- ions in the water and initiate the nucleation process. At these nucleation sites, calcium carbonate and magnesium carbonate start to form microscopic crystals (Watch® Water, n.d.). The reaction is demonstrated below:

Dissolved hardness → micro-crystal (insoluble)

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad\qquad\qquad \text{Equation } 15$$

$CaCO_3$ → stable micro-crystals

As the reaction proceeds, the crystals grow larger and finally leave the nucleation sites (Watch® Water, n.d.). The formed microscopic crystals are stable and remain suspended and do not stick to the surface while they are being transported by the water through the pipe (Watch® Water, n.d.; Home plus, 2017). It is also stated that microcrystals can sustain a temperature of up

to 380 °C (Watch® Water, n.d.). Therefore, when the water that contains microcrystals enters the scale formation environment (heating devices), scale deposit on the heating plate is prevented (Watch® Water, n.d.). Microcrystals would not revert into dissolved hardness ions (Home plus, 2017). Since hardness ions are not removed from the water, the crystals still form white spots onto the surface when the treated water is evaporated (Home plus, 2017). However, a study showed that the $CaCO_3$ precipitate from water that is treated by TAC is in aragonite form which can be easily wiped away as well as it does not stick onto the heating surface (Fox et al., 2014).

TAC technology does not remove water hardness but performs well on scale prevention (Fox et al., 2014). TAC passed the German standard test DVGW W512 (DVGW, 1996) which aims to test the scale formation of water conditioning devices. Standard tests done by Fox et al. (2011) showed that TAC treated water removes more than 88% scale. During the TAC process, no wet sludge is created, no chemical is added, and the pH does not change (Watch® Water, n.d.). Compared with conventional household level ion exchange softening process, no regeneration is needed, and no concentrated brine is generated. TAC materials are reported to be effective for 3-5 years which depends on the influent water quality and the equipment usage frequency (Watch® Water, n.d.). The purchase and maintenance price is comparable to or slightly higher than the ion exchange cost (Gombos, 2016).

Although not a lot of disadvantages are listed for TAC technology from the background information, the performance could be affected by several factors. For example, it is stated that NOM affects the removal of dissolved calcium to some degree (Mercer et al., 2005). NOM might compete for sites on the nucleation surface (Mercer et al., 2005). Other water quality parameters, such as iron, manganese, chlorine residual, could affect the unit performance. According to the product website, some water parameters are required to be below certain levels for a better TAC performance which reduces more scale formation.

In conclusion, TAC technology, as a newly applied scale prevention technology with little published literature has a great potential to be used at the household level. TAC prevents scale formation, and there is no chemical, no electricity, no regeneration, no control valve required. The sodium level is not elevated in finished water as well. However, TAC technology is not well studied, and more studies are needed in the future to analyze: what is the performance in household use, what is the lifespan of the media, how different hardness levels affect the performance, how pH affects the reaction, how NOM affects the performance, whether the lifespan of the media is affected by the characteristics of raw water, etc.

2.3.2 Ion exchange

Ion exchange (IX) unit is certified by NSF 61. Basic procedures, advantages, and disadvantages are described in Section 2.2.4. House-hold ion exchange devices do not have a separate process to treat concentrated brine which contains high chloride concentration. The concentrated brine is discharged directly into the sewage system and then enters the wastewater treatment system (or into a septic tank, if the house has one). However, wastewater treatment plants are not equipped to remove highly soluble chloride. Hence, chloride, together with treated effluent, is discharged into the natural water system. Elevated chloride concentration in the natural water system has a potential effect on aquatic life (Siegel, 2007). In addition, the softened water generated by an ion exchange unit contains a high level of sodium. Excess Sodium in drinking water will lead to some health problems as well; for example, high sodium intake might cause issues in people who have hypertension. While there are no health-related guidelines for chloride or sodium, the Ontario Drinking Water Objectives (Ontario MOE, 2003) and Guidelines for Canadian Drinking Water Quality (Health Canada, 2017) indicate chloride concentrations should be lower than 250 mg/L, and sodium concentration in drinking water should be less than 200 mg/L for aesthetic reasons.

2.3.3 Nanofiltration and reverse osmosis

Both nanofiltration and reverse osmosis technology have products that could be installed in the household. Nanofiltration unit is certified by NSF 61. Nanofiltration technology performs well on hardness removal, while reverse osmosis not only applies for softening purpose but also to create ultrapure water. Basic procedures, advantages, and disadvantages of nanofiltration technology in water softening are described in Section 2.2.3. However, at the household level, nanofiltration is less commonly applied than ion exchange technology, although it has high water hardness removal efficiency and also assists in removing other unfavorable components (American Water Works Association, 2007). Another difference of centralized nanofiltration is that household unit does not require house owner to do the chemical cleaning for membrane. If the membrane gets exhausted, the cartridge will be replaced.

2.3.4 Electrically induced precipitation

Electrically induced precipitation (EIP) technology causes microscopic particles to form before the water enters a scale-forming environment. The EIP unit utilizes the direct current to create an electric field and disrupt/affect dissolved bicarbonate (HCO_3^-) (Cho et al., 2005). Together with the electric field applied, the process of HCO_3^- dissociation is accelerated, and hydroxide ions (OH^-) are generated (Cho et al., 2005). When enough OH^- formed on the surface, carbonate ions are formed and then induces the precipitation of microscopic $CaCO_3$ particles on the electrode surface (Cho et al., 2005). EIP passed German DVGW W512 standard test, and reactions (Cho et al., 2005) are listed as follows:

$$HCO_3^- \rightarrow OH^- + CO_2 \hspace{4cm} \text{Equation 16}$$

$$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O \hspace{3cm} \text{Equation 17}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \ (s) \hspace{3.5cm} \text{Equation 18}$$
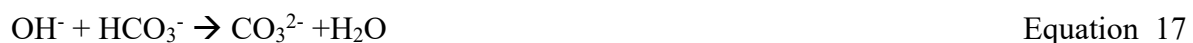
Microscopic particles formed ($CaCO_3$) also suspend in the water and act as nucleation sites (Fox et al., 2014). When water enters a heating environment, dissolved calcium carbonate will precipitate onto the surface of these nucleation sites rather than on the equipment surface (Fox et al., 2014). Although the precipitate will settle down, it is soft and can be easily wiped out. A study showed that the suspended solids in the water after being treated by EIP increased by 160-540% (Tijing et al., 2007), which indicates the microparticle formation in the water.

EIP is a physical scale prevention technology. Thus, no chemical or salt is added, and no sludge is created. Similar to TAC technology, EIP does not produce soft water, but does remove some hardness and reduces the scale formation. According to results from Fox et al. (2011), scale formation was reduced by 50% after treated by EIP. The reduction percentage is relatively low compared to TAC, ion exchange, and nanofiltration. In addition, electrodes used in EIP units need to be cleaned periodically because of the precipitate accumulation. EIP also requires electricity input which will increase the operational cost.

EIP is commercially available but not widely used. EIP technology used for scale prevention purpose at household still needs more research on its performance.

2.3.5 Magnetic water treatment

A magnetic water treatment unit utilizes an induction coil and wraps it externally around the water supply pipeline, as presented in Figure 2.6. Using an external signal box/electricity supply, an electrical current is created along with the coil which creates a magnetic field in the water pipe. With the magnetic field, anions concentrate on the pipe wall and cations concentrate in the center of the pipe or vice versa. Reversing the current causes anions and cations to move toward each other, which increases collision opportunities and forms sub-microscopic clusters (Aqua Rex, n.d.). These clusters act as nucleation seed which makes the water form "soft precipitate" aragonite ($CaCO_3$) that will not attach to the surface when the water is heated (Fox et al., 2014; Aqua Rex, n.d.).
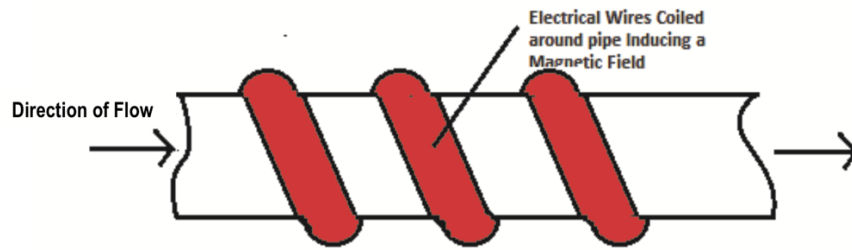
Figure 2.6 Schematic of magnetic water treatment (Fox et al., 2014). Reprinted with permission. © WateReuse Research Foundation.

A study showed that with the magnetic field applied, the reduction in scale formation ranges from 17% to 70% (Smith et al., 2003). Under heating conditions, a visible precipitate formed in the untreated water while no visible precipitate formed in the treated water (Smith et al., 2003). The experiment done by Fox et al. (2011) showed that the treated water reduced scale formation by 56%. Studies also showed that several variables might affect the performance of the unit such as corrosion caused by the magnetic device, dissolved oxygen concentration and other factors (Fox et al., 2014; Ozeki & Otsuka, 2006).

The magnetic water treatment process is also a physical scale prevention process. Similarly, no salt or chemical input, no brine or sludge generated. This process does not produce soft water either. Instead, it changes the calcium precipitation form from hard to soft scale. The technology also requires electricity input which increases the operational cost. As mentioned before, this technology is not well studied. The mechanism of the process, the influential factors, the stability and feasibility of magnetic water treatment to deal with hard water need more research.

2.3.6 Capacitive deionization process

Capacitive deionization process (CDP) is also called electrochemical demineralization or electrodeionization. CDP is an environmentally friendly technology used in the water softening process. CDP technology has commercial products available. It uses electrodes that have a high capacity to absorb ions from the water. The commonly used electrode material is porous carbon because of its high surface area (Fox et al., 2014). Two electrodes are connected to a battery, and

a potential difference is created between two electrodes. Ions in the water can be absorbed into pores on the electrode, as shown in Figure 2.1. Positively charged ions move and attach on the negatively charged electrode and vice versa (Zou et al., 2008). This process is not specific to hardness ions; in contrast, it targets all charged ions in the water. Then through a backwash or cleaning process, by reversing the battery charge, absorbed ions are forced out of electrodes pores and being washed out (Fox et al., 2014).
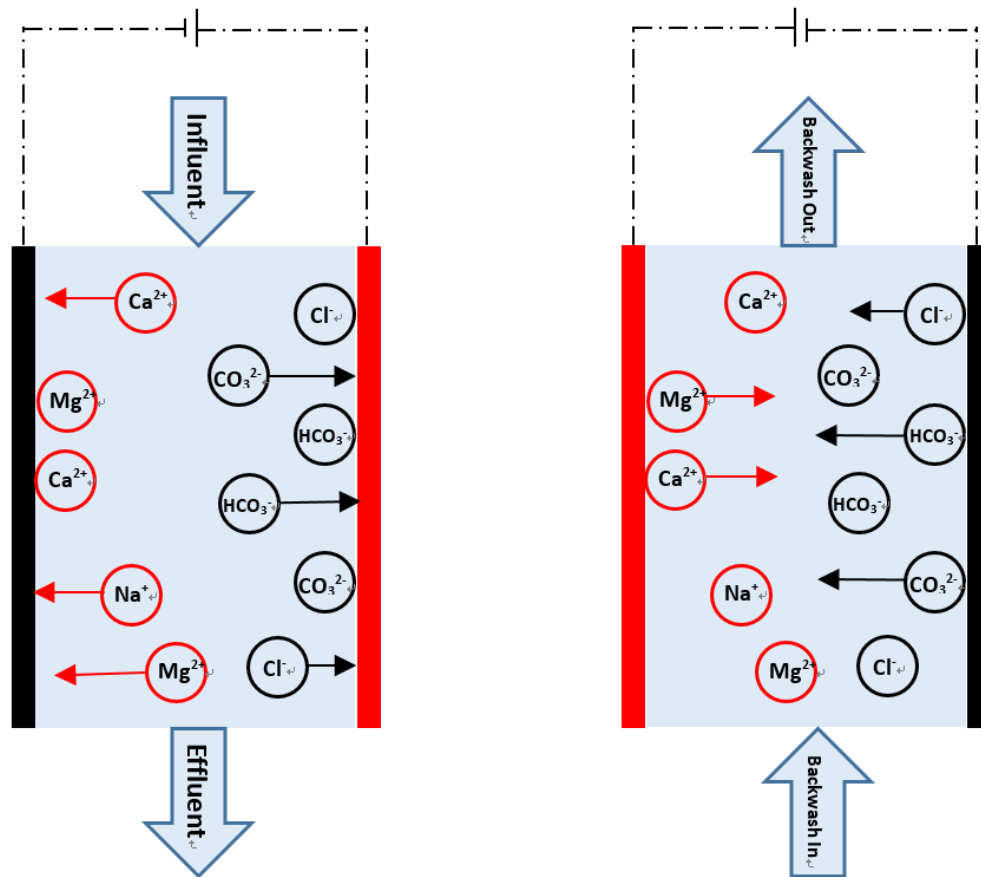
Figure 2.7 Capacitive deionization process working schematic. The left figure shows the normal operation condition. The right figure shows the backwash/cleaning process.

CDP is another possible physical scale prevention technology, and similar to ion exchange, CDP removes scale-forming ions. The scale reduction efficiency is around 80% (Fox et al., 2014). CDP unit does not utilize expensive membranes, does not require high-pressure input, does not require any chemical input, and does not need salt input. Since the principle of this

technology is to use electric potential difference to attract ions from the water, besides hardness ions removal, the treated water is almost pure with very little amount of ions. CDP may also be applied for desalination which can be used as an alternative to traditional reverse osmosis or electrical membrane methods.

Researchers have different opinions on preferential ion removal by CDI. Some research showed that monovalent ions are more preferred to be removed than divalent ions (Gabelich et al., 2002), while others reported that divalent ions are easier to be removed (Xu et al., 2008). Another study focusing on using CDI for hardness removal stated that in the continuous working phase, Ca^{2+} and Mg^{2+} ions removal showed higher efficiency than Na^+ ion removal (Seo et al., 2010). Moreover, problems such as finding a suitable electrode material to ensure the feasibility and the continuous reaction need to be studied in the future (Oren, 2008). Besides, the treatment unit requires the consumption of electricity and also needs running water to complete backwash procedure which generates concentrated brine. In addition, because of the high purity of the treated water, further treatment might need to be done to prevent the damage to the plumbing system.

CDI has the potential to be applied at the household level to prevent scaling problems. It has distinct advantages such as no chemical input, no salt input, no pressure requirement, and can assist in other minerals removal. However, the high requirement on electricity, brine generated, and the significant knowledge gap of CDI are main disadvantages.

Overall, this chapter described and summarizes four centralized technologies and six household technologies that are applied for softening or scale prevention purpose. All technologies have their unique advantages and disadvantages. Four centralized technologies are quite well studied; however, for household level, only ion exchange and membrane filtration are well studied and installed. Therefore, more research is needed for the other possible household scale prevention technologies as potential environmental friendly treatment options.

Chapter 3 Evaluation of Water Softening/Scale Prevention Technologies Using Multi-criteria Method

3.1 Introduction

As environmental problems become more complex, sustainability is increasingly important in solving problems and solutions that are environmentally friendly and energy saving are preferred. However, to meet sustainability goals, not only the effect and performance of a specific treatment needs to be considered, but also factors that will affect all stakeholders. Therefore, environmental decision making, technology comparison, and assessment require multi-disciplinary considerations which include socio-economic effects and ecological effects.

Decisions that depend solely on formal technical assessment tests or procedures are being questioned by representatives and stakeholders as they demand sustainable development, equity and trust, and many other factors that require input from all stakeholders (Antunes et al., 2006). What should be protected or sustained, and which factor should have higher weight also needs to be taken into account, instead of simply considering technical facts and performance of the solution itself (Forester, 1999).

Dealing with water-related problems is typically a complex undertaking influenced by many aspects. In order to design a suitable water treatment process, various factors need to be considered and assessed concurrently. Water quality, technical limitations, regulatory requirements, economic concerns as well as sustainability considerations will all affect the design and the decision making. Because of these multidisciplinary aspects that need to be considered, a systematic analysis such as a multi-criteria assessment (MCA) can be helpful. MCA is a decision-making tool which can be applied to compare different treatment choices in order to select the most applicable approach (Kiker et al., 2005). It is suited particularly well for those problems that have different options and need to evaluate different criteria. Generally, no

option is the most optimized with respect to all requirements; all alternatives have advantages and disadvantages. The goal of using the MCA method is to find a compromise or a more appropriate solution that can maximize the level of cost-benefit and socio-economic analysis results (Munda, 2012).

The MCA framework can be explained as an n×m evaluation matrix for which n represents a finite set of alternatives or options (in this chapter, it refers to different treatment technologies), while m represents different evaluation criteria which are used to evaluate the various alternatives (Hajkowicz & Collins, 2007).

The MCA method can quantify not only numerical factors but also qualitative factors. Thus, all factors that potentially affect the decision-making process can be included and considered. MCA is influential in policy-making regarding environmental sustainability related problems because this method aims for feasible multidisciplinary solutions. Besides, instead of only relying on experts' suggestions based on technical test results, stakeholders can also participate in the process and share their interests (Dodgson et al., 2009).

To proceed with the MCA process, the first step is to choose alternatives (treatments) that are of interest, and to decide on the criteria that will affect the decision. Then, the relative importance of each criterion is analyzed and a specific weight (W_n) is assigned to each criterion. The weight assignment is subjective, and this depends on which criterion is more important in the assessment. Then, according to the information collected for each alternative, relative indicator scores (S_n) are assigned for each criterion. Similarly, the score assignment is also subjective. The score only compares one treatment performance on this specific criterion in relation to the other alternative treatment options. Finally, the score (S_n) is multiplied by the weight (W_n) for each criterion for one treatment; and the scores are summed up to get the total score (Tn) for this treatment. Thus, $T_n = \sum_1^m (S_n \times W_n)$. The next step is to compare the final scores

of all treatment technologies which forms the basis for making decisions on which treatment is more preferred under the set of circumstances chosen.

Sensitivity analysis (SA) is a commonly applied method for a model or a system which aims to test the model/system robustness and uncertainty. SA results show the extent of the output variation (in this chapter, the total score) with the influential parameters changing in a specific range or under certain conditions (in this chapter, the criterion weight change) (Delgado & Sendra, 2004). For an MCA analysis, the subsequent SA analysis helps explain which criterion is most influential within the evaluation process.

As described in Chapter 2, there are many available technologies for both centralized and household scale. Because each technology has its unique advantages and disadvantages, it is difficult to make an informed decision except using a systematic assessment method.

The objectives of this chapter were to 1) use the MCA method to assess centralized, and household level water softening/scale prevention technologies, 2) propose preferences among all alternatives based on results of 1), and 3) do a sensitivity analysis on both centralized and household technologies assessments.

3.2 Method

3.2.1 Treatment options selected for assessment

This chapter assessed centralized and household softening technologies according to the background information provided in Chapter 2. Although reverse osmosis (RO) and nanofiltration (NF) both could remove water hardness, only nanofiltration is evaluated in this chapter. This is because RO removes almost all ions and is not applied solely for softening purpose (American Water Works Association, 2007). Centralized softening technologies being assessed in this chapter are: lime softening, pellet softening, nanofiltration, and ion exchange. Household softening/scale prevention technologies being assessed are: template assisted

crystallization (TAC), ion exchange (IX), nanofiltration (NF), electrically induced precipitation (EIP), magnetic water treatment, and capacitive deionization (CDI).

3.2.2 Criteria/Indicators selected to assess treatment alternatives

In this chapter, criteria that were chosen to proceed the treatment technology assessment are listed here: waste disposal, energy requirement, life-cycle cost, efficiency, whether further treatment is needed, whether chemicals are added, easy to use, and whether the technology is valid in practice.

The waste disposal relates to the regeneration of treatment residuals such as sludge that needs further treatment or has potential environmental effects, rejection from the membrane treatment, or concentrated brine from the regeneration of ion exchange resins. For water softening treatment technologies, brine concentrate refers to the water that discharged into the sewer system contains high salt concentration. Waste disposal is an essential part of sustainability considerations. Less waste correlates to a smaller environmental impact and thus is preferred to be used. Treatment that has the minimum environmental impact is preferred.

The energy requirement criterion considers pressure and electricity input requirements for a specific treatment technology. Some treatment technologies require pressurized operation conditions, and some other softening/scale prevention devices need to be connected to a power supply. The energy requirement is also an essential part of sustainability development. Generally, a technology that requires less energy requirement is the better choice. Lower or no energy input requirements also gives fewer restrictions on the unit operation which makes the unit more flexible to be used, for example in remote locations.

The life-cycle cost criterion is related to the users' expenses. It includes capital cost as well as operational and maintenance (O&M) cost. Capital cost refers to the first-time purchase and installation cost, and it is a one-time setup cost. However, this is not the total cost of the equipment, because O&M cost could affect the total expense spend as well. Operational cost

refers to any charge related to the unit operation, such as the cost caused by the electricity input, pressure addition, and treats unwanted residuals. Maintenance cost is generated by any manipulation that is done to maintain the unit, such as change media/membrane cartridge.

The 'subsequent treatment needed' criterion means whether the treated/finished water needs further treatment. For example, centralized pellet softening results in the softened water has a high pH which then requires pH adjustment before it can be distributed. Thus, this is also an important factor to be considered in technology selection. This criterion is applied to centralized technology assessment only because all selected household technologies do not require post-treatment on finished water.

The efficiency criterion focused on the technology performance or treatment efficiency (percentage reduction of scale formation) and used data provided by standard technology tests. Efficiency is also a non-negligible factor when deciding which technology to choose. In this chapter, the efficiency of different softening/scale prevention technologies was compared using the data from published reports. Efficiency criteria were only assessed for household technologies because all centralized technologies applied in water treatment plant have relatively high efficiency.

The 'easy to use' criterion focused on whether the technology and unit are easy to be operated by the user. This included whether the technology is too complicated to understand as well as whether the equipment itself is easy to install. This criterion was selected explicitly for the household level technology assessment since this is not a critical factor for centralized treatment.

The chemical addition criterion referred to whether any chemicals are required, and the amount needed during the unit process operation. Chemical addition increases the risk and thereby safety concerns and also increases the labor intensity. Besides, the chemical requirement also increases the operational cost. The chemical addition criterion was only used for the

centralized technology assessment since the household technologies assessed here do not require chemicals (except for ion exchange which uses sodium chloride to regenerate resin).

The certified or validated technology criterion reflected whether the technology is well-studied and whether data are available in published journals or reports. This criterion also considered if the technology has only been studied in research labs or if it has been applied widely.

3.2.3 Weight and score assignment

In order to compare different drinking water softening methods, several criteria/indicators were selected, as explained in section 3.2.2. However, not all criteria share the same importance in the assessment. The relative importance of the chosen criterion depends on the stakeholder's interest; therefore, different criteria are assigned different weight. Weight assignment is subjective; for a more crucial indicator, a higher weight is assigned to it. Total weights for both assessments were set at 100 in this assessment.

In this chapter's evaluation (initial assessment), more emphasis was put on sustainable goals (waste and energy input) as well as on cost and efficiency, because sustainable development and environmentally friendly technologies are gaining increasing attention currently. In addition, cost and efficiency are two commonly considered and also critical criteria when comparing different technologies. In contrast, other four criteria (subsequent treatment needed, chemical addition, and for household systems easy to use and validated/certified technology) were assigned a lower weight, because they were relatively less important in this evaluation compared to other criteria. Weight assignment summaries for centralized and household technologies are presented in Table 3.1 and Table 3.2.

