Evaluation of Alternatives to Domestic Ion Exchange Water Softeners

About the WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the California Energy Commission, and the California Department of Water Resources. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations.

Evaluation of Alternatives to Domestic Ion Exchange Water Softeners

Project Report

Peter Fox, PhD (Principal Investigator)
Arizona State University

Mara Wiest
Arizona State University

Timothy M. Thomure, PE, PMP
HDR Engineering, Inc.

Wontae Lee, PhD
HDR Engineering, Inc.

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For more information, contact:
WateReuse Research Foundation
1199 North Fairfax Street, Suite 410
Alexandria, VA 22314
703-548-0880
703-548-5085 (fax)
www.WateReuse.org/Foundation

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Foreword

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect public health, and improve the environment.

An Operating Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities including water professionals, academics, and Foundation subscribers. The Foundation's research focuses on a broad range of water reuse research topics including:

- Defining and addressing emerging contaminants
- Public perceptions of the benefits and risks of water reuse
- Management practices related to indirect potable reuse
- Groundwater recharge and aquifer storage and recovery
- Evaluation and methods for managing salinity and desalination
- Economics and marketing of water reuse

The Operating Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The primary objective of this study was to provide technical data to identify credible alternatives to ion exchange water softeners that would provide consumers with the ability to reduce the impacts of hard water without creating negative salinity impacts on reclaimed water. Secondary objectives were to evaluate the alternative technologies with different types of waters and to assess the technologies from a life-cycle cost perspective to determine their impacts on water and energy use.

Joseph Jacangelo
Chair
WateReuse Research Foundation

G. Wade Miller
Executive Director
WateReuse Research Foundation

Acknowledgments

Principal Investigators
Peter Fox, Ph.D. (Principal Investigator), *Arizona State University*
Mara Wiest, *Arizona State University*
Timothy M. Thomure, PE, PMP, *HDR Engineering, Inc.*
Wontae Lee, Ph.D., *HDR Engineering, Inc.*

Project Team
Stefani McGregor, *WateReuse Research Foundation*
Jonathan Boitano, P.E., *HDR Engineering, Inc.*

Participating Agencies
Brandy Kelso, *City of Phoenix (AZ)*
Chris Hassert, *City of Scottsdale (AZ)*
Ray Wong, *Santa Clara Valley Water District (CA)*
Steve Wittry, *City of Hollister (CA)*
Stephen R. Maguin, *Sanitation Districts of Los Angeles County (CA)*
Jeff Biggs and Dan Quintanar, *Tucson Water (AZ)*
Tom Poulson, *U.S. Bureau of Reclamation Phoenix Area Office*

Project Advisory Committee
Kim F. Wilhelm, P.E., *California Department of Public Health*
Erik Jorgensen, *U.S. Bureau of Reclamation*
Harold Bailey, Ph.D., P.E., *Bailey Environmental Associates, LLC.*
Margaret H. Nellor, P.E., *Nellor Environmental Associates, Inc.*
Bruce Dvorak, Ph.D., P.E., *University of Nebraska, Lincoln*

Executive Summary

This research project was performed by a team of scientists, faculty, and graduate students at Arizona State University and engineers from HDR Engineering, Inc. It was funded by the Cities of Phoenix and Scottsdale, Arizona; Santa Clara Valley Water District, San Jose, California; the County Sanitation Districts of Los Angeles County and the WateReuse Research Foundation. Waters used for testing were provided by the Cities of Scottsdale and Tempe, Arizona.

Research Objectives
The water sources in the Southwest United States are frequently classified as hard waters, resulting in a desire to counteract the negative impacts of scale forming minerals present in the water. This is typically done by installing a water conditioning device that will treat all the water coming into the home. The use of domestic ion exchange water softeners can become a major source to the overall urban contribution of TDS in wastewater due to the concentrated brine discharged during regeneration of ion exchange water softeners. Increasing TDS at water reclamation facilities will ultimately hinder the reuse of reclaimed water. The problem can be particularly severe for agriculture and landscape irrigation, which are important reuse applications. In the Southwest United States where water is scarce, water reuse is an important water conservation measure. The reduction of the use of ion exchange water softening systems is a practical way consumers can improve wastewater quality, but there is currently very limited research on salt free water conditioning methods.