Table 3.1 Weight assignments of criteria for centralized softening technologies

Criteria		Weight
Waste Disposal	Salt (Concentrate Brine)	14
	Sludge	14
Energy Requirement	Pressure	14
	Electricity	14
Life-cycle Cost	Capital Cost	14
	O&M Cost	14
Subsequent Treatment Needed		8
Chemical Addition		8
Total Weight		100

Table 3.2 Weight assignments of criteria for household softening/scale prevention technologies

Criteria		Weight
Waste Disposal	Salt (Concentrate Brine)	12
	Sludge	12
Energy Requirement	Pressure	12
	Electricity	12
Life-cycle Cost	Capital Cost	12
	O&M Cost	12
Efficiency		12
Easy to Use		8
Validated Technology		8
Total Weight		100

Similarly, score assignment is also subjective, and relative scores were assigned depending on the actual performance of one technology compared to the other technology alternatives. Assessment scores used in this chapter ranged from 0 to 5. A score closer to 0 meant that the technology had a relatively worse performance for that specific criterion, and closer to 5 indicated that the technology had a relatively better performance than others. For qualitative criteria that can be answered by yes or no, the score assigned 0 to yes and 5 to no or a sliding

scale from 0-5 (worst to best) was used based on the extent of the criterion. For quantitative criteria (life-cycle cost and efficiency), first, alternatives were ranked based on the data from literature, and then a score (from 0 to 5) was assigned accordingly. Score assignment summaries of both centralized and household technologies are presented in Table 3.3 and Table 3.4.

Table 3.3 Centralized softening technology: criteria score assignment

Criteria		Type	Score
Waste Disposal	Salt (Concentrate Brine)	Yes/No	Yes - 0 No - 5
	Sludge	Yes/No	Yes - 0 No - 5
Energy Requirement	Pressure	Yes/No	Yes - 0 No - 5
	Electricity	Yes/No	Yes - 0 No - 5
Life-cycle Cost	Capital Cost	Low/Medium/High (pairwise comparison)	Low – 3 to 5 Medium – 1 to 3 High – 0 to 1
	O&M Cost	Low/Medium/High (pairwise comparison)	Low – 3 to 5 Medium – 1 to 3 High – 0 to 1
Subsequent Treatment Needed		Yes/No	Yes - 0 No - 5
Chemical Addition		Subjectively defined according to the hazards and the amount required	0-5, a lot amount added to no addition

Table 3.4 Household softening technology: criteria score assignment

Criteria		Type	Score
Waste Disposal	Salt (Concentrate Brine)	Yes/No	Yes - 0 No - 5
	Sludge	Yes/No	Yes - 0 No - 5
Energy Requirement	Pressure	Yes/No	Yes - 0 No - 5
	Electricity	Yes/No	Yes - 0 No - 5
Life-cycle Cost	Capital Cost	Low/Medium/High (pairwise comparison)	Low – 3 to 5 Medium – 1 to 3 High – 0 to 1
	O&M Cost	Low/Medium/High (pairwise comparison)	Low – 3 to 5 Medium – 1 to 3 High – 0 to 1
Efficiency		Low/Medium/High (pairwise comparison)	Low - 0 to 1 Medium - 1 to 3 High - 3 to 5
Easy to Use		Subjectively defined according to how difficult to use	0-5, hard to easy
Validated Technology		Subjectively defined according to how developed the technology is	0-5, not certified to well developed

Waste disposal was a criterion for centralized and household softening technology evaluations. This is a qualitative factor, and it involves sludge and brine generation. If no sludge (brine) is created, the score is 5. In contrast, if sludge (brine) is created, the score is 0.

Energy requirement was a criterion for centralized and household softening technology evaluations. This is a qualitative factor, and it involves electricity and pressure input. If the process does not need electricity (pressure) input, the score is 5. In contrast, if the process needs electricity (pressure), the score is assigned 0.

Life cycle cost was a criterion for centralized and household softening technology evaluations. This is a quantitative factor, and it involves capital cost, and operational and maintenance cost. All cost data presented in the results summary tables (Table 3.5 and Table 3.6) were collected from the literature. According to their relative cost from high to low, scores of 0 to 5 were assigned accordingly. Lower cost for capital, operation, and maintenance is preferred. For centralized technologies, there was no article that summarized and compared the cost of all selected technologies, because the cost of centralized treatment is usually related to capacity, volume and many other, often site-specific factors. Therefore, it is difficult to compare the cost using exact numbers directly. In this section, based on various report and articles, a relative comparison was used to compare the cost of different technologies.

'Subsequent treatment needed' was a criterion for centralized softening technologies evaluation only, because none of the selected household technologies need further treatment of the finished water. This is a qualitative factor. If the process does not require any subsequent treatment, the score is 5. In contrast, if the process requires subsequent treatment, the score is 0.

Efficiency was a criterion for household technologies assessment only, because all four centralized technologies have relatively high hardness removal performance, and therefore, their efficiencies are also high and do not differ too much. Efficiency is a quantitative factor. According to efficiency data presented in Table 3.6, with a higher percentage hardness removal reported, the score is closer to 5.

Chemical addition was selected for centralized softening only because all selected household technologies do not require chemical input for the treatment process except for salt

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addition for ion exchange media regeneration. This is a qualitative factor but with a sliding scale. If no chemical is added during the process, the score is assigned 5. If chemicals are needed, the more chemical added or the more hazardous, the lower the score.

'Easy to use' was a criterion for household softening only. This is a relatively subjective qualitative factor and with a sliding scale. Comparing the technologies, if the technology is more straightforward for residents to install and use, the score assigned is closer to 5.

Validated/certified technology was a criterion for household softening only because all four centralized technologies are well developed, studied, and are widely applied, thus, they are all validated technologies. This is a qualitative factor with a sliding scale. If the technology is well studied and has reports in the peer-reviewed literature, commonly used and has a commercial product available on the market, then its score is high and closer to 5. In contrast, if the technology is not widely applied and still under research, then the corresponding score is low

Summaries of score assignment for centralized softening technologies criteria and household softening/scale prevention technologies criteria are listed in Table 3.3 and Table 3.4**.**

3.3 Assessment results and discussion

After setting the criteria that will be considered in the assessment process, the next step was to collect information and data in terms of these criteria for each alternative. In this section, information and data of selected centralized softening technologies and household softening technologies were collected from published literature or test results which are stated in Chapter 2: Literature Review. A summary of technologies' technical details is shown in Table 3.5 and Table 3.6. Information selected and summarized in the table is according to the criteria used in this assessment.

According to the report created by Finnesgaard et al. (2017), the capital cost of nanofiltration was higher than ion exchange, but the cost of two technologies was converging with higher flow requirements. Bergman (1995) stated that nanofiltration softening capital cost

was higher than lime softening, but they became similar with higher production capacity. Wilbert et al. (1999) stated that lime softening had higher capital cost than ion exchange. Pellet softening had lower capital cost than lime softening (Hofman et al., 2006). Therefore, the rank (from high to low) of capital cost for centralized technologies is nanofiltration, lime softening, ion exchange, and pellet softening. In terms of O&M cost, according to Bergman (1995), nanofiltration had higher O&M cost than lime softening. From the report prepared by the U.S. Department of Interior (2009), pellet softening had slightly higher O&M cost than ion exchange. Therefore, these two technologies were assigned the same score for the O&M criteria. Comparing the O&M cost of lime softening and pellet softening, it is obvious that lime softening cost more than pellet softening, mainly because of the extensive wet sludge treatment and transportation needed for lime softening. In contrast, pellet softening residuals can be more easily reused and more cost-effective to dispose, as described in Chapter 2. Therefore, the rank (from high to low) of O&M cost for centralized technologies is nanofiltration, lime softening, pellet softening, and ion exchange.

Table 3.5 Summary information for centralized softening technologies

Criteria		Lime Softening	Pellet Softening	Nanofiltration	Ion Exchange
Waste Disposal	Salt (concentrate brine)	No	No	Yes	Yes
	Sludge	Yes -Wet sludge (huge amounts)	No -Only dry pellets produced, can be recycled	No	No
Energy Requirement	Pressure	No	No	Yes	No
	Electricity	No	No	No	No
Life-cycle Cost	Capital Cost	Medium	Low	High (much higher than IX)	Medium (lower than lime softening)
	Operation and Maintenance cost	Medium (higher than pellet softening and IX)	Medium (similar to IX)	High (much higher than IX)	Medium
Subsequent Treatment Needed		Yes -Softened water needs pH adjustment	Yes -Softened water needs pH adjustment	Yes -Need to add corrosion inhibitors to stabilize the water	No

Table 3.5 (continued). Summary information for centralized softening technologies

Criteria	Lime Softening	Pellet Softening	Nanofiltration	Ion Exchange
Chemical Addition	Yes -Lime $Ca(OH)_2$ Soda-ash Na_2CO_3 as the main reactant	Yes -Add NaOH or lime to facilitate crystallization	No - But might need chemicals for cleaning of membranes.	No -But need NaCl salt for resin regeneration
Other Components Removed	-Radium 226 & 228 -Arsenic -Uranium -Heavy metals -TOC	-Iron/Magnesium -Phosphorus -Sulfate -Heavy metals	-Organics/inorganics -Bacteria/virus -TOC -Cryptosporidium -NOM thereby reducing DBP formation -Partial TDS -Pesticides	Almost all divalent cations
Major Concerns	-Sludge generation -Softened water needs pH adjustment -Chemical addition -Large footprint -Increased PH	-Increase pH for crystallization -Softened water needs pH adjustment -Smaller footprint than lime softening	-Membrane fouling -Membrane cleaning -Membrane capacity and lifetime -High cost	-Concentrated brine created -A large amount of salt needed -High cost

Table 3.6 Summary information for household softening technologies

Criteria		Template Assisted Crystallization	Ion Exchange	Nanofiltration	Electrically Induced Precipitation	Magnetic Water Treatment	Capacitive Deionization
Waste Disposal	Salt (concentrate brine)	No	Yes	Yes	No	No	Yes
	Sludge	No	No	No	No	No	No
Energy Requirement	Pressure	No	No	Yes	No	No	No
	Electricity	No	No	No	Yes	Yes	Yes
Life-cycle Cost* (Fox et al., 2014)	Capital Cost	Medium $1098	Medium to high $2048	High (Much more than IX)	High $2375	Low $760	High $4000
	O&M	Low CAD 76	Low to medium CAD 168	Medium (Much more than IX)	Medium CAD 194	Low CAD 11	Low to medium CAD 102
Efficiency (Fox et al., 2014)		>88%	>90%	>90%	~50%	17%-70%	~80%
Easy to Use		-Easy to install -Very low requirements on daily maintenance	-Easy to install and widely applied -Need to add salt regularly to regenerate the resin	-Require pressure generated unit	-Not that easy compared to TAC, IX, and NF -Needs frequent electrode cleaning	-Not easy to install, wires need to be across the pipe properly -Control the electricity current	-Not that easy compared to TAC, IX, and NF -Special requirements on installation

*: Cost data are calculated for 10-year usage. Electrical devices are powered 24/7. All systems were analyzed for a single-family residence with water hardness around 150 grains per gallon (2.56 kg/m^3) and daily water usage 300 gallons (1136 L) per day

Table 3.6 (continued) Summary information for household softening technologies

Criteria	Template Assisted Crystallization	Ion Exchange	Nanofiltration	Electrically Induced Precipitation	Magnetic Water Treatment	Capacitive Deionization
Validated Technology	Commercially available -Newly applied at the household level -Not well studied	Yes Commercially available -Quite popular -Well studied	Yes Commercially available -Well studied	Not quite commercially available, but not widely used	Not quite Commercially available, but not widely used	Not quite Commercially available, but not widely used
Major Concerns	-Hardness remains in the water in the form of micro-crystals	-NaCl salt as regenerant -Concentrated brine created during resin regeneration	-Pressure needed -Membrane replacement -High cost	-High energy requirement -Low efficiency	-High energy cost -Not stable -Low efficiency	-High energy cost -Appropriate electrode material needed

On the basis of information summarized in Table 3.5 and Table 3.6, as well as score assignment guidelines provided in section 3.2.3 (Table 3.3 and Table 3.4), each technology was assigned a score according to the performance of each criterion. The score assignment and total score results are shown in Table 3.7 and Table 3.8.

From Table 3.7 which shows the centralized technology assessment results, pellet softening has the highest score 402, which means it is the most applicable or the preferred centralized technology based on this assessment. Pellet softening has the full score (5) for most of the criteria selected. Only two main concerns need to be considered: the first one is the cost for the entire treatment unit. Due to the large unit size and relatively high labor and expertise required, capital and O&M cost cannot be ignored. However, considering a high volume throughput of this treatment technology, the cost is not extremely high. Another concern of pellet softening is that it requires some chemical input. As described in Chapter 2, pellet softening generally requires the addition of lime or NaOH to promote $CaCO_3$ precipitation. Because of this chemical addition, the treated water pH needs to be adjusted by CO_2 or other acid addition to neutralize the softened water and to meet regulations.

The second-ranked technology of centralized softening processes is ion exchange. This technology is not commonly used on a centralized scale. Its main drawback is the large volume of concentrated brine created during regeneration that has potential environmental impacts on natural water system because chloride is not well removed in receiving wastewater treatment plants and is therefore discharged in the receiving surface water body.

The third highest score of centralized softening technology is lime softening. Even though it is the earliest and most mature centralized softening technology in use, its high chemical demand, the large amount of wet sludge created and the high cost related to further treatment resulted in its low total score.

Nanofiltration gets the lowest score among all technologies selected. The main drawback is the high cost which is a common disadvantage for membrane treatments.

The high cost comes from membrane purchase and also replacement cost caused by membrane fouling. As a centralized application, nanofiltration treatment unit needs chemical cleaning and also need to dispose the concentrate. Another distinct disadvantage is the high energy requirement because of the high-pressure demand. However, the main advantage of nanofiltration is that it can remove many other substances in the water, which can assist in generating high-quality drinking water. In particular, it can remove NOM and thereby reduce DBP formation in the finished drinking water. Its high hardness removal efficiency is also an advantage that should not be ignored.

All four technologies for centralized treatment discussed above are successfully used in many drinking water treatment plants.

The household technologies assessment results shown in Table 3.8 indicate that template assisted crystallization (TAC) has the highest score. However, its main problem is that it should be working well in theory, and it is not widely applied in the real world. There is a relatively low quantity of published literature available. The most attractive character of TAC is that it is environmentally friendly and easy to operate at home. TAC only requires media for the treatment process with no by-products generated and no energy input required. Another unique quality of TAC is that it does not remove hardness ions from water, and it rather prevents scale formation in pipes and on the heating surface. To some extent, no hardness removal character is also good for some individuals that are restricted to a low-sodium diet. However, this advantage is not listed in the criteria for the assessment because it is not a concern for everyone. Moreover, if test results confirm the performance of TAC technology, it will have the potential to be widely applied, because it is the most environmentally friendly process among all alternatives.

Ion exchange is the second highest scoring technology. It is currently widely used in households with quite a high efficiency in hardness ions (Ca and Mg) removal. Ion exchange is also straightforward to use. Its main disadvantage is the high use of NaCl salt as the resin regeneration chemical. Regeneration of resins generally

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creates a large amount of brine which is typically discharged into the sewer system. As mentioned in Chapter 2, water with a high chloride concentration could pose a potential threat to the freshwater ecosystem. As this surface water may be used as raw water for drinking water production and because traditional drinking water treatment processes cannot efficiently remove chloride, it can be a potential threat to drinking water quality as well.

Electrically induced precipitation, magnetic water treatment, and capacitive deionization are three physical softening treatment technologies with relatively low marks in this assessment. They are not commonly used by residents, although there are commercial products available. The main disadvantages are that electricity input is required and the high cost. All three treatment processes depend mainly on electricity input to work. Because of their unique treatment unit structures and the general need to be installed inline, the cost of these physical treatment technologies could be high. In addition, physical softening treatments are still under investigation because the efficiency is highly affected by influential factors. Therefore, the hardness removal efficiency of these technologies still needs further testing and research. Also, optimizations such as using better performing electrode materials need to be considered and tested as well.

Nanofiltration has the lowest score. Nanofiltration has high efficiency in water hardness removal. However, there are three main disadvantages of nanofiltration at the household scale. The first one is the high cost of the treatment unit and the subsequent change of membrane cartridge. The second drawback is that nanofiltration needs a continuous pressurized operating condition. For a household unit, pressure input requires additional plumbing changes. Another problem related to nanofiltration is that the unit generates a concentrate that contains high ion concentration (rejected by the membrane).

Table 3.7 Centralized technologies assessment results

Total Score = Sum (Weight × Score)

Criteria		Weight	Lime Softening		Pellet Softening		Nanofiltration		Ion Exchange	
			Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal
Waste Disposal	Salt (Concentrate Brine)	14	5	70	5	70	0	0	0	0
	Sludge	14	0	0	5	70	5	70	5	70
Energy Requirement	Pressure	14	5	70	5	70	0	0	5	70
	Electricity	14	5	70	5	70	5	70	5	70
Life-cycle Cost	Capital Cost	14	2	28	4	56	1	14	3	42
	O&M Cost	14	2	28	3	42	1	14	3	42
Subsequent Treatment Needed		8	0	0	0	0	0	0	5	40
Chemical Addition		8	0	0	3	24	4	32	4	32
Total Score		100	N/A	266	N/A	402	N/A	200	N/A	366

*Score 5 is the best score and score 0 is the worst score.

Table 3.8 Household technologies assessment results

Total Score = Sum (Weight × Score)

Criteria		Weight	Template Assisted Crystallization		Ion Exchange		Nanofiltration		Electrically Induced Precipitation		Magnetic Water Treatment		Capacitive Deionization	
			Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal
Waste Disposal	Salt (Concentrate Brine)	12	5	60	0	0	0	0	5	60	5	60	0	0
	Sludge	12	5	60	5	60	5	60	5	60	5	60	5	60
Energy Requirement	Pressure	12	5	60	5	60	0	0	5	60	5	60	5	60
	Electricity	12	5	60	5	60	5	60	0	0	0	0	0	0
Life-cycle Cost	Capital Cost	12	4	48	3	36	1	12	3	36	5	60	0	0
	O&M Cost	12	5	60	2	24	0	0	2	24	5	60	3	36
Efficiency		12	4	48	5	60	5	60	1	12	0	0	3	36
Easy to Use		8	4	32	4	32	4	32	3	24	1	8	3	24
Validated Technology		8	1	8	5	40	5	40	2	16	1	8	2	16
Total Score		100	N/A	436	N/A	372	N/A	264	N/A	292	N/A	256	N/A	232

*Score 5 is the best score and score 0 is the worst score.

3.4 Sensitivity analysis

A sensitivity analysis (SA) is a helpful tool to evaluate how the variance of factors will affect the decision-making process (Pannier et al., 2018) and it is a typical follow-up process for assessments. Therefore, a sensitivity assessment was performed in this research as well. In this section, the main aim of this SA was to analyze if the assessment result (technology ranks) was affected by the stakeholder's perceived importance of the various criteria. SAs that were done for both centralized and household levels in this section were to keep the total score (100) same and changed the percentage weight according to different cases.

3.4.1 Sensitivity analysis for centralized technologies

The original assessment put more weight on waste, energy requirement, cost and efficiency criteria as presented in Table 3.7. In order to do the SA by changing the percentage weight of the different criteria, three cases were chosen, and the weight assignment is presented in Table 3.9. Case 1 assumed that sustainability development related factors gain more focus even though the stakeholder needs to spend more money on the treatment. Case 2 represented a situation that with excellent softening performance, the cost is a primary consideration. In Case 3, all criteria share the same importance in the assessment.

Calculated results for each case are presented in Appendix A Tables A.1, A.2, and A.3. The SA results considered the original case and the three new cases, an overview is presented in Figure 3.1. As can be seen from the figure, pellet softening always had the highest score under different case conditions, although the score fluctuated because of the weight change. Therefore, pellet softening was always the best solution and was not affected by the weight change. Ion Exchange was always the second best option and had the least up and down variation. Lime softening score changed up and down for different cases but kept at rank 3. Nanofiltration got the lowest mark for all cases that analyzed. Although nanofiltration has great advantages in water softening and other treatment, based on the criteria selected in this chapter,

nanofiltration was always the least preferred. In summary, for all three scenarios considered in the SA, the overall scores fluctuated, but the relative ranks did not change.

Table 3.9 Weight assignment for sensitivity analysis for centralized technologies

Criteria		Weight			
		Original	Case 1	Case 2	Case 3
Waste Disposal	Salt (Concentrate Brine)	14	17	8	12.5
	Sludge	14	17	8	12.5
Energy Requirement	Pressure	14	17	8	12.5
	Electricity	14	17	8	12.5
Life-cycle Cost	Capital Cost	14	8	26	12.5
	O&M Cost	14	8	26	12.5
Subsequent Treatment Needed		8	8	8	12.5
Chemical Addition		8	8	8	12.5
Total Weight		100	100	100	100
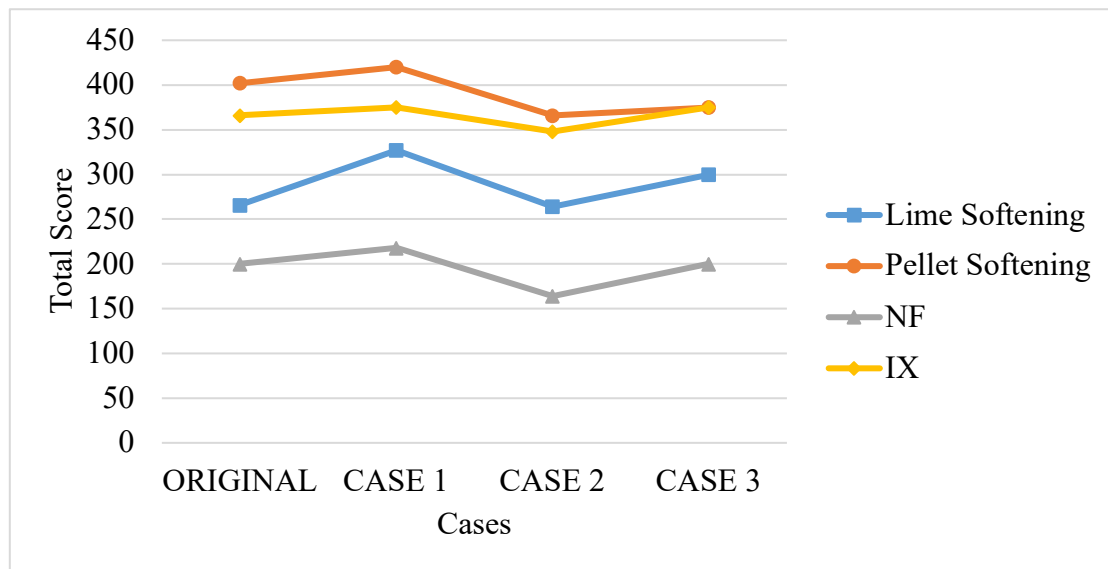
Figure 3.1 Sensitivity analysis results of centralized technologies

3.4.2 Sensitivity analysis for household technologies

Similarly, as for the centralized technologies assessment, the same SA approach was used for the household technologies. As presented in Table 3.10, since the total score was kept at 100 and some of the criteria were different than for the centralized technologies, the assigned weights differed from centralized technology assessment. Because efficiency is always the important factor one need to consider when purchasing the softening unit, efficiency criterion weight was kept at a relatively high value (12) and was maintained throughout three different cases.

Detailed calculated results for each case are presented in Appendix A Tables A.4, A.5, and A.6. SA results considering the original and three new cases are presented in Figure 3.2. Results showed that even with different weight assignments, TAC always had the highest score which was much higher than all other treatment options. TAC also showed the least fluctuation pattern under different case conditions. This meant that TAC is the preferred option using the selected criteria. Ion exchange was the second best choice in all assessment cases. Magnetic water treatment method got the third highest score for the original case and case 2, and in case 2, the score of magnetic water treatment method is close to ion exchange. While for the other two cases, three technologies seem to cluster together. Case 2 emphasized on cost criteria as well as efficiency, which indicates that if only care about cost and efficiency, magnetic water treatment method is the most preferred among these three physical methods. Nanofiltration got the second lowest score for all three cases analyzed. This is because for the criteria used in this chapter, nanofiltration performed terrible for most of criteria. From the sensitivity analysis results, the total score or preference rank was affected by which criteria the user cares more about. In summary, for all three scenarios considered in the SA, the overall scores fluctuated, but the relative ranks did not change.