The primary objective of this study is to provide technical data to identify credible alternatives to ion exchange water softeners that would provide consumers with the ability to reduce the impacts of hard water without creating negative salinity impacts on reclaimed water. The testing that was done focused on the formation of scale, since this can be scientifically quantified. Aesthetic factors such as residue/scale left on fixtures where water evaporates was not addressed as no credible testing procedures could be identified. Concerns regarding the effectiveness of detergents in hard water have been addressed by the development of synthetic detergents that remain hydrophilic in the presence of hardness [1]. Hardness will reduce the effectiveness of soaps commonly used for body washing. A secondary objective was to evaluate the alternative technologies with different types of waters. Two different surface waters, including Colorado River water (the most widely used water in the Southwest United States), and a groundwater were tested. Another secondary objective included assessing the technologies using life cycle assessment to determine their impacts on water energy use.

Testing focused on the ability of a water treatment device to reduce scale formation. Water softening devices are known to reduce scale formation and provide other benefits. Many of the benefits are aesthetic in nature and not easily quantifiable. These benefits include reduced spotting on dishes, more effective use of detergents, and pleasant feeling skin after a shower. Scale formation can be scientifically studied and quantified. An existing protocol for evaluating devices to prevent scale formation existed and was used as the basis for this research study.

Alternative Treatment Devices
The brine discharged from domestic ion exchange water softeners is highly concentrated with sodium, chloride, magnesium, and calcium ions which will cause problems for reuse applications such as agricultural irrigation, groundwater recharge, and cooling tower waters. The use of no-salt water conditioning devices would reduce the salinity load on reclaimed water, improving the quality for these reuse applications. Alternative devices may be effective at preventing scale by several possible methods.

Physical water treatment devices alter the interaction between ions in water. One method of physical water treatment is to convert soluble calcium into microscopic calcium carbonate crystals that remain suspended in water. As the water enters a more scale-forming environment, such as a hot water heater, the microscopic crystals provide the lowest energy surface for crystallization. Therefore, scale forming reactions will occur on the suspended crystals and scale formation on surfaces can be prevented. Template assisted crystallization (TAC) works by forming microscopic crystals and this technology was evaluated during this study. Another method of physical water treatment is scale induction, where an electrical field can induce scale formation on an electrode and reduce the scale forming potential of a water. Electrically induced precipitation (EIP) is an example of a scale inducing technology that was evaluated as part of this study. An electromagnetic device that can create microscopic crystals was also evaluated as part of this study. Other alternatives to ion exchange include devices that use capacitive or electro-deionization. These devices remove almost all ions at equal efficiencies, however, at the time of this study the devices had a low water recovery rate. One test was done to evaluate the ability of a capacitive deionization system to prevent scale formation.

Finally, alternative technologies that add chemicals such as complexing agents or phosphonates can prevent scale formation without the addition of salt. These devices were not evaluated during this study.

Testing Methodology
The testing methodology used in this study was based on the German DVGW-W512 protocol. The main components of the experimental apparatus consisted of a water supply tank, a pump, treatment lines, the treatment device, a check valve, a water heater, and an open drain. A timer was used to control the flows and periodically turn water on and off during the day. An 8 hour rest period with no flow through the system occurred each evening. Two identical systems in parallel were constructed to run two tests at a time.

The capacity of the water supply tank was 350 gallons, which was refilled once during the experiment, for a total of 700 gallons used for each test. Testing consisted of water intermittently being pumped though the system at 1gpm throughout the day to simulate the turning on and off of faucets in a home setting. The total volume was pumped through the system over a period of 21 days. For the controls with no water treatment, the water treatment device was simply removed or bypassed. The water heater has a total volume of 14 liters. The wattage of the heating element was 1200W and it had a surface area of 738 cm^2 giving it a total watt density of 1.6 W/cm^2. All devices were installed according to the manufacturer's instructions.

Testing was done with three different waters. The two surface waters included Tempe tap water originating from Salt/Verde River system and Colorado River water from the Central Arizona Project (CAP) Canal. Both waters were treated by conventional coagulation and flocculation typical of surface water treatment plants. Groundwater from Scottsdale, Arizona was also used. The groundwater was treated by air stripping to remove volatile organic compounds. Scaling within the stripping towers requires acid cleaning of the media on an annual basis. The treated groundwater is actually blended with Salt/Verde water to provide customers with water lower in hardness. The groundwater used in this study was not blended. The scaling potential of the groundwater was the greatest and the scaling potential of the Salt/Verde water was the least of the waters tested.