Table 3.10 Weight assignment for sensitivity analysis of household technologies

Criteria		Weight			
		Original	Case 1	Case 2	Case 3
Waste Disposal	Salt (Concentrate Brine)	12	14	8	11
	Sludge	12	14	8	11
Energy Requirement	Pressure	12	14	8	11
	Electricity	12	14	8	11
Life-cycle Cost	Capital Cost	12	8	20	11
	O&M Cost	12	8	20	11
Efficiency		12	12	12	12
Easy to Use		8	8	8	11
Validated Technology		8	8	8	11
Total Weight		100	100	100	100
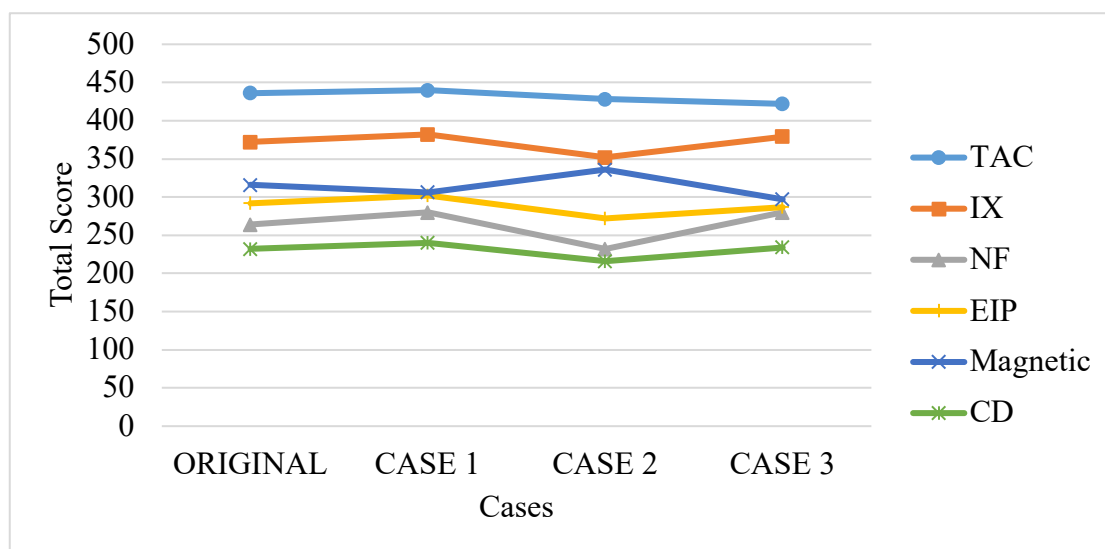
Figure 3.2 Sensitivity analysis results of household technologies

3.5 Conclusions

Currently, solving environment-related problems commonly require multi-disciplinary consideration. Besides treatment efficiency and technical performance aspects, sustainability factors are increasingly important in decision making. Drinking water related treatments are no exception. Manufacturers, operators, policymakers, and even residents are looking for treatment

methods that can integrate treatment goals as well as sustainable development and environmentally friendly goals. Multi-criteria assessment (MCA) methodology is a useful assessment tool to compare different treatment alternatives, regarding selected criteria that combine sustainability evaluations as well.

MCA assessment was used in this chapter to evaluate centralized and household level softening/scale prevention technologies by selected quantitative (life-cycle cost and efficiency) and qualitative (waste disposal, energy requirement, whether further treatment is needed, whether chemicals are added, easy to use, and whether the technology is validated) criteria. Different weights were assigned to different criteria, and scores were assigned based on the technology performance. Sensitivity analysis (SA) was also done for centralized and household technologies. Weights of criteria were changed based on different assessment cases.

Centralized water softening technology assessment results showed:

- Pellet softening scored highest and is a widely used and well-developed process applied in European countries, with high efficiency and relatively low environment impacts. SA results showed that pellet softening got the highest rank for all cases selected.

- Ion exchange gave the second highest total score although it is not usual to be implemented in a centralized scale. SA results showed that under certain cases, the score could be close to pellet softening.

- Lime softening has the third highest score and the rank did not change in SA cases, although it is well developed and applied.

- Nanofiltration received the lowest score, and the rank did not change in SA cases.

Household water softening/scale prevention technology assessment results showed:

- Template assisted crystallization (TAC) gained the highest score and the rank did not change in SA cases. The particular concern for this salt-free scale prevention technology is that this is a newly developed and applied technology with insufficient published literature.

- Ion exchange received the second highest score, and the rank did not change in SA cases. It is the most commonly used household softening technology currently with concerns

about potential threats caused by chloride salt.

- Nanofiltration and three physical treatment options received relatively low scores. According to SA results, the relative rank was affected by the criteria weight assignment.

Chapter 4 Performance of Template Assisted Crystallization (TAC) for Scale Prevention in Drinking Water

4.1 Introduction

In Ontario, a major drinking water source is groundwater, which generally has high mineral content. Therefore, drinking water supplied by groundwater typically encounters high water hardness levels. It is not unusual for a natural groundwater source to have calcium concentrations up to 100 mg/L (250 mg/L $CaCO_3$ equivalent) or in some cases even higher. Magnesium, which is another hardness component present in the natural groundwater, typically has lower concentrations, which can range from negligible to 50 mg/L (World Health Organization, 2010). Thus, calcium hardness generally is the predominant part of the total water hardness.

The Region of Waterloo has a drinking water hardness of 291-651 mg $CaCO_3$/L (Water Softener Facts, 2018); the City of Guelph's drinking water hardness level ranges from 320 to 550 mg $CaCO_3$/L (City of Guelph, 2018); the City of Cambridge has a drinking water hardness level ranges from 340 to 548 mg $CaCO_3$/L (Water Softener Facts, 2018); Oxford County has a drinking water hardness level ranges from 189 to 1390 mg $CaCO_3$/L. According to the hardness level categorization stated in Chapter 2, all areas mentioned have a very hard water supply. In order to minimize side effects caused by hard water (more detergent consumption and scaling problems), softening/scale prevention technologies are needed. Centralized softening technologies such as the lime softening and the pellet softening are widely used in Europe and some parts of the United States, respectively. The most commonly applied softening technology in Ontario is ion exchange, and ion exchange units are commonly installed at the household level. However, with ion exchange units being more widely applied, two problems have to be taken into consideration: excessive chloride salt discharge into the municipal sewer during regeneration and elevated sodium levels in softened drinking water.

Ion exchange unit uses sodium chloride salt to regenerate the resin, the concentrated brine generated after the regeneration process is discharged into the sewer system and contains high Cl^- concentration. Although the groundwater chloride input mostly comes from the widespread use of road salt during the winter period, industrial and residential water softener application is causing drinking water sources to become more saline as well (Flodman & Dvorak, 2012).

According to Gombos (2016), Waterloo Region and Guelph generate a billion liters backwash water per year and 51,000 tonnes salt is discharged into the environment per year. Therefore, the overall amount of Cl^- salt discharged by household ion exchange units can be quite significant. The major part of wastewater NaCl flow comes from industrial and residential softeners' waste (Sanitation Districts of Los Angeles County, 2005). Other studies also showed that chloride might seriously affect surface water and groundwater quality (Hoffman et al., 1981; Wilcox, 1986; Panno et al., 1999). Chloride is soluble and mobile, and it is not subject to any natural removal or water treatment processes (NH Department of Environmental Service, n.d.). Once chloride is discharged into natural water sources, it remains in the watershed until it passes to a downstream watershed. Especially for groundwater which has a long residence time, adverse effects such as causing saline groundwater wells can be non-negligible (Duke & Erickson, 2003; NH Department of Environmental Service, n.d.). An elevated chloride concentration is harmful to many forms of aquatic flora and fauna. Excess chloride intake by flora and fauna causes problems in their growth, reproduction, and survival (Siegel, 2007). Elevated chloride levels in drinking water sources also cause taste and odor problems, and corrosion problems in distribution systems if over 250 mg/L (Health Canada, 2017). Chloride is not regulated by a maximum acceptable concentration (MAC) value, but EPA sets an acute chloride value at 860 mg/L and a chronic value 230 mg/L for aquatic ecosystems (USEPA, 1988). Health Canada and Ontario Drinking Water Objectives also target 250 mg/L as the suggested maximum chloride level for an aesthetic objective in drinking water (Ontario M.O.E, 2003; Health Canada, 2017).

Hard water that contains high calcium concentration is likely to affect those individuals who are prone to milk-alkali syndrome and hypercalcemia (World Health Organization, 2010). With the application of a softener, the calcium ion concentration of water is reduced substantially while the sodium concentration is elevated. Excess sodium intake has potential adverse effects on human health, and it can be of particular concern to people who are restricted to a low-sodium diet because of for example, high blood pressure (Siegel, 2007). Suggested levels for sodium and chloride are summarized in Table 4.1.

Table 4.1 Summary table of suggested sodium and chloride levels. (N/A: not available; AO: aesthetic objective)

	Sodium (Na$^+$)	Chloride (Cl$^-$)	Water Source	Reference
Human Health	200 mg/L (AO) Need to notify residents if Na$^+$ exceeds 20 mg/L	250 mg/L (AO)	Drinking water	Health Canada, 2017; Ontario M.O.E, 2003
Aquatic Organisms	N/A	Acute: 860 mg/L Chronic: 230 mg/L	Surface water	USEPA, 1988
Wildlife	N/A	600 mg/L (recommended maximum)	Surface water	Napgal, Levy & MacDonald (2003)

Because of these potential problems, salt-free softening or scale prevention technologies are becoming more popular. According to the information and the assessment done in Chapter 3, template assisted crystallization (TAC) achieved a high evaluation result as a salt-free and environmentally friendly scale prevention technology. The TAC unit only uses polymer beads with plenty of nucleation sites on the beads' surface, and no other chemical input is required. The up-flow system allows free Ca^{2+}, and Mg^{2+} to nucleate on the media surface (nucleation sites) and to form chemical stable microcrystals which eventually slough off (Fox et al., 2014). These microcrystals help prevent hard scale formation in kettles, pipelines, and other house appliance as they flow through the pipes (Watch® Water, n.d.; Home plus, 2017). Since the treated water still has all hardness ions in the water, it avoids some of the negative effects of softened water. In a report prepared by C3 Water Inc. (2015) for the City of Guelph, TAC treatment was mentioned as a salt-free scale prevention method. Fox et al. (2011) also conducted research which showed good performance in scale prevention using DWGW W512 standard test method (DVGW, 1996). Cost and efficiency analysis also showed a great application prospect (Fox et al., 2014).

The application of nucleation theory in household drinking water scale prevention is relatively new, and there is a need to evaluate the performance scientifically.

Parameters that can represent the scale-forming and scale-dissolving tendencies of water are calcium carbonate ($CaCO_3$) saturation indices. Two commonly used indices are the Langelier Saturation Index (LSI) and Calcium Carbonate Precipitation Potential (CCPP). Negative index values represent water undersaturated with $CaCO_3$ and prone to dissolve scale and vice versa, positive index values represent water saturated with $CaCO_3$ and prone to precipitate scale.

The main objectives of this chapter were to evaluate the performance of the TAC technology with respect to 1) changes in water quality after treatment, 2) quantification and determination of the approximate size of the microcrystals, and 3) changes in scale formation after treatment. With respect to 1), the following parameters were investigated: reduction in total and free Ca ions; change in other metal ion concentrations; and change in scaling indices. With respect to 3), a simplified scale test method was developed to measure scale formation for TAC treated and untreated water.

4.2 Materials and methods

4.2.1 Material

The template assisted crystallization (TAC) anti-scale treatment system used in this experiment consisted of two parts: the tank and the media. According to the desired flow rate of 3-5 US gallons per minute (GPM) (1.89×10^{-4}-3.15×10^{-4} m^3/s), a specific water tank was selected. The tank was a model 844 OneFlow (Watts®, ON, Canada) with a maximum flow rate requirement of 12 GPM. The tank volume was 38 L, and the pipe thread size is 3/4 inch. The media used in this experiment was produced in Germany in the form of double layered coated modified ceramic beads. The media appearance was that of white opaque solid granules; the approximate media effective size was 0.55-0.75 mm. According to the selection guideline, with an expected flow rate of 3-5 GPM and an influent hardness level of 200-550 mg/L $CaCO_3$, 3.3 L of TAC media were placed in the treatment tank.

The operational requirements for the anti-scale system used in this experiment are listed in Table 4.2. The approximate lifespan of the media used was estimated to be about 3-5 years based

on the information provided by the producer. The lifespan of the media depends on the source water quality and the volume of house water treated.

Table 4.2 TAC unit operation requirements (according to user manual)

Parameter	Operating Range
Operating Temperature	3°C- 90°C
pH Range	6.5 - 9.5
Maximum Hardness (as $CaCO_3$)	1400 mg/L
Maximum Salinity	35000 mg/L
Maximum Fe^{2+} Concentration	0.2 mg/L
Maximum Mn^{2+} Concentration	0.05 mg/L
Maximum Free Chlorine Concentration	3 mg/L
Maximum Cu^{2+} Concentration	1.3 mg/L

4.2.2 Experimental set-up and sampling plan

In this experiment, two source waters with different water qualities were used to test the TAC unit performance. At location A, two units (unit A and unit B) were tested in parallel to ascertain comparability between two different treatment trains from June 2018 until August 2018. Because of the site limitation, only unit B was moved to location B and testing continued from September 2018 to October 2018. The experimental steps were the same at both locations.

For the first phase, TAC units were set up in location A. Two brand new TAC units with 3.3 L media in each tank were set up in parallel as presented in Figure 4.1. Figure 4.2 shows the unit setup at each location. The two units were fed the same source water. All pipes used in this set-up were made from soft PVC. On both influent lines, valves were installed to control the water flow rate of the two TAC units within 12-14 L/min. This was done to ensure that the two units

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were run under the same conditions. Both flowmeters were the Burkert® type 8030 inline flow sensors which were connected to a Burkert® 8619 data logger with one-time flow rate display.

There were two sampling points for each unit, one on the influent line and another on the effluent line. 2 L influent (untreated) and 2 L effluent (treated) water samples were taken twice per week using wide-mouth polyethylene plastic bottles. At location A, the experiment was run for three months (from June 2018 to August 2018). The units were run sporadically, and on each sampling day, units were started and run for 2 hours at a flow rate 12-14 L/min before taking samples. At location B, the experiment was run for three weeks and unit B was operated continuously at a flow rate 12-14 L/min. The parameters measured for each water sample are listed in Section 4.2.3.
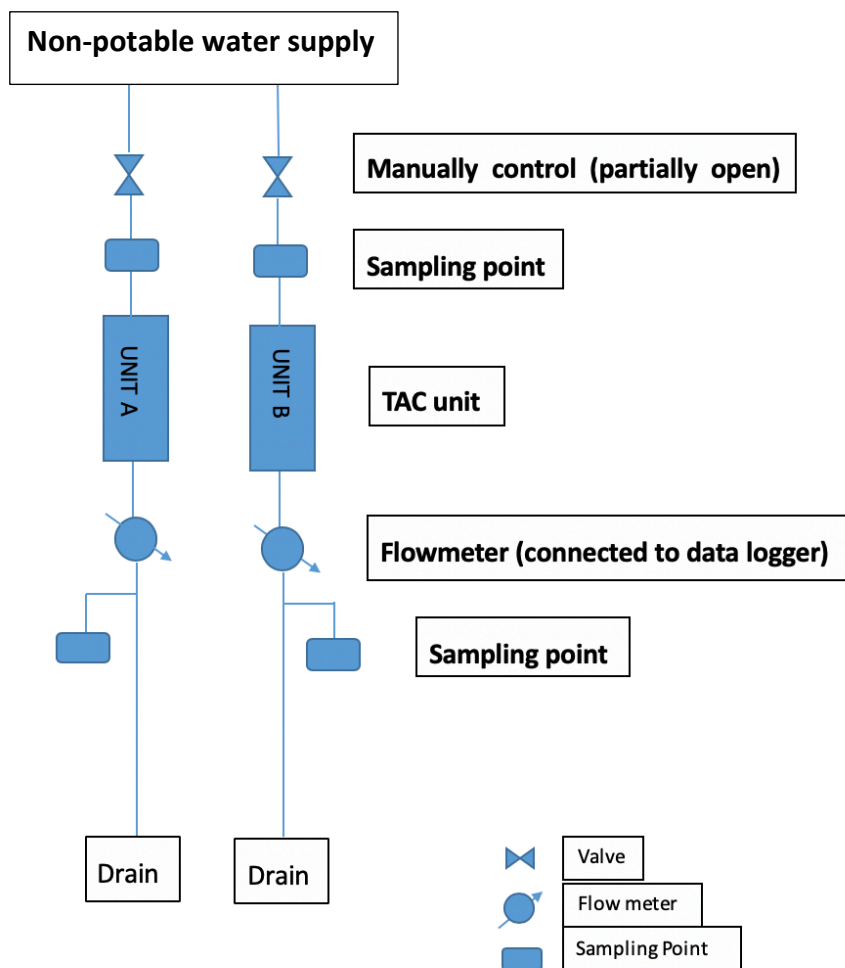
Figure 4.1 Experimental set-up diagram for location A. Two trains were set up in parallel using the same water source. At location B, only the train with unit B was set up.
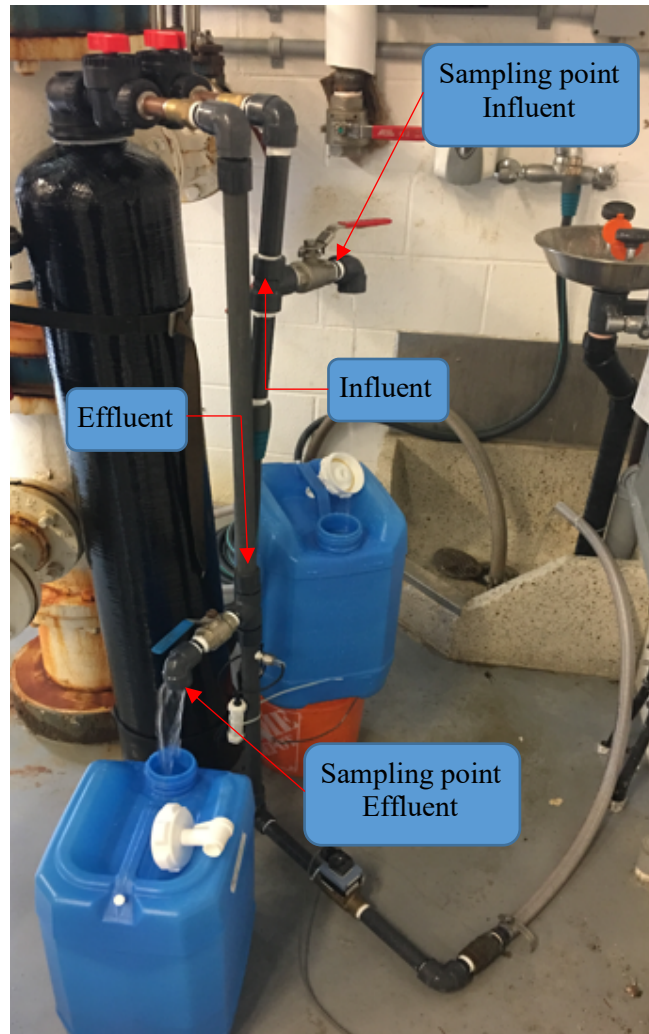
Figure 4.2 TAC unit setup at location B

The second phase of the experiment was to set up one TAC unit in location B, thereby testing a source water with different water quality. As reproducibility between units had already been tested at location A, only unit B was moved to location B, and the train was built the same as the train in location A. Sampling frequency was two or three times per week, and measurements were the same as in the first phase.

4.2.3 Water quality parameter measurements

Water sample pH, temperature, and conductivity were measured by YSI Professional Plus multi-parameter instrument (YSI Inc., USA). The pH and conductivity probes were calibrated in the lab right before water samples were taken. Conductivity and pH are parameters that can be affected by temperature changes; therefore, water pH, temperature, and conductivity were

measured immediately on-site after the water sample was taken. All other parameters mentioned in this section were measured after water samples were taken back to the lab.

The turbidity was measured using a Hach 2100Q Portable Turbidimeter (Hach ®, USA). Calibration was done every time prior to measuring samples, and the calibration standards used are Hach StablCal® Calibration Set (Hach ®, USA) for 2100Q. The calibration standards had the following turbidity values: 10, 20, 100, and 800 NTU.

Free chlorine residuals were measured using a Hach Portable Spectrophotometer DR1900 (Hach ®, USA). The test used Hach DPD Free Chlorine Reagent Powder Pillows (10 mL test chemical kit) and measures chlorine residuals from 0.02 to 2.00 mg/L.

Total alkalinity was measured according to Standard Methods (22nd edition, 2012) 2320B. Alkalinity values are expressed in mg/L $CaCO_3$,

Anion concentration measurements were done using Thermo Scientific Dionex^{TM} ICS-1100 equipment according to ASTM standard D4327-17 (ASTM International, 2017). Anions being analyzed included: chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}). All samples were filtered through 0.45 μm polyethersulfone (PES) syringe filters. Calibrations used for anion concentration measurement are presented in Table 4.3. Dilution was made if needed according to the calibration range.

Table 4.3 Range of calibration standards for anion concentrations measured by ion chromatography

Standard	Anion Concentration (mg/L)				
	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Blank	0	0	0	0	0
1	1	1	1	2	1
2	2	2	2	4	2
3	5	5	5	10	5
4	20	20	20	40	20
5	50	50	50	100	50

Total cation concentration measurements were done using Thermo Scientific Dionex^{TM} cation analyzer equipment. The suppressor used is Dionex^{TM} CDRS^{TM} 600, the column used is

Dionex^{TM} IonPac^{TM} CS16 IC column. The eluent was 26 mM methanesulfonic acid. Measurements were done according to ASTM standard D6919-09 (ASTM International, 2009). Cations being analyzed include: sodium (Na^+), magnesium (Mg^{2+}), potassium (K^+) and calcium (Ca^{2+}). All samples were filtered through 0.45 μm PES syringe filters. For water samples collected from location A, samples were diluted 1:3. For water samples collected from location B, because of the high Ca concentration, samples were diluted 1:5 for cation measurements. Each sample was measured four times and then the average value was used. Calibrations used for cation concentration measurement are presented in Table 4.4.

Table 4.4 Range of calibration standards for cation concentrations measured by ion chromatography

Standard	Cation Concentration (mg/L)				
	Na^+	NH_4^+	Mg^{2+}	K^+	Ca^{2+}
Blank	0	0	0	0	0
1	1	1	1	2	2
2	2	2	2	4	4
3	5	5	5	10	10
4	20	20	20	40	40
5	50	50	50	100	100

Free calcium ion concentrations weres measured using a Thermo Scientific Orion^{TM} Calcium Electrode (Thermal Fisher Scientific, USA). Calibration solutions had Ca^{2+} concentration of 10 mg/L, 50 mg/L and 100 mg/L. For location B water samples were diluted 1:2 in order to be within the calibration range.

Metal ion concentrations were also measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). For each water sample, calcium (Ca), magnesium (Mg), iron (Fe) and manganese (Mn) were measured in the department lab using ICP made by Spectro Analytical Instruments. Each sample was measured three times and the average value was calculated. Calibrations used for cation concentration measurement are presented in Table 4.5.

Table 4.5 Range of calibration standards for metals concentration measured by ICP

Standards	Metal Concentration (mg/L)			
	Ca	Mg	Mn	Fe
Blank	0	0	0	0
1	1	1	0.1	0.1
2	10	10	1	1
3	20	20	2	2
4	40	40	4	4
5	60	60	6	6

Some water samples from both locations were sent to ALS Global lab for full metal analysis. Specifically, location A water samples (both units) were sent to ALS Global lab on May 29, 2018 and September 16, 2018; location B water samples (unit B) were sent to ALS Global lab on September 16, 2018 and October 3, 2018.

4.2.4 Simplified scale test

Because of time and equipment constraints, a simplified scale test was developed mimicking some of the principles in the DVGW W512 standard test (DVGW, 1996). Instead of the flow-through system designed for the standard test, this test used two identical stainless steel kettles which are commonly used at home to boil the water. The kettles used were Aicok electric kettles (1.7 L) with variable temperature settings.

The first test measured total scale formed (i.e. solid deposit that is not floating in water). This test was done three times for source water A and three times for source water B. The following procedure was applied: Measure 1 L of TAC treated tap water into one kettle and 1 L of untreated water into the other kettle, and boil the water until reaching the boiling point and the kettles switched to off. Cool down for about 2 min and then empty out the water. Gently rinse the kettles inside three times with ultrapure water (Milli-Q). Then repeat these steps 20 times, therefore, for one test, 20 L of treated and 20 L of untreated water was boiled. After boiling 20L, 3% nitric acid (HNO_3) was used to dissolve the solid precipitates formed on the walls and the bottom of the kettle). 90 mL of 3% HNO_3 was added in three portions (30 mL, 30 mL, 30 mL) using glass pasteur pipettes by tilting the kettle and letting the acid run down the kettle wall drop

by drop. The kettle was then left standing for 30 min so that the acid dissolved the remaining scale at the bottom. The acid was then poured into a 100 mL volumetric flask. Add 3% HNO_3 to the mark and mixed well. Then measure the prepared samples on the ICP machine. For location A, samples were diluted 1:30, and for location B, samples were diluted 1:45. The Ca concentration (C_1 mg/L) measured by ICP can be used to calculate the mass of calcium carbonate scale precipitate (m_{scale}) formed in each kettle (after boiling 20 L water) and is expressed in mg Ca, Mg, Fe, Mn, and mg $CaCO_3$:

$$m_{scale} = C_1 \times 0.1L$$

Another scale test was done only once for each location water and aimed to measure the "sticky scale" formed in each kettle. The boiling procedure was the same as described in the last paragraph. The difference was that, after boiling 20 L of treated water in one kettle and 20 L of untreated water in the other kettle, three layers of Kimtech® Kimwipes were used to wipe the inside of each kettle three times. This step was to wipe out the relative loosely attached scale. Then Milli-Q water was used to rinse the kettles. The remaining scale was dissolved using 3% HNO_3 as described previously. Then the prepared samples were measured on the ICP machine. For location A, samples were diluted 1:30 dilution, while for location B, samples were diluted 1:45. The measured the Ca, Mg, Fe, and Mn concentrations were converted into a mass of sticky scale formed in each kettle expressed as mg Ca, Mg, Fe, Mn, and mg $CaCO_3$.

4.2.5 Isolation of microcrystals by sequential ultrafiltration

In a preliminary 0.45/0.22 μm filtration test, it was attempted to isolate and quantify microcrystals formed during the TAC treatment process, but these tests did not show any Ca ion concentration differences between filtered and unfiltered samples. Thus, in order to quantify crystal formation and estimate the approximate crystal size, pressurized ultrafiltration was set up. Amicon® Stirred Cells, as well as compressed air (act as pressure input), were used for the ultrafiltration process. Membranes used in the experiment are presented in Table 4.6.

Table 4.6 Membranes used in the sequential ultrafiltration experiment

Membrane Name	Membrane size (MWCO[*])	Membrane material
Millipore®	3000 Da	Regenerated Cellulose
Ultrafiltration	1000 Da	Regenerated Cellulose
Membrane	500 Da	Cellulose Acetate

[*]MWCO: Molecular Weight Cut-Off

TAC treated water samples were filtered with sequentially smaller filter sizes i.e. the filtrate of the 3000 Da membrane was filtered through the 1000 Da membrane and that filtrate was then filtered with the 500 Da membrane. ICP was then used to measure the Ca and Mg ions that remained in each filtrate and the original sample. If a distinct reduction between raw water samples and filtrate samples was observed, microcrystal formation could be confirmed. Moreover, if an obvious decrease between untreated and treated water samples is shown in one filtrate, the approximate microcrystal size could be anticipated to be larger than this membrane size MWCO. For comparison purposes, this same procedure was also applied to the untreated water sample.

4.2.6 LSI and CCPP calculation

LSI and CCPP are two indices that are used to indicate the calcium carbonate precipitation tendency. According to Standard Method 2330B (22nd edition, 2012), LSI is calculated using the equation:

$$LSI = pH - pH_s \hspace{3cm} \text{Equation 19}$$

Where pH is the measured pH, and pH_s is the pH of water in equilibrium with $CaCO_3$ at the existing Ca^{2+} and HCO_3^- ion concentrations.

According to the standard method 2330D (22nd edition, 2012), CCPP is calculated using computerized models rather than hand calculation. In this chapter, CCPP values were calculated using PHREEQXCEL which was developed and modified by Dr. Peter de Moel at the Delft University of Technology. Stimela.dat (version 3.1.7) and PHREEQC.DAT were used in this calculation sheet. Parameters that are needed to do the CCPP calculation using PHREEQXCEL

are temperature, pH, cations (calcium, magnesium, sodium, and potassium) concentration, anions (chloride, nitrate, sulfate) concentration, alkalinity.

4.3 Results and Discussion

4.3.1 Source water quality

Two different drinking water sources were used. Water was taken from the tap in two different municipal drinking water distribution systems. Source water qualities (average values of the entire experimental period) are listed in Table 4.7. The measured raw data are presented in Appendix B Table B.1 and Table B.2.

Table 4.7 Water quality of the two water sources. For Location A parameters, n = 23 except for Cl₂ residual (n=15), turbidity (n=15), TOC (n=19), Mn²⁺ (n=15) and Fe²⁺ (n=8). For Location B parameters, n = 7

Parameters	Location A		Location B	
	Average	Standard Deviation	Average	Standard Deviation
Temperature (^{o}C)	17	1	19	1
pH	7.2	0.2	7.1	0.1
Alkalinity (mg/L $CaCO_3$)	206	11	233	3
Cl_2 Residual (mg/L)	0.06	0.03	0.98	0.18
Turbidity (NTU)	0.18	0.06	0.86	0.15
Conductivity (μS/cm)	600	25	1391	93
TOC (mg Carbon/L)	2.3	1.2	1.1	0.2
Mn^{2+} (mg/L)	0.03	0.01	0.1	0.02
Fe^{2+} (mg/L)	0.06	0.02	0.2	0.05
Mg^{2+} (mg/L)	21.2	1.6	51.5	5.4
Ca^{2+} (mg/L)	67.7	5.8	256	27.0
Hardness (mg/L $CaCO_3$)	169	14	640	67

Location A had its drinking water supply from mixed groundwater and surface water (mostly from groundwater) while location B had its drinking water supplied from one particular

groundwater well. In part for this reason, location B had much higher water hardness compared to location A, and calcium ion concentrations in location B water samples were about four times higher than in location A. Location B had much higher conductivity values as well which indicated that location B is richer in mineral ions compared to location A, which is typical for a groundwater. Location B also had higher chlorine residuals, iron, and manganese concentrations, but they still meet the operational requirements of the TAC unit (however, close to the high end). For the manganese level in drinking water supply, the maximum acceptable concentration is 0.12 mg/L, while the AO value is 0.02 mg/L (Health Canada, 2019). Based on the limited sampling in this research, both source waters show higher manganese concentrations than the new AO value, but these data were obtained before the new guideline values were in effect. It would be useful to conduct additional sampling.

4.3.2 Performance of TAC unit with respect to hardness ions and metal ions

4.3.2.1 Total Ca and Mg ion concentration

Total Ca and Mg ion concentrations were measured by cation IC for both treated and untreated water samples. Total Ca ion concentrations measured are shown in Figure 4.3 and Figure 4.4 for both locations. Total Mg ion concentrations measured are shown in Figure 4.5 and Figure 4.6. Reduction of Ca^{2+} and Mg^{2+} concentration is shown in Figure 4.7. Raw measured data and supplementary information are presented in Appendix B Table B.3.

Total Ca^{2+} did not show much reduction after passage through the TAC unit at both locations. At location A, the average reduction was 2.99 mg/L for unit A and 2.77 mg/L for unit B (Figure 4.3 and Figure 4.7). The Ca^{2+} percentage removal at location A was 4.42% for unit A and 4.09% for unit B. As presented in Figure 4.4, for location B, the first sample result from September 16, 2019 gave a reduction value of 33.6 mg/L which was much higher than all other data points collected. This could be an outlier caused by several possible reasons: since this is the first data point after unit B was moved to location B, the media might not have gotten used to the new water by that time. The abnormal reduction value could also be caused by measurement error, though the measurements were reproducible as indicated by the standard deviations, and concentrations of the untreated and treated samples were in the same range as samples taken

later. If this first point is taken out, the average reduction of location B (Figure 4.4 and Figure 4.7) was about 7.02 mg/L (unit B), and the average percentage removal was 2.73% (unit B).
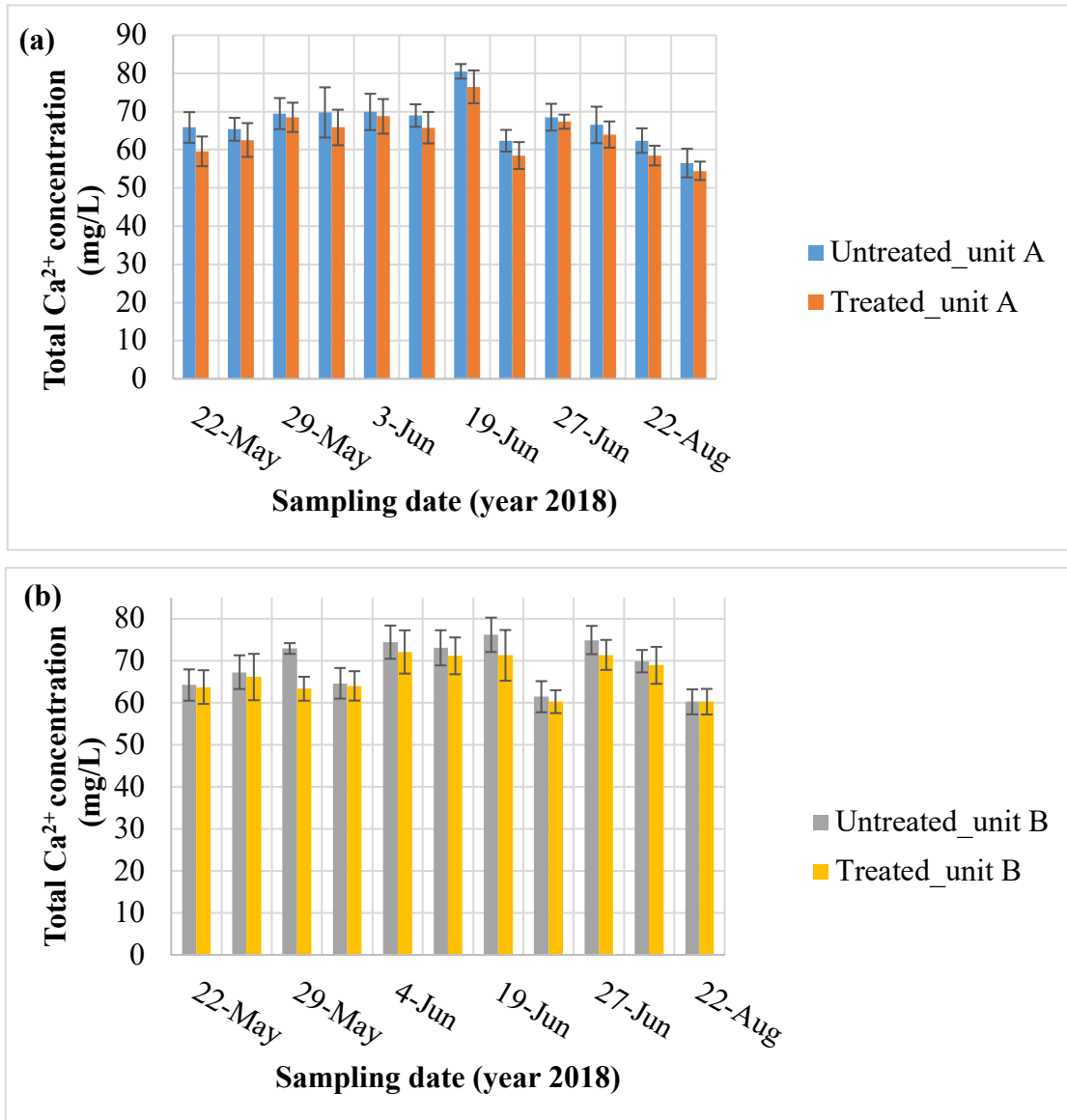
Figure 4.3 Total Ca²⁺ concentrations measured for location A (a) unit A and (b) unit B. Each sample was measured 4 times by IC (n=4), and error bars show standard deviations.
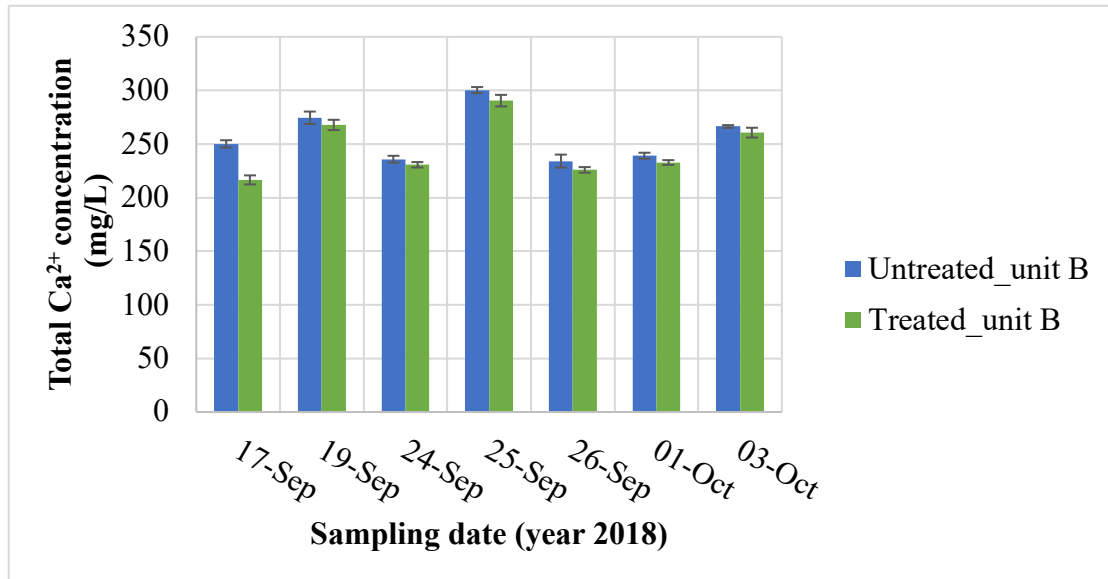
Figure 4.4 Total Ca^{2+} concentrations measured for location B unit B. Each sample was measured 4 times by IC (n=4), and error bars show standard deviations.

Total Mg^{2+} concentrations in untreated and treated water were quite close (Figure 4.5) for location A samples, while location B (Figure 4.6) showed some reduction but not much. Mg^{2+} reduction data showed some negative values. Negative values could be caused by measurement error or these indicate that no reduction occurred after the water had been treated by the TAC unit. For location A, the average Mg^{2+} reduction was 0.85 mg/L (unit A) and 0.96 mg/L (unit B). The corresponding average Mg^{2+} percentage removal was 4.0% (unit A) and 4.5% (unit B). For location B, the average Mg^{2+} reduction was 3.56 mg/L, and the average Mg^{2+} percentage removal was 6.9% (unit B).
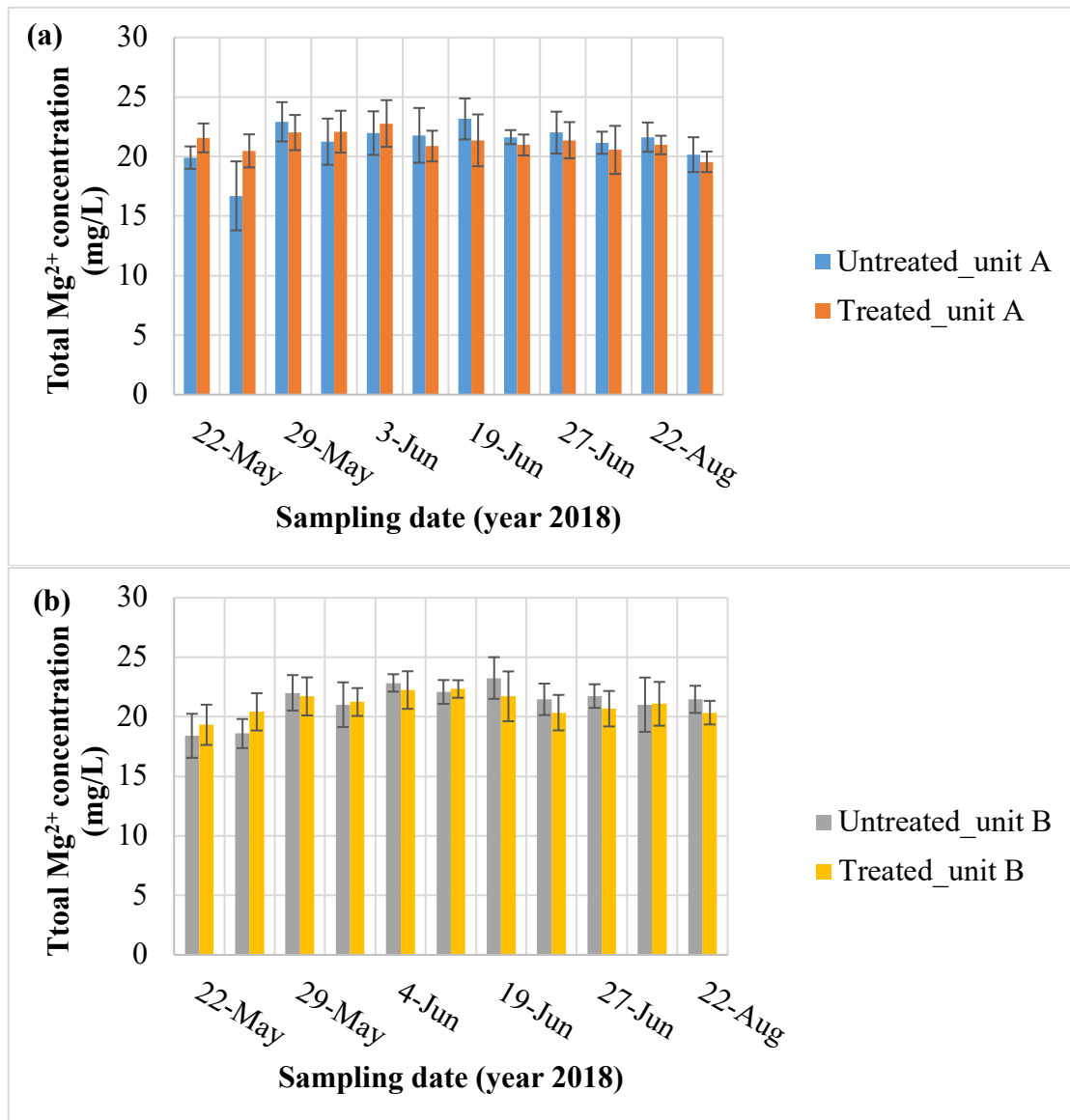
Figure 4.5 Total Mg²⁺ concentrations measured for location A (a) unit A and (b) unit B. Each sample was measured 4 times by IC (n=4), and error bars show standard deviations.
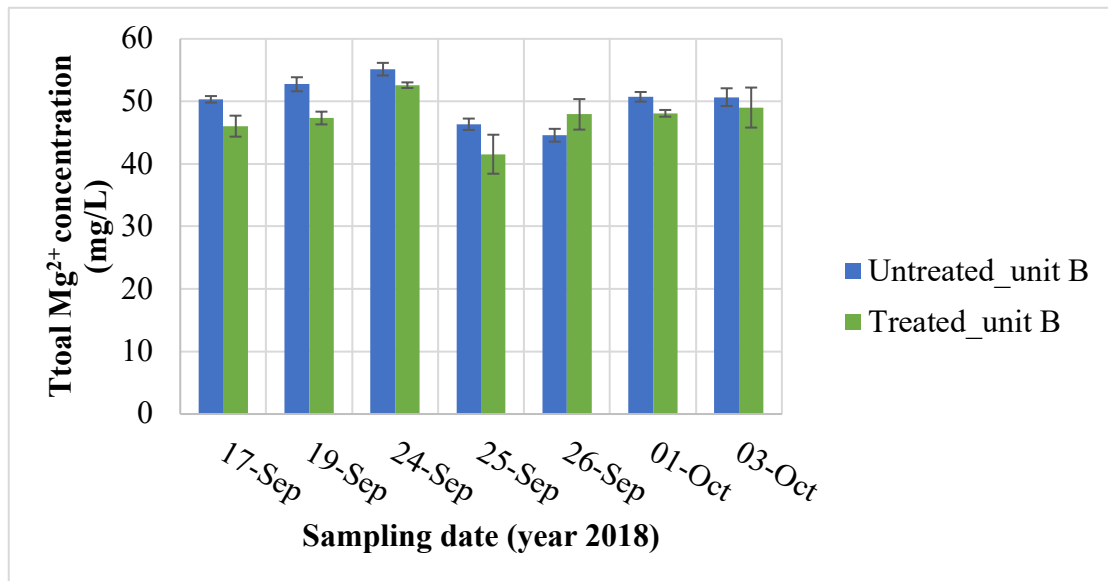
Figure 4.6 Total Mg^{2+} concentrations measured for location B unit B. Each sample was measured 4 times by the IC machine (n=4), and error bars show standard deviations.
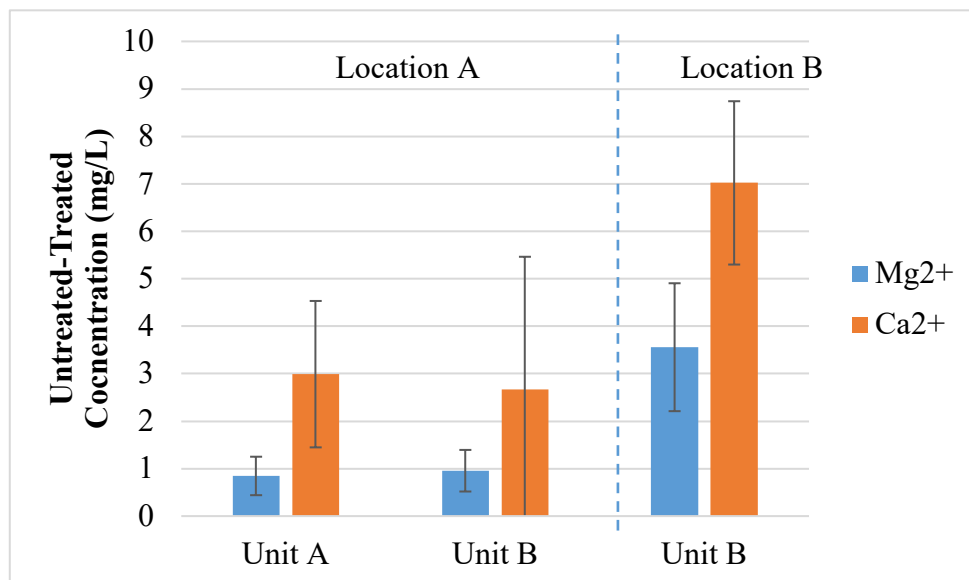
Figure 4.7 Average reductions (untreated – treated) of total Ca^{2+} and Mg^{2+} concentrations after treatment by TAC units for the two source waters. Error bars show standard deviations. For location A, n=12 for unit A and n=11 for unit B. For location B, n=7.