The majority of testing was done at 80 ^{o}C, which is the temperature used in the DVGW-W512 protocol. This temperature increases the quantity of scale formed during testing; however, it is greater than the maximum temperature of 60 ^{o}C that would be expected in a domestic hot water

heater. Therefore, one set of tests was done at 60 $^{\circ}$C to verify that results were consistent with actual conditions in a domestic hot water heater.

Tempe tap water was used for initial testing at a temperature of 80 $^{\circ}$C. All five technologies were evaluated with Tempe tap water at 80 $^{\circ}$C, including ion exchange and capacitive deionization. All other testing was done only with the three alternative devices, since the expected efficacy of ion exchange and capacitive deionization was established. The three alternative devices were template assisted crystallization, electromagnetic, and electrically induced precipitation. The next set of tests was done with Tempe tap water at a temperature of 60 $^{\circ}$C to simulate the maximum temperature expected in a domestic hot water heater. Testing with Colorado River water and Scottsdale groundwater was then completed.

The quantity of scale formed during each test was determined by a combination of gravimetric measurements and acid dissolution. The ability of a device to reduce scale was evaluated by comparing the total scale formed during a test with the scale formed with the no treatment control using the same water. Scale was also characterized by x-ray diffraction, scanning electron microscopy, and light microscopy.

Results
All of the devices tested were able to reduce scale formation. Capacitive deionization and ion exchange efficiently reduced scale formation, as expected. Template assisted crystallization reduced scale formation by greater than 88 percent. Both electromagnetic treatment and electrically induced precipitation reduced scale formation by approximately 50 percent. The ability to reduce scale formation was not a function of the water type, although there were major differences in the quantities of scale formation between water types. In the no treatment controls, Colorado River water produced approximately 1.5 times the scale as compared to Tempe tap water, and the Scottsdale groundwater produced approximately 2.25 times the scale as compared to Tempe tap water.

Scale formed with Tempe tap water and Colorado River water was primarily calcite. The scale formed with no treatment controls was a hard scale and acid washing was necessary to remove the majority of the scale. The scale formed after electromagnetic and electrically induced precipitation was a "soft" scale that was easily removed by brushing. A comparison of X-ray diffraction results for the different calcite scales exhibited a difference in peak intensities. These differences represent a difference in the layering and orientation of the calcite peaks and the differences were greatest for the electromagnetic treatment. Scanning electron microscope images also exhibited differences in the calcite scale. The no treatment controls had calcite crystals oriented in the same directions. The electromagnetic and the electrically induced precipitation had calcite crystals in random orientation and the crystals were also more variable in size. The results are consistent with scale formation directly on the heating coils with the no treatment controls. The formation of calcite in suspension and subsequent deposition on the heating coils would be consistent with calcite formed with electromagnetic treatment and electrically induced precipitation. This could also explain the "soft" nature of the scale formed with these treatment technologies. The large amount of scale formed with the no treatment control using Scottsdale groundwater was aragonite. The scale formed was also a hard scale. While aragonite has sometimes been considered be responsible for "soft" scale development, the results of this study demonstrate that "soft" scale is not due to aragonite formation. Aragonite was the primary form of scale formed during all testing with Scottsdale groundwater. The same trends regarding the formation of hard and "soft" scales were observed in the Scottsdale groundwater tests as compared to the other tests even though aragonite was formed. The high scaling potential was likely responsible for the formation of aragonite instead of calcite. The

amount of "soft" scale formed when template assisted crystallization was used with Scottsdale groundwater could be qualitatively assessed. During other testing with template assisted crystallization, the quantity of scale was too small for qualitative assessment.

Conclusions

The results of this study show that scale can potentially be reduced in home water heaters with physical water treatment devices. Similar scale reduction was observed at two different temperatures and with different water qualities. The ability of the devices to perform with different water qualities is critical, since different water chemistries can alter the type of scale that is formed.

The water conditioning devices included in this study were capable of reducing scale by 46 to 99 percent as compared to the untreated case. Both the electromagnetic and electrically induced precipitation devices reduced scale formation by approximately 50 percent. Template assisted crystallization reduced scale formation by greater than 90 percent. Both capacitive deionization and ion exchange effectively reduced scale formation, as expected.

The primary component of the scale was calcium carbonate. For both Tempe tap water and Colorado River water, the calcium carbonate formed scale as calcite. Both the electromagnetic and electrically induced precipitation devices resulted in the formation of a "soft" scale that was easily removed. The calcite in the "soft" scales was variable in size and orientation, which could be from deposition of calcite particles formed in suspension. The calcite in the no treatment controls was more uniform in orientation, which is consistent with scale formation directly on the heating elements. Aragonite formation with Scottsdale groundwater followed the same trends as other testing when calcite was formed.