From Figure 4.7, location B showed a higher reduction in Ca concentrations. However, as for the percentage removal, the two locations showed similar values which were relatively low. It was also evident that location B showed a higher reduction in Mg^{2+} concentrations compared with location A, but given the relatively high standard deviations, these were quite similar on a percentage basis. Overall, reductions in total Mg were quite low.

In order to determine whether the reduction of the total dissolved Ca concentration is zero, paired t-tests were done for each location water and each unit. This test utilizes the difference between treated and untreated average values on a given day. The null hypothesis is that there is no difference, so the test examines whether the average difference is significantly different from zero. The summarized results are presented in Table 4.8 and Table 4.9. All paired t-test results showed that for each location and each unit, the reduction in Ca was not zero (statistically significant at a 5% significance level). These results represent a situation where the reduction was significantly different from zero. However the observed reduction was small and therefore not likely to be of much practical benefit.

Table 4.8 Paired t-test to compare the total Ca concentration reduction (untreated-treated) using a 5% significance level. Calculated t and P values are also listed in the table.

Location and Unit compared		t value	P value	Result
Location A	Unit A	6.7	$3.3 \times e^{-5}$	concentration difference $\neq 0$
	Unit B	2.9	0.0160	
Location B	Unit B	10	0.0002	

Table 4.9 Paired t-test to compare the total Mg concentration reduction (untreated-treated) using a 5% significance level. Calculated t and P values are also listed in the table.

Location and Unit compared		t value	P value	Result
Location A	Unit A	5.9	0.0006	concentration difference $\neq 0$
	Unit B	5.3	0.0031	
Location B	Unit B	5.9	0.0020	

4.3.2.2 Free Ca ion concentration

Free Ca^{2+} concentrations in water samples were measured by a Ca^{2+} ion selective electrode. Free Ca^{2+} in treated water represented the Ca^{2+} that remained in the water and was not transformed to microcrystals. According to the theory, because of the microcrystal formation, free Ca^{2+} ions concentration should decrease when comparing untreated to treated water. Free Ca^{2+} concentrations measured for location A are shown in Figure 4.8 and for location B in Figure 4.9. For location A, the average free Ca^{2+} reduction was 3.26 mg/L (5.0%) for unit A and 3.14 mg/L (4.7%) for unit B. For location B, the average free Ca^{2+} reduction is 8.8 mg/L (4.0%) for

unit B. Although free Ca^{2+} was reduced at both locations, the amount was not very substantial. Location B showed a slightly smaller percentage removal compared to location A. Reduction of free Ca ion concentration is represented in Figure 4.10. Supplementary and raw data measured are presented in Appendix B Table B.4.
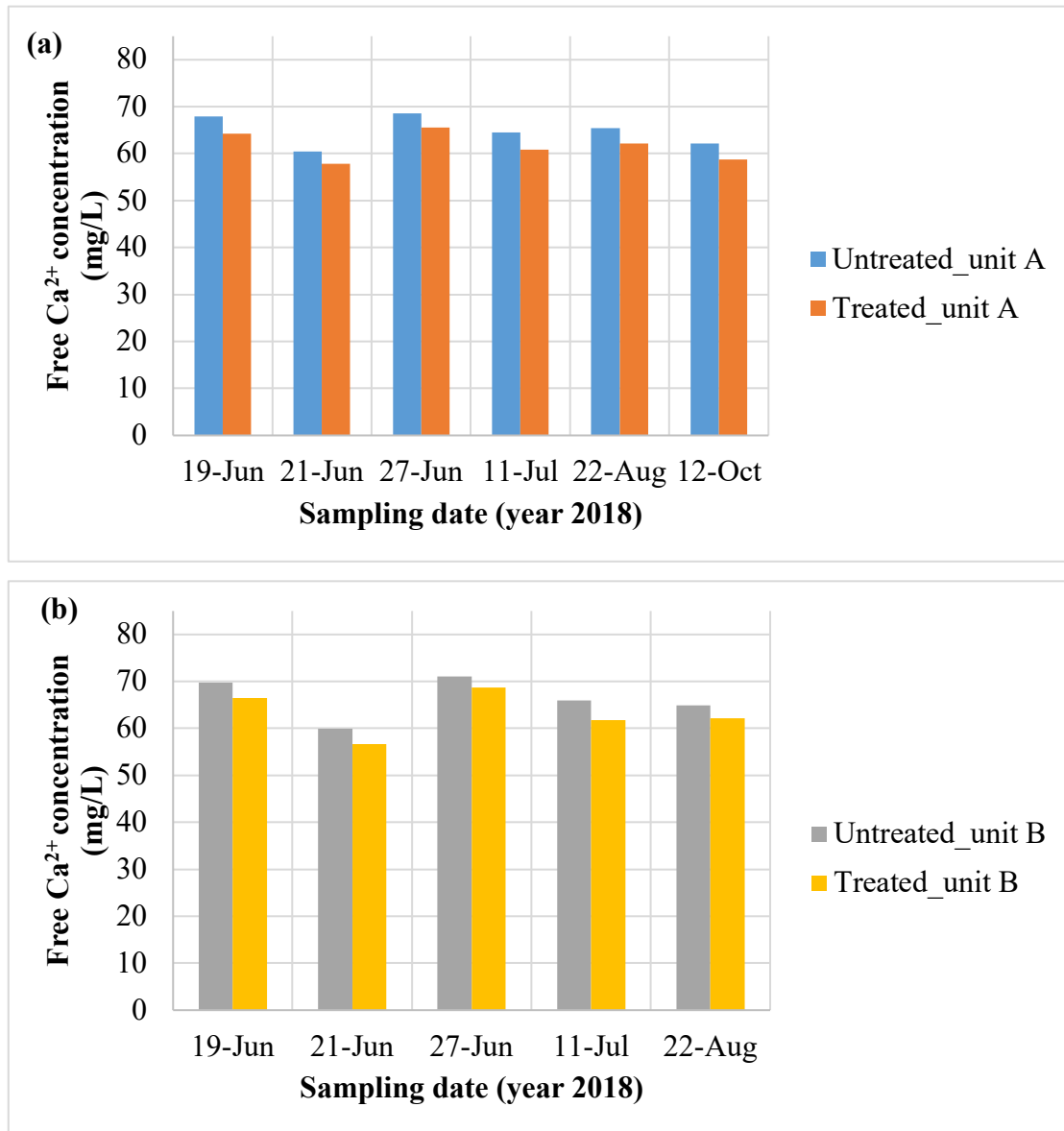
Figure 4.8 Free Ca^{2+} concentrations measured by ion selective electrode for location A unit (a) A and (b) unit B. Each sample was measured once.
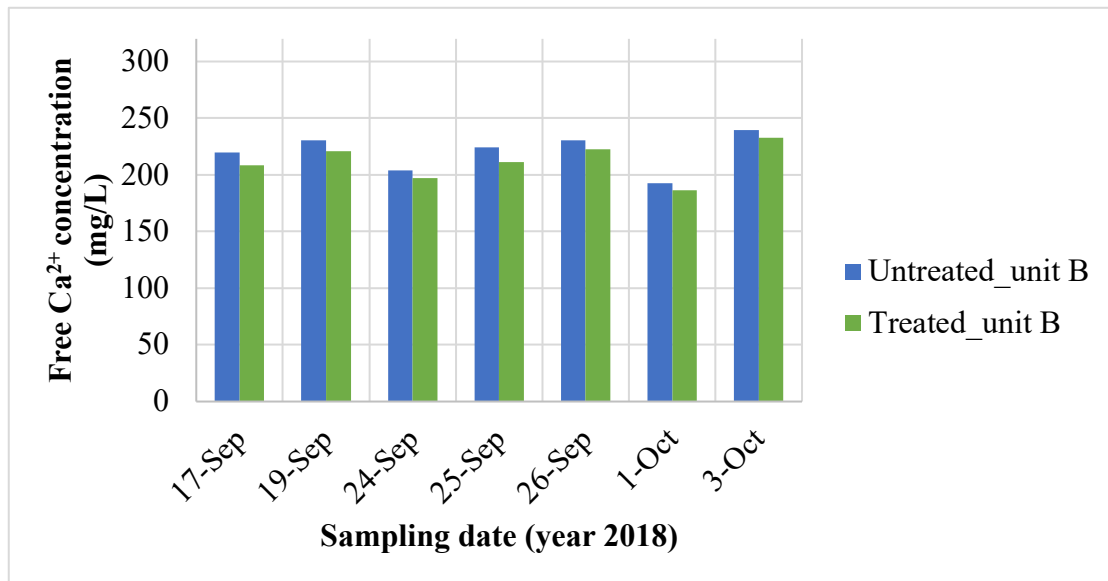
Figure 4.9 Free Ca²⁺ concentration measured by ion selective electrode for location B unit B. Each sample was measured once.
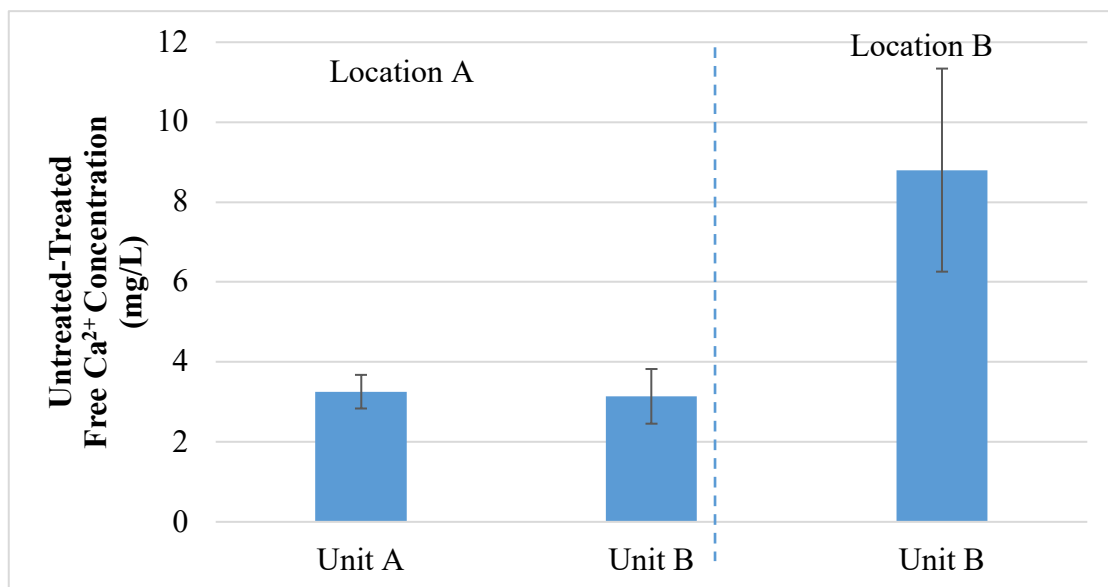
Figure 4.10 Average reductions (untreated – treated) in free Ca²⁺ concentrations after treatment by TAC units for the two source waters. For location A, n=6 for unit A and n=5 for unit B. For location B, n=7. Error bars show standard deviations

In order to determine whether the reduction of total free Ca concentration is zero, paired t-tests were done for each location water and each unit. The summarized results are presented in Table 4.10. All paired t-test results showed that for each location and each unit, the reduction in free Ca was not zero (statistically significant at a 5% significance level). Again, these results

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represent a situation where the reduction was significantly different from zero. However the observed reduction was small and therefore not likely to be of much practical benefit.

Table 4.10 Paired t-test to compare the free Ca concentration difference (untreated-treated) using a 5% significance level. Calculated t and P values are also listed in the table

Location and Unit compared		t value	P value	Result
Location A	Unit A	19	$7.5 \times e^{-6}$	concentration difference $\neq 0$
	Unit B	10	5.1×10^{-4}	
Location B	Unit B	9.2	$9.5 \times e^{-5}$	

4.3.2.3 Total Fe and Mn ion concentration change

For each treated and untreated water sample, total Fe and Mn concentrations were measured by ICP in the University of Waterloo Labs. According to the company website, the TAC unit is also able to remove some Fe and Mn ions from water (Watch® Water, n.d.). This ICP test was done to figure out to what extent the TAC unit could reduce Fe and Mn concentrations. Average concentration reduction values for both ions at the two locations are shown in Figure 4.11. The raw measured data are presented in Appendix B Table B.5, and Figures B.1 and B.2 present the Mn concentrations measured, and Figures B.3 and B.4 present the Fe concentrations measured.
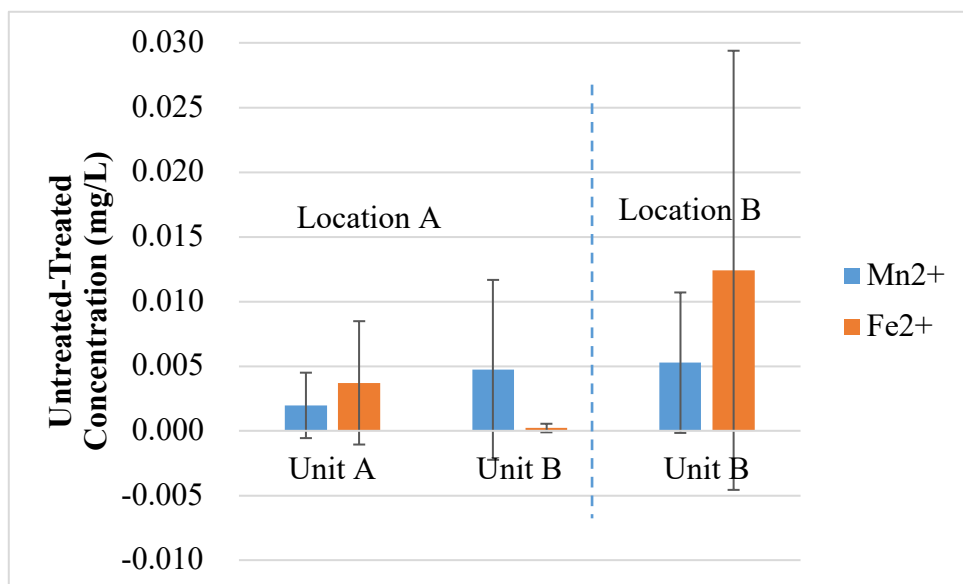
Figure 4.11 Average reduction (untreated – treated) in total Mn²⁺ and Fe²⁺ concentrations after treatment by TAC units for the two source waters. For location A, n=6 for unit A and n=5 for unit B. For location B, n=7. Error bars show standard deviations

For Mn concentration, the amount of Mn removal was similar at both locations though location B had a much higher Mn concentration level than location A. Location A had the average Mn reduction of 0.002 mg/L (unit A) and 0.005 mg/L (unit B) and the percentage removal was 6.7% (unit A) and 16.7% (unit B). Location B had an average Mn reduction of 0.005 mg/L, and the percentage removal was 5%. Although the percentage removal showed a difference between the two locations, the standard deviations were relatively high in comparison to the measured reductions which means the data varied a lot and the observed reductions are likely not true differences.

For Fe ion concentration, location B showed greater average reduction value than location A, however, with a huge error bar. The average Fe concentration of location B treated water was 0.15 mg/L, while the average concentration for untreated water was 0.16 mg/L. Treated water lowered the Fe concentration by 0.01 mg/L, and the percentage removal was 4%. Location A unit A had an average Fe reduction value of 0.004 mg/L and a percentage removal of 6.7%, while unit B showed no reduction after being treated by TAC. Overall, the standard deviations were very high in comparison to the measured reductions which indicates that the observed reductions are highly variable and likely not true differences. Although a difference was expected, basically the experiments could not confirm any reductions in Fe and Mn concentrations.

4.3.2.4 Full metal analysis

During the TAC experiments process, a few samples (treated and untreated water, unit A and B, two locations) were sent to a commercial lab for full metal analysis (ICP-MS). In total, three pairs of water samples taken from location A (May 29 and September 16, 2018) and two pairs of water samples taken from location B (September 16 and October 3, 2018) were measured for full metal analysis. Test results are shown in Appendix B Table B.6 and Table B.7 (only measurable metals). In total, 39 metals were measured, but most metals had very low concentrations which were lower than the method detection limits (MDLs). Only Strontium (Sr) and Sulfur (S) showed some reduction for both locations. Location A water samples also showed some reduction in copper (Cu), arsenic (As), and selenium (Se).

4.3.2.5 Preliminary test

A preliminary experiment was performed where 1 L of untreated and 1 L of treated water were held for three weeks in an 85°C oven. Different forms of crystal deposition were observed though no other analysis was done on these crystals as there were not sufficient crystals formed for further analyses.

4.3.3 LSI and CCPP

As stated in Section 4.2.6, LSI and CCPP are two parameters that are calculated to represent the scale formation potential. Water with a lower scale precipitation potential has lower LSI and CCPP values (Table 4.11). For each pair of water samples (untreated and treated), LSI and CCPP were calculated using the PHREEQXCEL. All calculated data are presented in Appendix B Table B.8 and Table B.9. As can be seen from Table B.8 and Table B.9, most LSI and CCPP values are negative and quite low in value. For location A, some treated water samples had slightly lower LSI and CCPP values, while some had slightly higher values. For location B water, all showed somewhat higher LSI and CCPP values for treated water.

Table 4.11 LSI and CCPP Categories

LSI/CCPP values	Trend	
LSI (CCPP) >0	Water oversaturated with $CaCO_3$	Tends to precipitate $CaCO_3$
LSI (CCPP) < 0	Water undersaturated with $CaCO_3$	Tends to dissolve $CaCO_3$
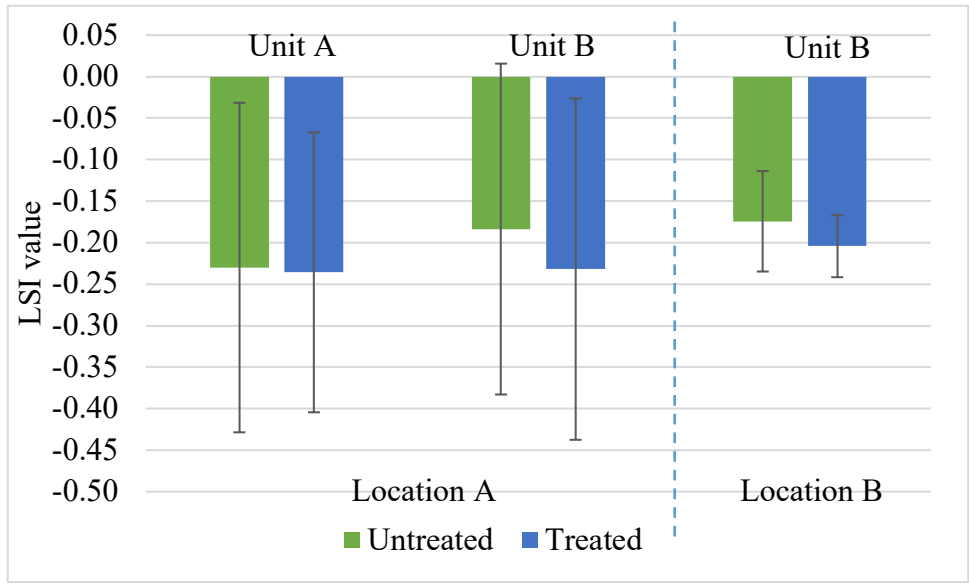
Figure 4.12 Average LSI values calculated for both locations and both units. For location A, n=12 for unit A and n=11 for unit B. For location B, n=7. Error bars show standard deviations
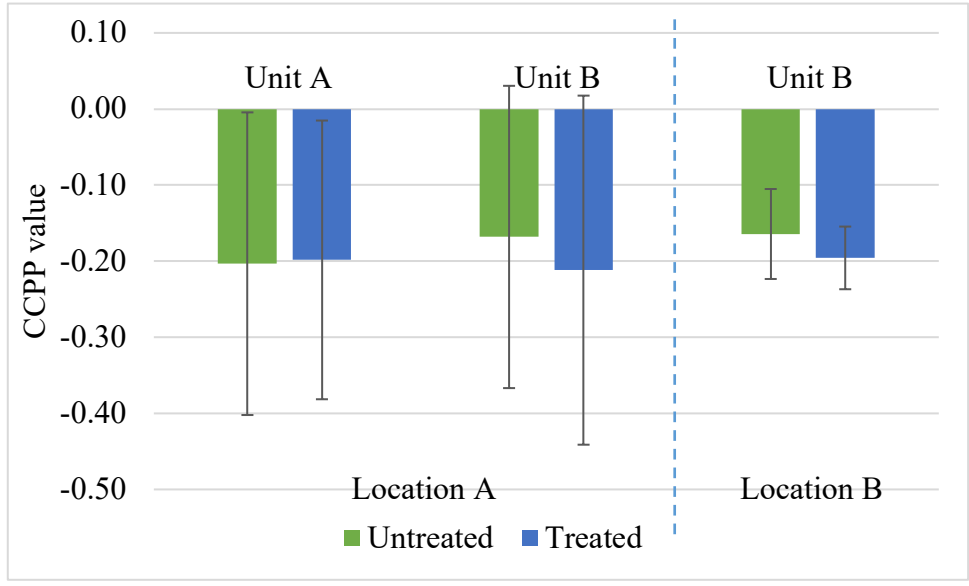
Figure 4.13 Average CCPP values calculated for both locations and both units. For location A, n=12 for unit A and n=11 for unit B. For location B, n=7. Error bars show standard deviations

The average LSI and CCPP values calculated for untreated and treated water at both locations are presented in Figure 4.12 and Figure 4.13. Although average index values showed negative values, they all within 0 to -0.3. According to Millette et al. (1980), water is very corrosive if LSI is lower than -2.0. Therefore, waters measured are still around balanced

conditions. All untreated and treated water had slightly negative values with high standard deviations. No apparent differences between untreated and treated water were found for both locations.

The values for differences (untreated – treated) in average LSI and CCPP values are shown in Table 4.12. Positive values indicate that untreated water has higher LSI and CCPP values which also meant that the treated water had less scale formation potential. However, standard deviations calculated for difference (reduction) values were still quite high and higher than the reduction values. Both locations showed a similar trend. This indicates that there was essentially no change in both indices after TAC treatment.

Table 4.12 Summary table of differences (untreated-treated) in average LSI and CCPP values with standard deviations. LSI and CCPP values were calculated using PHREEQXCEL.

Location and unit	Location A				Location B	
	Unit A		Unit B		Unit B	
	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
LSI	0.01	0.05	0.05	0.05	0.03	0.03
CCPP	0.00	0.05	0.04	0.06	0.04	0.02

4.3.4 Simplified scale test results

4.3.4.1 Total amount of scale formed in kettles

One goal of the TAC unit treatment is to prevent or reduce the scale formation in pipes and heating devices. A study has shown that TAC treated water generates almost no scale on 60°C and 80°C heating plate in a flow-through system according to DVGW W512 standard test method (Fox et al., 2014). DVGW W512 (DVGW, 1996) standard test method aims to evaluate the effectiveness of a non-cation exchange scale prevention unit's performance. Duplicate test/control rigs are used. The water is continuously heated in this flow-through system. After the test period, the procedure is to collect the scale formed in the water heaters (treated water and untreated water) and compare the amount formed. Because of the time limitation and the complicated setup, this study did not reperform the DVGW W512 standard test.

In order to test the effect on scale formation in this study, a simplified scale test using kettles was developed, albeit it is not a flow-through system. For homes which have a hard water supply, white and hard scale formed in heating kettles that is difficult to clean can cause problems and concerns. This experiment was designed to mimic using kettles to boil the water in a home and measure the actual total scale formation. In each phase of the test, 1 L of water was boiled, which also aimed to mimic the daily water boiling at home. For one boiling test, 20 L of water in total were boiled. Because the main component of the white scale is $CaCO_3$, total scale formation was measured and presented as the mass of $CaCO_3$ formed after boiling 20 L of water. See section 4.2.4 for details. Figures 4.14 and 4.15 show the kettle heating plates after boiling 20 L of untreated and 20 L of treated water for both locations. From the photos, TAC treated water still forms obvious scale on the heating plate of the kettle (boiling temperature: 100°C). In contrast, some spots with detached scale were observed on the treated water heating plate for both locations, which indicates that treated water formed less scale than untreated water.
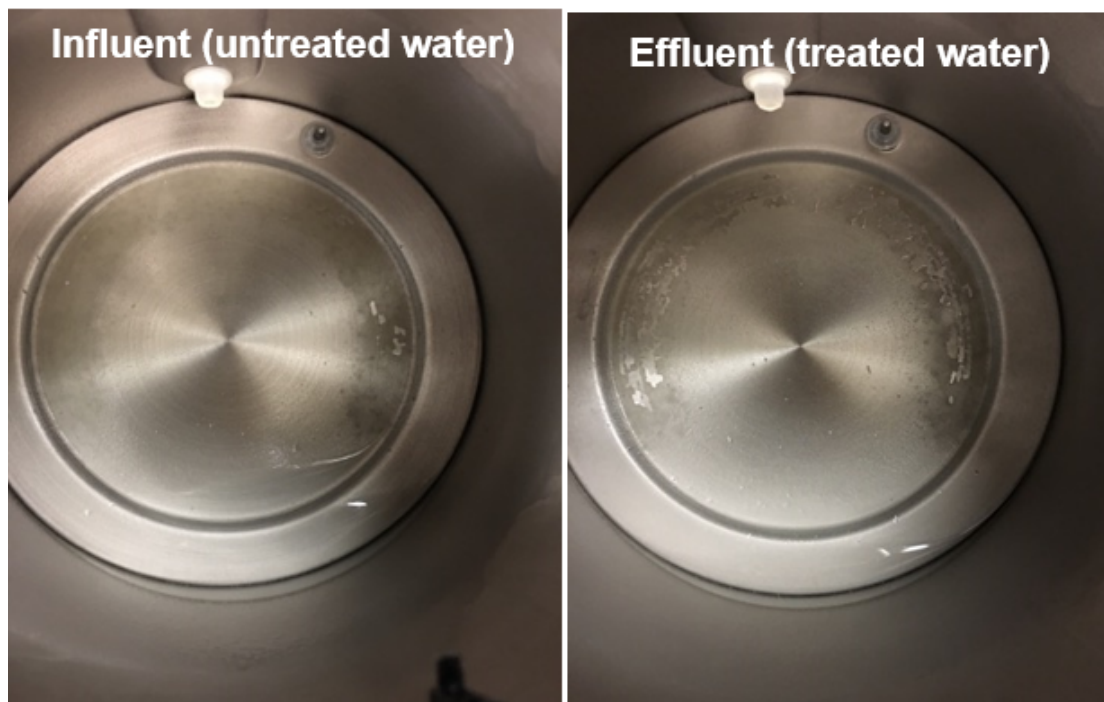
Figure 4.14 Heating plate of kettles after boiling 20 L of location A water
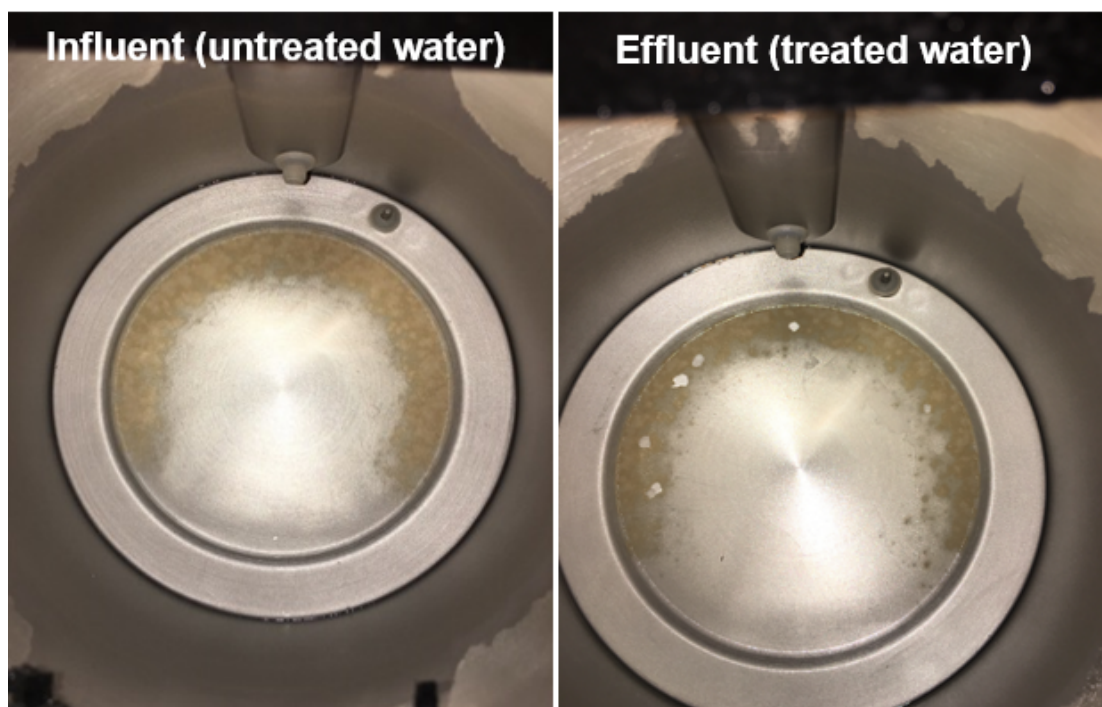
Figure 4.15 Heating plate of kettles after boiling 20 L of location B water

The scale was dissolved, and Ca concentrations were measured on the ICP. In addition, Mg, Fe and Mn concentration in dissolved scale were also measured, and differences (untreated - treated) were calculated. Finally, concentrations were converted to mass of scale per 20 L of water boiled. These data are presented in Appendix B Table B.10. Calculated differences in scale formation are presented in Table 4.13.

In total, three simplified boiling tests were done for water units at each location. Mg did not see much removal for both locations (Table 4.13). Mn and Fe did not show obvious removal for location A either (Table 4.13). Referring back to Section 4.3.1, the raw water of location A had little Mn and Fe content, which were close to the MDLs. However, the location B water simplified boiling test results showed some detectable Mn and Fe removal, the amount of which was however not much.
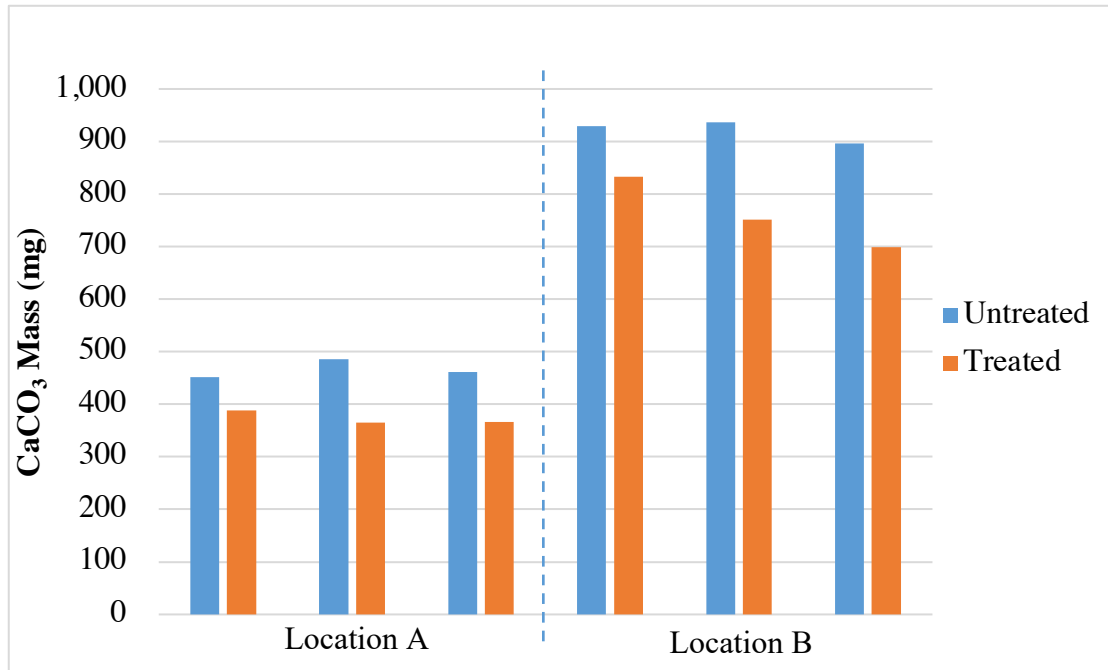
Figure 4.16 Calculated amount of CaCO₃ scale mass formed after boiling 20 L of treated and untreated water respectively

Table 4.13 Difference in metal mass (untreated-treated) of the scale deposit and the calculated mass of CaCO₃ scale formation. ND means not detectable in the treated and/or untreated waters.

Location	Unit	Time Measured	Difference (untreated-treated)				
			Mg	Ca	Mn	Fe	CaCO₃ Scale
			mg	mg	mg	mg	mg
Location A	A	23-Aug-18	0.0	25.4	ND	0.01	63.6
	B	23-Aug-18	0.5	48.2	ND	-0.01	121
	A	12-Oct-18	0.2	38.4	0.00	-0.02	96.0
Location B	B	17-Sep-18	0.1	38.5	0.03	0.02	96.2
	B	24-Sep-18	0.1	74.1	0.04	0.01	185
	B	12-Oct-18	-0.3	79.1	0.03	0.05	198

It is obvious that the main component in the scale is Ca and the calculated amount is presented in Table 4.13 and Figure 4.16. From the test results of both locations, reduction of Ca scale could be seen and location B had higher reduction than location A. Because all 6 boiling

tests were not performed on the same day as well as the nature of the experiment, Ca scale measured for each day did not generate a consistent value. This test seems more semi-quantitative in nature. As for values themselves, the amount of reduction was not as substantial as expected.

4.3.4.2 "Hard scale/Sticky scale" formation in kettles

This experiment was done to test if the TAC treatment changes the nature of $CaCO_3$ scale e.g. making it easier to be removed. As stated in section 4.2.4, the only different manipulation was to use Kim wipes to wipe off the so-called "soft scale" (not stuck tightly on the surface) and then dissolve the remaining scale that was tightly stuck to the surface in nitric acid. In this experiment, only Ca scale results are presented. Unlike the boiling test that measured total scale formation, only one boiling test was done at each location to examine the "hard scale/sticky scale". The raw measured and calculated data is presented in Appendix B Table B.11. The calculated Ca scale formation difference values are presented in Table 4.14 and Figure 4.17.

As can be seen, a similar trend was shown for this experiment compared to the total scale measurement test. At both locations, the hard scale did not show much difference. With higher supply water hardness (location B), the reduction was higher. However, considering the total hardness level, the reduction amount was not substantial either.
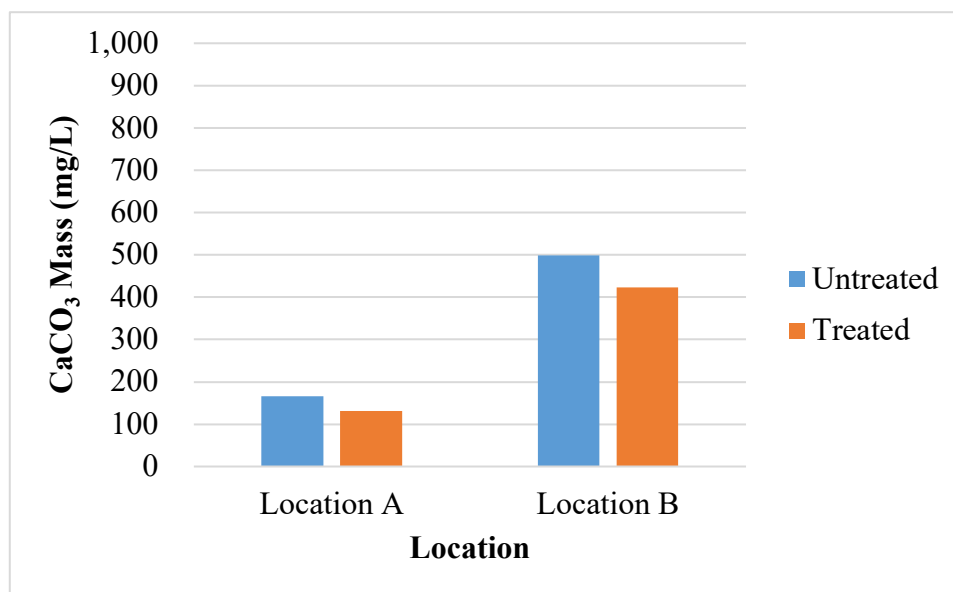
Figure 4.17 Calculated amount of $CaCO_3$ hard scale mass formed after boiling 20 L of treated and untreated water (for both location A and B)

Table 4.14 Difference of metal mass (untreated-treated) of the sticky scale deposit and the corresponding mass of hard CaCO$_3$ scale formation.

Location	Unit	Time Measured	Difference (untreated-treated)				
			Mg^{2+}	Ca^{2+}	Mn^{2+}	Fe^{2+}	CaCO$_3$ scale
			mg	mg	mg	mg	mg
Location A	A	15-Aug-18	0.2	13.7	0.00	0.00	34.18
Location B	B	26-Sep-18	-0.1	29.9	0.02	0.01	74.81

4.3.5 Ultrafiltration test results

According to the basic theory of TAC treatment, when hard water passes through the media, hardness ions will nucleate on nucleation sites and form stable microcrystals. In order to dig deeper into the microcrystals that should form a sequential ultrafiltration test was designed which aimed to categorize the approximate microcrystal size and quantify them. For each location, one sequential ultrafiltration test was done using 3000 Da, 1000 Da and 500 Da ultrafiltration membranes on untreated and TAC treated water samples. As a control, untreated water samples were also measured, because microcrystals formation was not expected. According to the literature of TAC treatment theory, the major components of the microcrystal should be CaCO$_3$ and some MgCO$_3$. Therefore, if microcrystals were filtered out, a distinct Ca concentration reduction should be detected between treated and untreated water filtrate. In order to measure the Ca concentration, samples were acidified with nitric acid and measured by ICP. Not only Ca, but also other metals (Mg, Fe, and Mn) were also measured. Raw measured ICP data are presented in Appendix B Table B.12 and bar charts for the results for the two location waters are shown in Figure 4.18.

For location A water samples, ultrafiltration results for all three membranes did not show a significant decrease between treated and untreated water in Ca concentration. 3000 Da and 1000 Da showed similar values to raw water. However, 500 Da filtrate showed a much lower Ca concentration. For location B water samples, a similar trend as location A water, 3000 Da, and 1000 Da showed results close to raw water. 500 Da filter showed significantly lower Ca concentration on treated and untreated water; it also gave an obvious difference between treated and untreated water.

However, there was insufficient evidence to conclude that the microcrystal size is between 500 Da and 1000 Da because only location B water samples showed this result. One aspect that needs to be considered is that 500 Da is a membrane size that intrudes into nanofiltration filter size. Nanofiltration could filter out divalent ions as well. The difference showed in Figure 4.18 (B) could be caused by the small membrane size as well.

Comparing raw water measurement results and filtered water samples results, there was not a distinct difference for the 3000 Da and 1000 Da membranes. Although 500 Da showed great reduction compared to raw water, the reduction was because of the small membrane size which is likely to reject divalent ions as well.

In conclusion, the ultrafiltration test did not successfully detect the substantial formation of crystals, neither the approximate microcrystal size. Some possible reasons are listed below:

- There were not a lot of microcrystals formed through the TAC process or these few crystals can act as nucleation sites in a flow-though system to lower scale formation potential.

- Microcrystal size varied (every membrane result showed a bit of Ca concentration decrease in TAC treated water sample, though altogether these decreases were quite small).
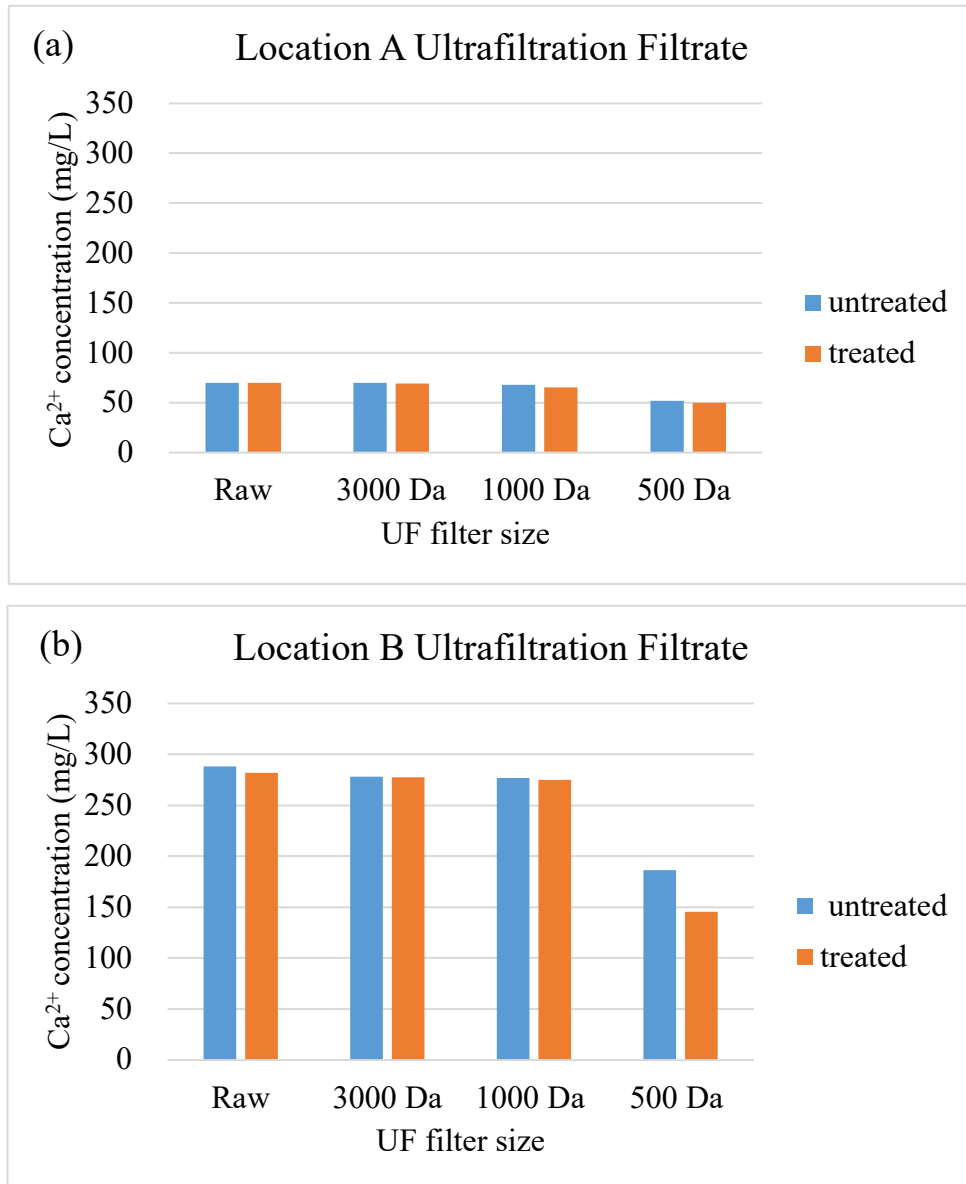
Figure 4.18 Ultrafiltration test results of (a) location A and (b) location B water samples (TAC treated and untreated) using ultrafiltration membranes

4.4 Conclusions

In this chapter, TAC treatment technology, which is a potentially environmentally friendly point-of-entry scale prevention method, was tested. Using two different drinking water sources, the performance of TAC units was tested using several methods thereby covering different aspects: change in total Ca concentrations, change in free Ca concentrations, change in metal ion concentrations, change in LSI and CCPP parameters, and scale formation using kettles with heating plates. In order to estimate the approximate crystal size and quantity, sequential ultrafiltration tests were performed as well. The key conclusions are summarized below:

- Total Ca showed slight reductions between TAC treated and untreated water with quite large standard deviation values. With higher water hardness level, the reduction value was higher as well. The percentage removal was not substantial. However, paired t-test results showed that the average reduction values were statistically not zero using a 5% significance level. Both locations showed a similar tendency.

- Free Ca concentration showed a small reduction for each pair of water samples (untreated and TAC treated). With higher water hardness level, reduction values were proportionally higher, although percent removals remained at 5% and 4% for location A and location B respectively. In a similar trend as total dissolved Ca, the percentage removal is not that much, but paired t-tests showed the average reduction values are statistically not zero using a 5% significance level. Location A and location B water showed the same tendency.

- Metal ion concentration analysis did not show much reduction in Mg, Fe, and Mn ions. Since the measured values were close to or lower than the MDL, the percentage removal varied. From full metal analysis results, other metals had very low concentration or were not detectable in the untreated and treated water samples.

- The average LSI and CCPP parameter values calculated showed that for both locations, TAC treated water had less scale formation potential than untreated water. However, the standard deviations were quite large.

- A simplified scale test was developed to measure the total and sticky scale formed in a boiling kettle (100°C). This test showed that TAC treated water formed slightly less scale

and slightly less sticky scale. This was more pronounced for location B with its much higher water hardness than location A. However, visible scale formation could still be observed in the kettle for TAC treated water which did not meet the expected target: no scale formation.

- Sequential ultrafiltration tests did not successfully separate the microcrystals formed after treatment by the TAC unit and could not estimate the approximate size of the microcrystals.

4.5 Disclaimer

Mention of commercial products and trade names does not constitute endorsement or recommendation for their use by the author.

Chapter 5 Conclusions and Recommendations

5.1 Summary and Conclusions

Currently, there are many softening/scale prevention treatment technologies available, and thorough assessments are required to decide on a suitable technology for a certain application. If focusing on household level treatment, the most popular applied softening technology in Ontario is ion exchange. Because of the potential side effects caused by elevated sodium concentration in the softened water as well as the high chloride concentration in the brine, an environmentally friendly salt-free treatment is highly attractive. Template assisted crystallization (TAC) as a new drinking water scale prevention treatment is promising, but there is not a lot of published research available. Therefore, to fill these research gaps, this research had two main goals: 1) assess and rank available centralized and household drinking water softening/scale prevention technologies, and 2) test the performance of TAC at the household level.

To achieve these two goals, this research was conducted in two phases. The first phase was to gather information about currently available softening/scale prevention technologies for both centralized and household treatments, and technologies were then evaluated and ranked using the multi-criteria assessment method. Centralized treatment options including lime softening, pellet softening, nanofiltration, and ion exchange were investigated. Household treatment options that were selected were template assisted crystallization (TAC), ion exchange, nanofiltration, electrically induced precipitation (EIP), magnetic water treatment method, and capacitive deionization (CD). Criteria that were considered in this evaluation were waste disposal (brine and sludge), energy usage, life-cycle cost, subsequent treatment needed, efficiency, easy to use, chemical addition and certified/validated technology. According to multi-criteria assessment theory, the weighting of criteria assignment is subjective, and it depends on which criteria are more critical with the specific case. Hence, sensitivity analyses were done for both centralized and household technologies, with consideration of different cases. Based on the assessment results, the following conclusions and findings are summarized:

Centralized technologies:

- The overall rankings (from the highest score to the lowest score) were pellet softening, ion exchange, lime softening, and nanofiltration.

- Pellet softening scored highest among all technologies assessed. It has a relatively high hardness removal efficiency. Chemical addition is needed during the process, but the chemical is easy to obtain, and the amount required is not as much as for lime softening. The cost is also competitive with other options.

- Ion exchange was ranked second. The main problems are the huge amount of concentrated brine discharge, and relatively high cost related to ion exchange when applied in a centralized water treatment plant. Lime softening was ranked third. The main problems related to lime softening are the substantial amount of wet sludge generated, high chemical input, and subsequent finished water and waste treatment requirements. Nanofiltration was ranked fourth. The main disadvantages are continuous pressure input, concentrated brine generation, and the high cost related to membrane maintenance.

- Sensitivity analysis results using cases with different weight assignments for each criterion showed that the rank of the four technologies did not change, albeit there were some variations in total scores.

Household (point-of-entry/point-of-use) technologies:

- Overall ranking (from the highest score to the lowest score): template assisted crystallization, ion exchange, electrically induced precipitation, nanofiltration, magnetic water treatment method, capacitive deionization.

- Template assisted crystallization gained the highest score. TAC is a relatively new treatment option but with very little critical assessment. However, it has great potential to effectively prevent scale formation at household level without harming the environment. Thus, it is a possible salt-free alternative to ion exchange if its performance claims can be confirmed.

- Ion exchange got the second highest mark, and its major issues are related to chloride being released into the environment, the elevated sodium concentration in softened water as it pertains to human health, and the disposal of the generated brine.

- Nanofiltration got the fourth rank. Considering nanofiltration applications at the household level, the main drawbacks are the pressure input requirement, brine generation, and the high cost related to membrane cartridge purchase and change.

- Electrically induced precipitation, a magnetic water treatment method, and capacitive deionization are three physical scale prevention approaches which were ranked third, fifth, and sixth, respectively. The main disadvantages for these physical methods are their high electricity requirements and the uncertainty related to their operational parameters which still need to be optimized.

- Sensitivity analysis results obtained using cases with different weight assignments showed that the relative ranks were not affected though the total scores showed some variations.

The second phase tested the TAC technology which was ranked highest in the Phase I assessment at the household level. Experiments were conducted to test the performance of the TAC unit in two different source waters. Compared to location A water, location B water had much higher hardness, free chlorine concentration, and Fe/Mn concentration. The TAC unit is supposed to form insoluble $CaCO_3$ crystals, which are assumed to prevent scale formation. Free Ca ion concentrations as an indirect measure of crystal formation. Total Ca and Mg ion concentrations, metal ion concentrations, and other standard water quality parameters were also measured before and after TAC treatment. LSI and CCPP values were calculated to represent the scale precipitation potential for both TAC treated and untreated water. In addition, a simplified scale test (not in a flow-through system) was developed to measure the scale deposit after boiling treated and untreated water. Finally, a sequential ultrafiltration test was designed to isolate and determine the approximate size of the microcrystal. Key conclusions and findings related to the second phase are listed below.

- Free Ca concentration showed a similar trend in both locations, some reduction was measured, but the percentage removals were relatively small. The percentage removals for location A unit A and unit B, and location B unit B were 5.0%, 4.7%, and 4.0% respectively. Location B treated water showed larger reduction values than location A.

- Total Ca and Mg concentrations were reduced slightly but were too small to be of practical value in TAC treated water. The TAC process was not expected to remove any hardness according to the theory. The percentage removal of Ca^{2+} ions for location A unit A unit B and location B unit B were 4.4%, 4.1%, and 2.7%, respectively. The percentage removal of Mg^{2+} ion for location A unit A unit B and location B unit B were 4.0%, 4.5%, and 6.9% respectively. Location B treated water showed higher reduction values of both

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Ca^{2+} and Mg^{2+} than location A.

- Mn and Fe ion reductions (especially for location B water) were highly variable. This was because the actual values of Fe and Mn in drinking water approached the MDL for the instrument used (ICP). A full metal analysis did not show any significant decrease in other metal concentration and most metals were not detectable.

- LSI and CCPP calculation results did essentially not show any difference between the treated and untreated waters.

- A new simplified scale test using household electric kettles was developed and it showed that TAC treated water formed a bit less scale. Some scale detachment was observed on the heating plates after boiling treated water. The fact that boiling treated water formed a visible amount of scale on the heating plate is still problematic.

- Sequential ultrafiltration tests were not able to identify any substantial crystal formation. One possible reason is that there were not a lot of crystals being formed and the methodology used was not sensitive enough to detect these.

5.2 Recommendations for future work

Recommendations for future work are as follows:

- Future research work could perform scale test according to DVGW W512 standard test using a flow through system. This is to provide more supportive information for TAC technology by testing different source waters, in addition to Fox et al. (2014) report.

- Water samples collected for this study were taken right after the TAC unit. According to the theory, the microcrystals formed were supposed to serve as nucleation surfaces for further $CaCO_3$ precipitation as the water flows through pipes. Therefore, future studies could design a setup to test the unit performance after the water has been transported a certain distance i.e. had a certain contact time after TAC treatment in a flow-through system.

- Although the contact time of the media of only five seconds is supposed to be sufficient for crystal formation, the flow rate could be controlled in future work to test if longer contact times such as several minutes would improve performance.

- Future studies could also do some media analysis, to ascertain differences in media

surfaces in brand new media and exhausted media.

- Further development of the simplified scale test would be appropriate because it gave different results than the standard DVGW W512 test which is designed for a flow-through system.

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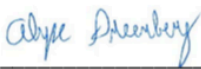
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Appendix A Supporting information for Chapter 3

Table A.1 Sensitivity analysis for centralized softening technologies. Case 1: more focus on sustainability related criteria (waste disposal and energy consumption) in the assessment

	Criteria	Case1 Weight	Lime Softening		Pellet Softening		Nanofiltration		Ion Exchange	
			Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal
Waste Disposal	Salt (Concentrate Brine)	17	5	85	5	85	0	0	0	0
	Sludge	17	0	0	5	85	5	85	5	85
Energy Consumption	Pressure	17	5	85	5	85	0	0	5	85
	Electricity	17	5	85	5	85	5	85	5	85
Life-cycle Cost	Capital Cost	8	2	16	4	32	1	8	3	24
	O&M Cost	8	2	16	3	24	1	8	3	24
Subsequent Treatment Needed		8	8	5	40	0	0	0	5	40
Chemical Addition		8	8	0	0	3	4	32	4	32
Total Score/Weight		100	■	327	■	420	■	218	■	375

Table A.2 Sensitivity analysis for centralized softening technologies. Case 2: more focus on life-cycle cost criteria in the assessment

	Criteria	Case 2 Weight	Lime Softening		Pellet Softening		Nanofiltration		Ion Exchange	
			Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal
Waste Disposal	Salt (Concentrate Brine)	8	5	40	5	40	0	0	0	0
	Sludge	8	0	0	5	40	5	40	5	40
Energy Consumption	Pressure	8	5	40	5	40	0	0	5	40
	Electricity	8	5	40	5	40	5	40	5	40
Life-cycle Cost	Capital Cost	26	2	52	4	104	1	26	3	78
	O&M Cost	26	2	52	3	78	1	26	3	78
Subsequent Treatment Needed		8	5	40	0	0	0	0	5	40
Chemical Addition		8	0	0	3	24	4	32	4	32
Total Score/Weight		100	■	264	■	366	■	164	■	348

Table A.3 Sensitivity analysis for centralized softening technologies. Case 3: every criterion shares the same importance in the assessment

	Criteria	Case 3 Weight	Lime Softening		Pellet Softening		Nanofiltration		Ion Exchange	
			Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal
Waste Disposal	Salt (Concentrate Brine)	12.5	5	62.5	5	62.5	0	0	0	0
	Sludge	12.5	0	0	5	62.5	5	62.5	5	62.5
Energy Consumption	Pressure	12.5	5	62.5	5	62.5	0	0	5	62.5
	Electricity	12.5	5	62.5	5	62.5	5	62.5	5	62.5
Life-cycle Cost	Capital Cost	12.5	2	25	4	50	1	12.5	3	37.5
	O&M Cost	12.5	2	25	3	37.5	1	12.5	3	37.5
Subsequent Treatment Needed		12.5	5	62.5	0	0	0	0	5	62.5
Chemical Addition		12.5	0	0	3	37.5	4	50	4	50
Total Score/Weight		100	■	300	■	375	■	200	■	375

Table A.4 Sensitivity analysis for household softening technologies Case 1: more focus on sustainability related criteria (waste disposal and energy consumption) in the assessment

Criteria		Case 1 Weight	Template Assisted Crystallization		Ion Exchange		Nanofiltration		Electrically Induced Precipitation		Magnetic Water Treatment		Capacitive Deionization	
			Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal
Waste Disposal	Salt (Concentrate Brine)	14	5	70	0	0	0	0	5	70	5	70	5	70
	Sludge	14	5	70	5	70	5	70	5	70	5	70	5	70
Energy Consumption	Pressure	14	5	70	5	70	0	0	5	70	5	70	5	70
	Electricity	14	5	70	5	70	5	70	0	0	0	0	0	0
Life-cycle Cost	Capital Cost	8	4	32	3	24	1	8	3	24	5	40	0	0
	O&M Cost	14	5	70	0	0	5	70	5	70	5	70	5	70
Efficiency		12	4	48	5	60	5	60	1	12	0	0	3	36
Easy to Use		8	4	32	4	32	4	32	3	24	1	8	3	24
Validated Technology		8	1	8	5	40	5	40	2	16	1	8	2	16
Total Score		100	■	440	■	382	■	280	■	302	■	306	■	310

Table A.5 Sensitivity analysis for household softening technologies. Case 2: more focus on life-cycle cost criteria in the assessment

Criteria		Case 2 Weight	Template Assisted Crystallization		Ion Exchange		Nanofiltration		Electrically Induced Precipitation		Magnetic Water Treatment		Capacitive Deionization	
			Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal
Waste Disposal	Salt (Concentrate Brine)	8	5	40	0	0	0	0	5	40	5	40	5	40
	Sludge	8	5	40	5	40	5	40	5	40	5	40	5	40
Energy Consumption	Pressure	8	5	40	5	40	0	0	5	40	5	40	5	40
	Electricity	8	5	40	5	40	5	40	0	0	0	0	0	0
Life-cycle Cost	Capital Cost	20	4	80	3	60	1	20	3	60	5	100	0	0
	O&M Cost	20	5	100	2	40	0	0	2	40	5	100	3	60
Efficiency		12	4	48	5	60	5	60	1	12	0	0	3	36
Easy to Use		8	4	32	4	32	4	32	3	24	1	8	3	24
Validated Technology		8	1	8	5	40	5	40	2	16	1	8	2	16
Total Score		100	■	428	■	352	■	232	■	272	■	336	■	256

Table A.6 Sensitivity analysis for household softening technologies. Case 3: every criterion shares the same importance in the assessment

Criteria		Case 3 Weight	Template Assisted Crystallization		Ion Exchange		Nanofiltration		Electrically Induced Precipitation		Magnetic Water Treatment		Capacitive Deionization	
			Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal	Score	Subtotal
Waste Disposal	Salt (Concentrate Brine)	11	5	55	0	0	0	0	5	55	5	55	5	55
	Sludge	11	5	55	5	55	5	55	5	55	5	55	5	55
Energy Consumption	Pressure	11	5	55	5	55	0	0	5	55	5	55	5	55
	Electricity	11	5	55	5	55	5	55	0	0	0	0	0	0
Life-cycle Cost	Capital Cost	11	4	44	3	33	1	11	3	33	5	55	0	0
	O&M Cost	11	5	55	2	22	0	0	2	22	5	55	3	33
Efficiency		12	4	48	5	60	5	60	1	12	0	0	3	36
Easy to Use		11	4	44	4	44	4	44	3	33	1	11	3	33
Validated Technology		11	1	11	5	55	5	55	2	22	1	11	2	22
Total Score		100	∎	422	∎	379	∎	280	∎	287	∎	297	∎	289

Appendix B Supporting information for Chapter 4

Table B.1 Raw water (influent water) quality data of location A. Two units (A and B) were set up at location A using the same source water. ND means not detectable by the machine. N/A means not available (not measured)

Measure Date	Unit	Temperature (℃)	Conductivity (μS/cm)	pH	Alkalinity (mg/L CaCO₃)	TOC (mg/L)	Cl₂ Residual (mg/L)	Turbidity (NTU)	Mg (mg/L)	Ca (mg/L)	Mn (mg/L)	Fe (mg/L)
22-May-18	A	17	553	7.3	206	1.3	0.07	0.12	19.9	68.8	0.03	ND
22-May-18	B	17	541	7.4	202	1.9	0.06	0.2	18.4	64.2	0.02	ND
23-May-18	A	16	568	7	216	N/A	N/A	N/A	16.7	62.6	0.02	ND
23-May-18	B	16	560	7.2	217	N/A	N/A	N/A	18.6	66.2	0.04	0.07
29-May-18	A	16	600	7	216	2.4	0.06	0.14	22.9	69.5	0.03	ND
29-May-18	B	16	598	6.9	218	1.9	0.08	0.17	22	72.9	0.03	ND
30-May-18	A	16	609	7.2	222	N/A	N/A	N/A	21.2	69.8	0.03	0.08
30-May-18	B	16	619	7.2	225	N/A	N/A	N/A	21	64.7	0.05	0.08
3-Jun-18	A	17	626	7.4	210	4.1	0.08	0.26	22	69.9	ND	ND
3-Jun-18	B	17	626	7.3	212	3.2	0.07	0.33	22.8	74.4	ND	ND
4-Jun-18	A	18	623	7.5	193	2.6	N/A	N/A	21.8	69	ND	ND
4-Jun-18	B	18	644	7.4	199	3.1	N/A	N/A	22.1	71.1	ND	ND
19-Jun-18	A	17	611	7.2	208	4.4	N/A	N/A	23.2	80.6	0.03	ND
19-Jun-18	B	17	612	7.3	210	4.2	N/A	N/A	23.3	76.2	0.03	ND
21-Jun-18	A	19	599	7.2	187	2.4	0.05	0.19	21.6	62.4	0.03	0.06
21-Jun-18	B	19	596	7.2	187	2.9	0.07	0.19	21.5	60	0.03	0.05
27-Jun-18	A	16	599	6.8	209	2.2	0.06	0.2	22	68.5	0.03	ND

Note: MDL of Mn and Fe measured by ICP at the University of Waterloo is 0.02 mg/L. Measurable Mn concentration exceeds AO value (0.02 mg/L) which is set by Health Canada (2019).

Table B.1 (continued). Raw water (influent water) quality data of location A. Two units (A and B) were set up at location A using the same source water. ND means not detectable by the machine. N/A means not available (not measured)

Measure Date	Unit	Temperature (℃)	Conductivity (µS/cm)	pH	Alkalinity (mg/L CaCO₃)	TOC (mg/L)	Cl₂ Residual (mg/L)	Turbidity (NTU)	Mg (mg/L)	Ca (mg/L)	Mn (mg/L)	Fe (mg/L)
27-Jun-18	B	16	603	6.8	207	2	0.04	0.13	21.7	74.9	0.03	ND
11-Jul-18	A	18	592	7.2	205	0.68	0.05	0.22	21.2	65.5	ND	ND
11-Jul-18	B	18	595	7.2	204	1.1	0.08	0.17	21	66.6	ND	ND
24-Aug-18	A	20	628	6.9	199	2	0.05	0.08	21.6	62.4	ND	0.04
24-Aug-18	B	17	603	7	204	1.2	0.05	0.13	21.5	60.2	ND	0.05
12-Oct-18	A	18	607	7.2	187	0.22	0.06	0.15	20.2	56.5	0.03	0.07

Note: MDL of Mn and Fe measured by ICP at the University of Waterloo is 0.02 mg/L. Measurable Mn concentration exceeds AO value (0.02 mg/L) which is set by Health Canada (2019).

Table B.2 Raw water quality data of location B

Measure Date	Sample Name	Temperature (℃)	Conductivity (µS/cm)	pH	Alkalinity (mg/L CaCO₃)	TOC (mg/L)	Cl₂ Residual (mg/L)	Turbidity (NTU)	Mg (mg/L)	Ca (mg/L)	Mn (mg/L)	Fe (mg/L)
16-Sep-18	B	20	1383	7.2	233	1.3	0.86	0.8	51.3	250	0.08	0.09
19-Sep-18	B	19	1446	7	234	1.3	1.08	1	53.7	273	0.09	0.1
24-Sep-18	B	20	1314	7.1	230	1.2	0.9	0.7	54.2	236	0.1	0.2
25-Sep-18	B	20	1568	7	237	1.3	1.25	0.74	59.3	304	0.1	0.1
26-Sep-18	B	19	1332	7.1	233	1	1.08	0.85	41.6	226	0.1	0.1
1-Oct-18	B	19	1298	7	235	0.95	0.69	0.79	49.7	237	0.1	0.2
3-Oct-18	B	18	1395	7.1	229	0.61	0.98	1.1	50.7	265	0.1	0.2

Note: MDL of Mn and Fe measured by ICP at the University of Waterloo is 0.02 mg/L. All location B water samples measured has Mn concentration exceed AO values (0.02 mg/L) which are set by Health Canada (2019).

Table B.3 Total Ca^{2+} and Mg^{2+} concentration in untreated and treated water measured by cation IC (two locations and two units). Each sample was measured 4 times (n=4) and calculated the average value

Location	Time Measured	Untreated (In)				Treated (Out)			
		Magnesium (mg/L)		Calcium (mg/L)		Magnesium (mg/L)		Calcium (mg/L)	
		Average	Standard deviation	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Location A Unit A	22-May-18	19.9	0.9	65.8	4.0	21.6	1.2	59.6	3.9
	23-May-18	16.7	2.9	65.4	3.0	20.5	1.4	62.6	4.4
	29-May-18	22.9	1.7	69.5	4.1	22.0	1.5	68.5	3.8
	30-May-18	21.2	1.9	69.8	6.6	22.1	1.8	65.9	4.7
	3-Jun-18	22.0	1.8	69.9	4.8	22.8	2.0	68.8	4.5
	4-Jun-18	21.8	2.3	69.0	3.0	20.9	1.3	65.8	4.1
	19-Jun-18	23.2	1.7	80.6	1.9	21.4	2.2	76.5	4.3
	21-Jun-18	21.6	0.6	62.4	2.8	21.0	0.9	58.5	3.5
	27-Jun-18	22.0	1.8	68.5	3.5	21.4	1.5	67.4	1.9
	11-Jul-18	21.2	0.9	66.5	4.8	20.6	2.0	64.0	3.4
	24-Aug-18	21.6	1.2	62.4	3.2	21.0	0.8	58.5	2.6
	12-Oct-18	20.2	1.5	56.5	3.8	19.6	0.9	54.5	2.4
Location A Unit B	22-May-18	18.4	1.9	64.2	3.7	19.3	1.7	63.7	4.0
	23-May-18	18.6	1.2	67.3	4.0	20.4	1.6	66.1	5.5
	29-May-18	22.0	1.5	72.9	1.3	21.7	1.6	63.4	2.9
	30-May-18	21.0	1.9	64.7	3.7	21.2	1.2	64.0	3.5
	3-Jun-18	22.8	0.7	74.4	4.0	22.2	1.6	72.1	5.2
	4-Jun-18	22.1	1.0	73.1	4.2	22.3	0.7	71.2	4.4
	19-Jun-18	23.3	1.8	76.2	4.1	21.7	2.1	71.3	6.0
	21-Jun-18	21.5	1.3	61.5	3.7	20.3	1.5	60.3	2.7
	27-Jun-18	21.7	1.0	74.9	3.4	20.7	1.5	71.4	3.6
	11-Jul-18	21.0	2.3	69.9	2.7	21.1	1.8	68.9	4.4
	24-Aug-18	21.5	1.1	60.2	3.0	20.3	1.0	60.3	3.1
Location B Unit B	16-Sep-18	50.3	0.5	250	3.4	46.0	1.7	217	4.2
	19-Sep-18	52.7	1.1	275	5.8	47.3	1.0	268	4.8
	24-Sep-18	55.2	1.0	236	3.2	52.6	0.5	231	2.5
	25-Sep-18	46.3	0.9	300	2.8	41.6	3.1	291	5.4
	26-Sep-18	44.6	1.0	234	6.1	47.9	2.4	226	2.6
	1-Oct-18	50.7	0.8	239	2.8	48.1	0.5	233	2.2
	3-Oct-18	50.7	1.4	266	1.3	49.0	3.2	261	4.6

Table B.4 Free Ca^{2+} concentration in untreated and treated water measured by Ca^{2+} ISE (two locations and two units)

Location	Time Measured	Untreated (In) Calcium (mg/L)	Treated (Out) Calcium (mg/L)
Location A Unit A	19-Jun-18	67.9	64.2
	21-Jun-18	60.4	57.9
	27-Jun-18	68.6	65.5
	11-Jul-18	64.5	60.9
	24-Aug-18	65.4	62.1
	12-Oct-18	62.2	58.8
Location A Unit B	19-Jun-18	69.7	66.5
	21-Jun-18	59.9	56.7
	27-Jun-18	71.1	68.7
	11-Jul-18	65.9	61.7
	24-Aug-18	64.9	62.2
Location B Unit B	16-Sep-18	220	209
	19-Sep-18	231	221
	24-Sep-18	204	197
	25-Sep-18	224	211
	26-Sep-18	231	223
	1-Oct-18	193	187
	3-Oct-18	240	233

Table B.5 Total Mn and Fe concentrations in untreated (in) and treated (out) water measured by ICP (two locations and two units). Each sample was measured 4 times (n=4) and calculate the average value. ND means not detectable and N/A means not able to calculate

| Location | Time Measured | Untreated (In) | | | | Treated (Out) | | | |
| | | Manganese (mg/L) | | Iron (mg/L) | | Manganese (mg/L) | | Iron (mg/L) | |
		Average	Standard deviation	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Location A Unit A	22-May-18	0.03	0.003	ND	N/A	0.02	0.003	ND	N/A
	23-May-18	0.02	0.004	0.07	0.02	0.03	0.003	0.07	0.02
	29-May-18	0.03	0.003	0.08	0.004	0.03	0.002	0.08	0
	30-May-18	0.03	0.002	0.08	0.014	0.03	0.005	0.07	0.006
	03-Jun-18	ND	N/A	ND	N/A	ND	N/A	ND	N/A
	04-Jun-18	ND	N/A	ND	N/A	ND	N/A	ND	N/A
	19-Jun-18	0.03	0.004	ND	N/A	0.03	0.004	ND	N/A
	21-Jun-18	0.03	0.003	0.06	0.011	0.03	0.002	0.05	0.013
	27-Jun-18	0.03	0.002	ND	N/A	0.03	0.004	ND	N/A
	11-Jul-18	ND	N/A	ND	N/A	ND	N/A	ND	N/A
	22-Aug-18	ND	N/A	0.04	0.003	ND	N/A	0.04	0.013
	12-Oct-18	0.03	0.008	0.07	0.028	0.03	0.007	0.07	0.019
Location A Unit B	22-May-18	0.02	0.003	ND	N/A	0.02	0.006	ND	N/A
	23-May-18	0.04	0.002	0.07	0.009	0.02	0.003	0.08	0.006
	29-May-18	0.03	0.002	0.06	0.001	0.03	0.004	0.06	0.001
	30-May-18	0.05	0.004	0.08	0.008	0.03	0.006	0.1	0.004
	03-Jun-18	ND	N/A	ND	N/A	ND	N/A	ND	N/A
	04-Jun-18	ND	N/A	ND	N/A	ND	N/A	ND	N/A
	19-Jun-18	0.03	0.003	ND	N/A	0.03	0.001	ND	N/A
	21-Jun-18	0.03	0.004	0.06	0.008	0.03	0.005	0.06	0.011
	27-Jun-18	0.03	0.002	ND	N/A	0.02	0.002	ND	N/A
	11-Jul-18	ND	N/A	ND	N/A	ND	N/A	ND	N/A
	22-Aug-18	ND	N/A	0.05	0.003	ND	N/A	0.05	0.003
Location B Unit B	16-Sep-18	0.08	0.009	0.09	0.024	0.07	0.006	0.10	0.007
	19-Sep-18	0.09	0.004	0.12	0.036	0.08	0.005	0.10	0.033
	24-Sep-18	0.11	0.009	0.17	0.037	0.10	0.003	0.17	0.029
	25-Sep-18	0.12	0.004	0.13	0.016	0.12	0.021	0.13	0.028
	26-Sep-18	0.11	0.004	0.15	0.056	0.11	0.004	0.14	0.023
	01-Oct-18	0.14	0.004	0.23	0.027	0.13	0.009	0.18	0.037
	03-Oct-18	0.13	0.006	0.21	0.022	0.13	0.005	0.20	0.025

Note: MDL of Mn and Fe measured by ICP at the University of Waterloo is 0.02 mg/L

Figure B.1 Total Mn²⁺ concentration measured for location A (a) unit A and (b) unit B. Each sample was measured 4 times by the ICP machine (n=4), and error bars show standard deviations

Figure B.2 Total Mn^{2+} concentration measured for location B unit B water. Each sample was measured 4 times by the ICP machine (n=4), and error bars show standard deviations
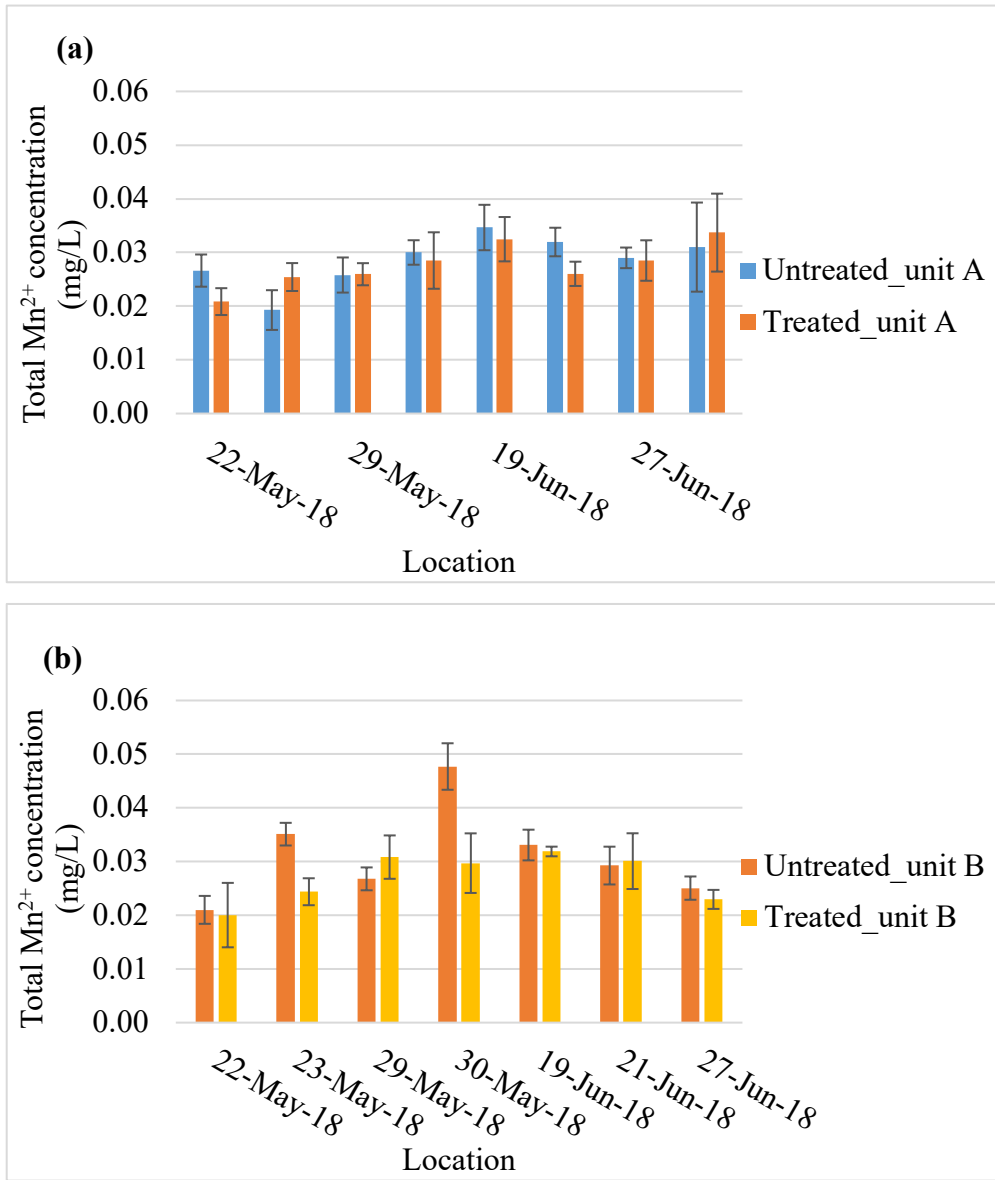
Figure B.3 Total Fe^{2+} concentration measured for location A (a) unit A and (b) unit B water. Each sample was measured 4 times by the ICP machine (n=4), and error bars show standard deviations
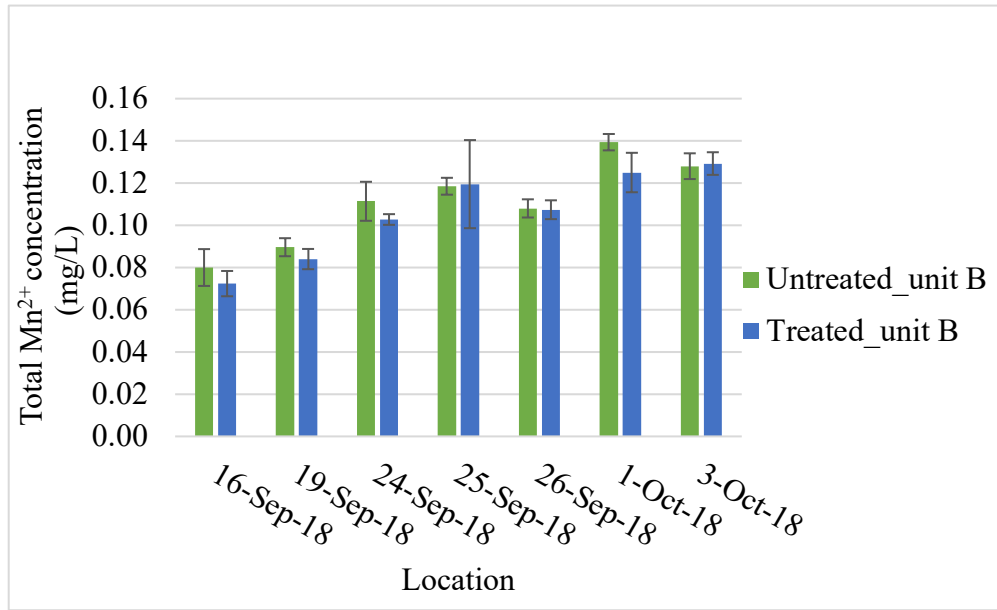
Figure B.4 Total Fe^{2+} concentration measured for location B unit B water. Each sample was measured 4 times by the ICP machine (n=4), and error bars show standard deviations
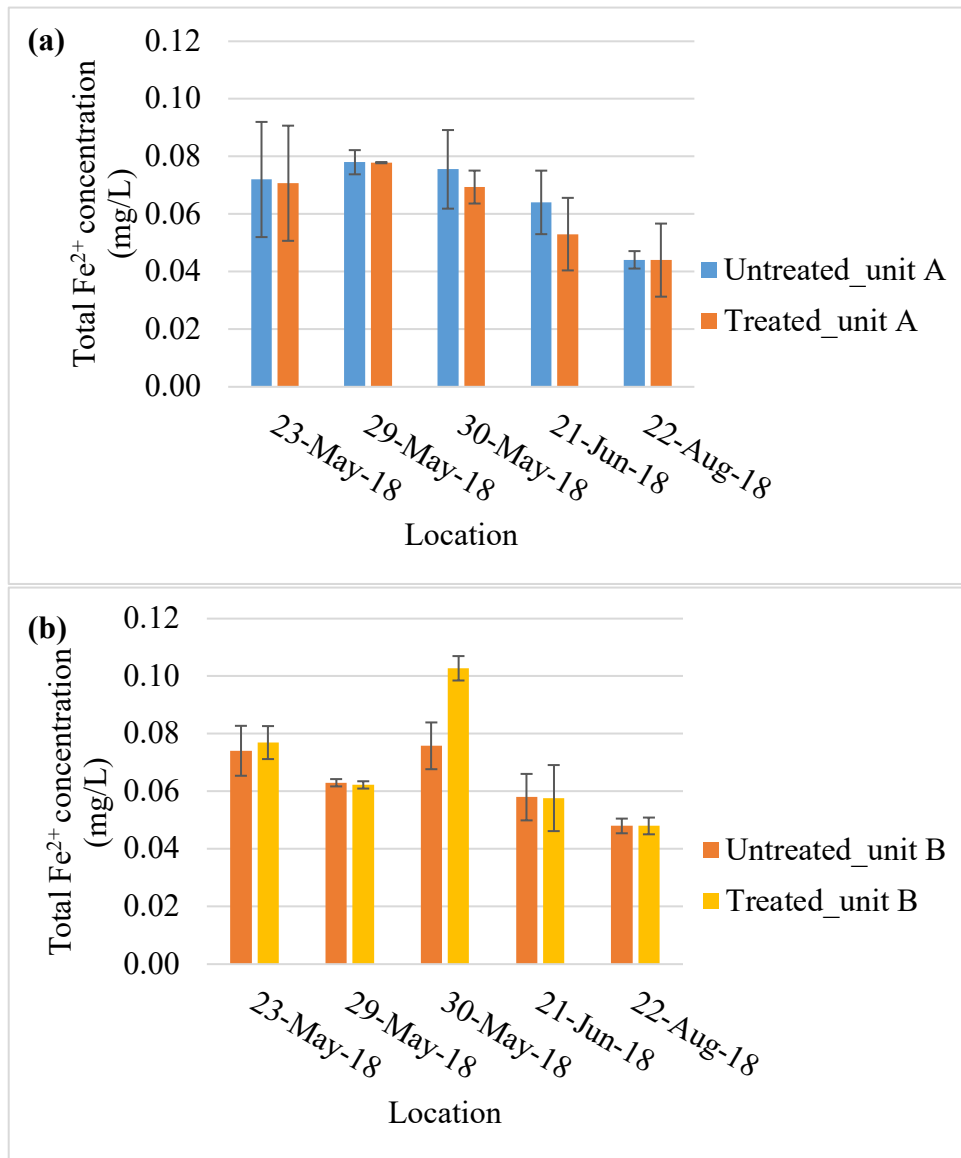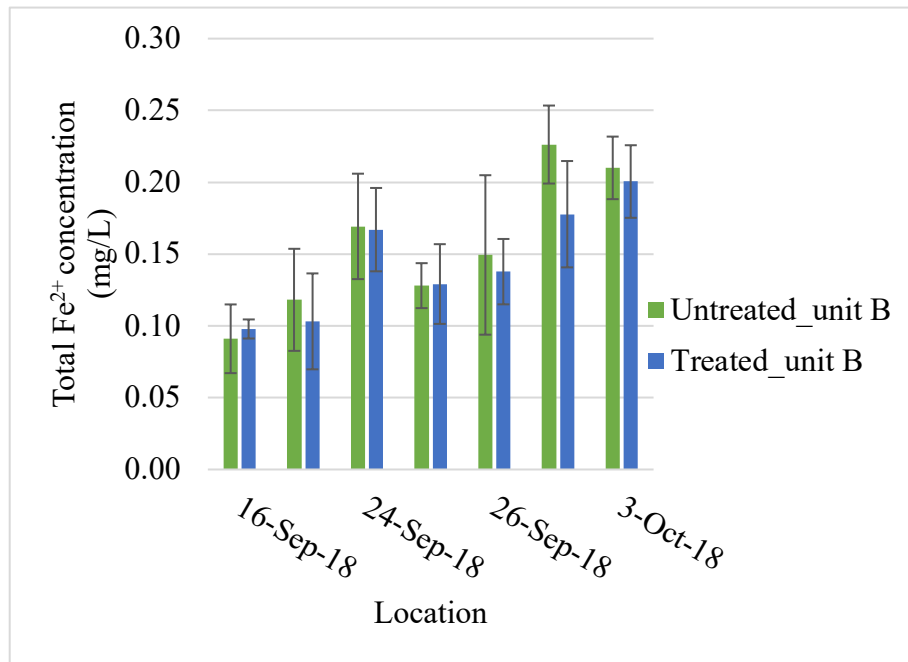
Table B.6 Full metal analysis results of both units of location A water samples measured by ICP-MS. "In" represents untreated water and "Out" represent treated water

Sample Name/date	29-May-18		29-May-18		16-Sep-18	
Total Metals (mg/L)	IN _unit A	OUT _unit A	IN _unit B	OUT _unit B	IN _unit A	OUT _unit A
Aluminum (Al)	0.103	0.104	0.104	0.379	0.0569	0.0545
Arsenic (As)	0.00032	0.00031	0.00032	0.00031	0.00034	0.00031
Barium (Ba)	0.0785	0.0793	0.0799	0.0794	0.0800	0.0798
Boron (B)	0.017	0.018	0.018	0.052	0.017	0.017
Cadmium (Cd)	0.0000094	0.0000096	0.0000081	0.0000094	0.0000078	0.0000067
Calcium (Ca)	81.6	81.9	79.5	77.3	71.4	70.7
Copper (Cu)	0.0159	0.0158	0.0255	0.0246	0.0184	0.0183
Iron (Fe)	0.014	0.014	0.015	0.018	0.019	0.021
Lead (Pb)	0.000067	0.000083	<0.000050	0.000330	0.000191	0.000540
Lithium (Li)	0.0029	0.0029	0.0028	0.0027	0.0033	0.0030
Magnesium (Mg)	22.7	22.9	23.3	22.8	20.3	20.5
Manganese (Mn)	0.00516	0.00561	0.00568	0.00562	0.00415	0.00847
Molybdenum (Mo)	0.000895	0.000889	0.000900	0.000847	0.000736	0.000727
Potassium (K)	2.20	2.21	2.24	2.20	2.38	2.42
Rubidium (Rb)	0.00090	0.00093	0.00096	0.00097	0.00105	0.00103
Selenium (Se)	0.000158	0.000144	0.000165	0.000154	0.000140	0.000098
Silicon (Si)	3.06	3.06	3.11	3.04	3.16	3.15
Sodium (Na)	35.5	34.8	35.6	35.0	29.6	29.8
Strontium (Sr)	0.266	0.265	0.261	0.269	0.276	0.241
Sulfur (S)	14.2	14.1	14.5	13.9	13.6	13.4
Uranium (U)	0.000698	0.000702	0.000688	0.000700	0.000692	0.000690
Zinc (Zn)	<0.0030	0.0034	0.0032	0.0119	0.0036	0.0168

Note: Total 39 metals were measured, the following metals were not detectable and the MDLs (mg/L) are in "()": Antimony (0.0001), Beryllium (0.0001), Bismuth (0.00005), Cesium (0.00001), Chromium (0.0005), Cobalt (0.0001), Nickel (0.0005), Phosphorus (0.05), Silver (0.00005), Tellurium (0.0002), Thallium (0.00001), Thorium (0.0001), Tin (0.0001), Titanium (0.0003), Tungsten (0.0001), Vanadium (0.0005), Zirconium (0.0003)

Table B.7 Full metal analysis results of location B water samples (unit B only) measured by ICP-MS. "In" represents untreated water and "Out" represent treated water

Sample Name/date Total Metals (mg/L)	16-Sep-18 IN _unit B	16-Sep-18 OUT _unit B	3-Oct-18 IN _unit B	3-Oct-18 OUT _unit B
Barium (Ba)	0.0835	0.0868	0.0821	0.0899
Boron (B)	<0.10	<0.10	0.13	0.12
Calcium (Ca)	255	265	309	302
Copper (Cu)	0.098	0.090	0.081	0.086
Lead (Pb)	0.00149	0.00134	<0.00050	<0.00050
Magnesium (Mg)	47.8	49.4	53.0	53.1
Manganese (Mn)	0.0247	0.0249	0.0285	0.0298
Molybdenum (Mo)	0.00330	0.00336	0.00363	0.00329
Potassium (K)	1.85	1.83	2.02	2.02
Silicon (Si)	4.6	4.6	4.8	4.7
Sodium (Na)	15.6	15.9	16.9	16.8
Strontium (Sr)	12.1	12.3	11.7	11.3
Sulfur (S)	205	201	257	251
Uranium (U)	0.00042	0.00046	0.00048	0.00048

Note: Total 39 metals were measured, the following metals were not detectable and the MDLs (mg/L) are in "()": Aluminum (0.005) Antimony (0.0001), Arsenic (0.0001), Beryllium (0.0001), Bismuth (0.00005), Cadmium (0.0000005), Cesium (0.00001), Chromium (0.0005), Cobalt (0.0001), Iron (0.01), Lithium (0.001), Nickel (0.0005), Phosphorus (0.05), Rubidium (0.0002), Selenium (0.00005), Silver (0.00005), Tellurium (0.0002), Thallium (0.00001), Thorium (0.0001), Tin (0.0001), Titanium (0.0003), Tungsten (0.0001), Vanadium (0.0005), Zinc (0.003), Zirconium (0.0003)

Table B.8 LSI and CCPP values calculated for location A water samples for unit A and B and the difference (treated-untreated)

Date	Unit	LSI			CCPP		
		Untreated	Treated	Difference	Untreated	Treated	Difference
22-May-18	A	-0.03	-0.06	-0.03	-0.02	-0.03	-0.01
	B	0.04	-0.01	-0.05	0.02	0	-0.02
23-May-18	A	-0.4	-0.3	0.1	-0.37	-0.26	0.11
	B	-0.2	-0.25	-0.05	-0.16	-0.2	-0.04
29-May-18	A	-0.37	-0.4	-0.03	-0.35	-0.4	-0.05
	B	-0.39	-0.44	-0.05	-0.39	-0.43	-0.04
30-May-18	A	-0.18	-0.14	0.04	-0.14	-0.11	0.03
	B	-0.13	-0.15	-0.02	-0.1	-0.12	-0.02
03-Jun-18	A	0.02	-0.08	-0.1	0.01	-0.05	-0.06
	B	-0.09	-0.09	0	-0.07	-0.06	0.01
04-Jun-18	A	0.07	-0.02	-0.09	0.04	-0.01	-0.05
	B	0.08	-0.05	-0.13	0.04	-0.03	-0.07
19-Jun-18	A	-0.11	-0.11	0	-0.08	-0.08	0
	B	-0.01	-0.06	-0.05	-0.01	-0.04	-0.03
21-Jun-18	A	-0.27	-0.29	-0.02	-0.18	-0.19	-0.01
	B	-0.2	-0.21	-0.01	-0.12	-0.13	-0.01
27-Jun-18	A	-0.57	-0.58	-0.01	-0.63	-0.64	-0.01
	B	-0.53	-0.52	0.01	-0.58	-0.57	0.01
11-Jul-18	A	-0.17	-0.17	0	-0.12	-0.12	0
	B	-0.14	-0.15	-0.01	-0.09	-0.1	-0.01
24-Aug-18	A	-0.45	-0.4	0.05	-0.4	-0.32	0.08
	B	-0.45	-0.62	-0.17	-0.39	-0.65	-0.26
12-Oct-18	A	-0.31	-0.28	0.03	-0.2	-0.17	0.03

Table B.9 LSI and CCPP values calculated for location B (unit B only) water samples and the difference (treated-untreated)

Date	Unit	LSI			CCPP		
		Untreated	Treated	Difference	Untreated	Treated	Difference
16-Sep-18		-0.08	-0.16	-0.08	-0.07	-0.14	-0.07
19-Sep-18		-0.19	-0.2	-0.01	-0.19	-0.19	0
24-Sep-18		-0.1	-0.15	-0.05	-0.09	-0.14	-0.05
25-Sep-18	B	-0.18	-0.21	-0.03	-0.18	-0.21	-0.03
26-Sep-18		-0.22	-0.23	-0.01	-0.2	-0.22	-0.02
01-Oct-18		-0.23	-0.23	0	-0.22	-0.23	-0.01
03-Oct-18		-0.22	-0.25	-0.03	-0.2	-0.24	-0.04

Table B.10 Calculated total mass of metals (Mg, Ca, Mn, Fe) in the scale deposit (for both locations). ND represents not detectable.

Location	Unit	Time Measured	Mg (mg)		Ca (mg)		Mn (mg)		Fe (mg)	
			Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Location A	A	23-Aug-18	2.1	2.1	180.8	155.4	ND	ND	0.10	0.09
	B	23-Aug-18	2.4	1.9	194.2	145.9	ND	ND	0.07	0.08
	A	12-Oct-18	2.0	1.8	184.7	146.3	0.02*	0.02*	0.14	0.16
Location B	B	17-Sep-18	2.3	2.2	371.6	333.1	0.15	0.12	0.23	0.21
	B	24-Sep-18	2.9	2.8	374.9	300.7	0.18	0.14	0.25	0.24
	B	01-Oct-18	2.6	2.9	358.5	279.5	0.17	0.14	0.32	0.27

Table B.11 Calculated total mass of metals (Mg, Ca, Mn, Fe) in the sticky scale deposit (for both locations)

Location	Unit	Time Measured	Mg (mg)		Ca (mg)		Mn (mg)		Fe (mg)	
			Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Location A	A	15-Aug-18	1.9	1.7	66.2	52.5	0.01	0.01	0.10	0.10
Location B	B	26-Sep-18	1.8	1.9	199.3	169.4	0.15	0.13	0.23	0.22

Table B.12 Calculated total metal (Mg, Ca, Mn, Fe) concentration of the raw water and filtrate after ultrafiltration procedure (both locations). Three different sizes of filter were used: 3000 Da, 1000 Da and 500 Da. Each sample was measured 4 times (n=4). ND means not detectable and N/A means not able to be calculated

Location and Date	Sample Name	Mg (mg/L)		Ca (mg/L)		Mn (mg/L)		Fe (mg/L)	
		Average	Standard deviation	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Location A 16-Jul-18	IN_Raw	22.3	0.2	70.0	0.3	ND	N/A	ND	N/A
	IN_30000 Da	22.2	0.1	70.0	0.3	ND	N/A	ND	N/A
	IN_1000 Da	21.5	0.1	67.6	0.3	ND	N/A	ND	N/A
	IN_500 Da	15.1	0.1	52.1	0.5	ND	N/A	ND	N/A
	OUT_Raw	22.5	0.1	70.0	0.3	ND	N/A	ND	N/A
	OUT_30000 Da	21.8	0.1	69.1	0.3	ND	N/A	ND	N/A
	OUT_1000 Da	20.7	0.2	65.4	0.6	ND	N/A	ND	N/A
	OUT_500 Da	14.7	0.1	50.1	0.5	ND	N/A	ND	N/A
Location B 3-Oct-18	IN_Raw	51.5	0.4	288	0.9	0.13	0.006	0.19	0.02
	IN_3000 Da	49.8	0.2	278	0.7	0.10	0.005	0.13	0.02
	IN_1000 Da	49.8	0.5	277	1.9	0.11	0.007	0.17	0.03
	IN_500 Da	32.3	0.2	186	1.3	0.10	0.006	0.17	0.02
	OUT_Raw	50.6	0.2	282	2.1	0.13	0.004	0.20	0.01
	OUT_3000 Da	49.4	0.3	277	2.5	0.11	0.005	0.16	0.03
	OUT_1000 Da	49.0	0.3	275	2.9	0.11	0.005	0.16	0.02
	OUT_500 Da	25.0	0.1	145	0.6	0.11	0.006	0.14	0.03