Recommendations

A more rapid testing procedure would be desirable to evaluate water conditioning devices. Research is currently being done to determine if a calcium ion selective electrode might be suitable for a rapid test. If a device is converting soluble calcium into pre-nucleate calcium carbonate clusters, the free calcium concentration should decrease.

A more rapid test could also lead to a method to monitor the performance of a physical water treatment device. There is currently no method to assess whether a physical water treatment device is working other than observing scale formation.

The development of an ANSI protocol to certify devices as preventing scale formation will greatly increase the reputation of alternative treatment devices. The protocol will be similar to the testing completed during this research study. One important difference is the protocol will allow a manufacturer to choose a watt density for the heating elements. This is necessary to certify a device for different types of hot water heaters including electric, gas-fired, and tankless hot water heaters. The testing of devices that add a chemical to the water will have to extend over the expected useful life of the device, which results in tests that could last 6 months or longer. This again points to the need for a more rapid test that could provide similar assurance for certification.

Chapter 1

INTRODUCTION

The rising need for water reuse in the Southwest United States has increased awareness of wastewater quality. The concentration of total dissolved solids (TDS) in wastewater has the potential to restrict the beneficial uses of reclaimed water. There are many sources that contribute to TDS in wastewater including industrial, commercial, and domestic activities. Most wastewater treatment plants do not treat wastewater for TDS due to the high energy costs involved with reverse osmosis or other salt-reducing technologies. Therefore, efforts must be made to reduce TDS levels at their source if TDS concentrations are to be reduced in reclaimed water.

Freshwater sources in the Southwest United States are considered very hard, ranging from 80 to 280 mg/L as calcium carbonate [2]. The problem with hard water is that the dissolved calcium in water forms solid calcium carbonate, otherwise known as scale, at higher temperatures so any place where water is heated or evaporates has the potential for scale formation on surfaces. This scale can cause unpleasant aesthetic effects such as spotted dishes and scale formation on faucets and shower heads. Also, scale can clog pipes and reduce the heating efficiency of water heaters. A recent independent study done by Battelle Memorial Institute showed that scale in water heaters can increase energy usage by up to 24 percent.

To control or prevent scale, scientists have tried sponge ball circulation devices, enhanced heat exchanger surfaces, and scale inhibiting chemicals such as dispersing and chelating agents [3]. A common practice both in industry and households is to prolong the life of heat exchangers (water heaters) and other appliances by using a water conditioning system as pretreatment. The ion exchange water softener is a popular product to reduce water hardness in the home. The ion exchange process starts when hard water enters into a tank filled with polymeric beads (also called resin beads) which are saturated with a monovalent cation solution (usually sodium or potassium). The calcium and magnesium ions (hardness) exchange places with the sodium ions on the bead. The effluent water has the same level of TDS, but the scale forming minerals have been removed and the effluent water is considered soft. Once the resin beads have been saturated with calcium and magnesium ions, the resin beads are soaked with a heavily concentrated monovalent cation solution called brine. This solution removes the calcium and magnesium from the beads and the brine is then flushed to the sewer. There are two basic types of self regenerating ion exchange water softeners: timer based and demand based. The timer based unit allows the user to manually program the regeneration times while the demand based timer regenerates based on the volume of water used. The demand based units will normally be more water efficient than the timer based. Both types of units, however, deposit additional salt into the wastewater stream.

The use of ion exchange water softeners has been identified as a potentially controllable source of TDS in wastewater. Some communities such as Santa Clarita Valley in California have already banned the use of ion exchange water softeners to reduce the degradation to the environment and to improve the wastewater quality for water reuse applications. For these communities and for consumers interested in reducing their environmental footprint, there is limited scientific evidence available to compare alternative water conditioning devices that do not require the use of salt in their processes.

This study provides a comparison of no-salt water conditioning devices in their effectiveness to reduce scale in a water heater. Four alternative technologies were studied and tested on three different water sources in the Southwest United States.

1.1 Background

Consumers desire softened water for a variety of reasons. The removal of calcium and magnesium ions has the potential to improve the properties of the water for a number of applications. Many of these perceived benefits are aesthetic in nature and cannot be easily quantified. An example of aesthetic benefits would include evaluating the effectiveness of detergents for cleaning clothes or how a shampoo makes a person's hair look and feel. The focus of this research is on scale formation. Scale formation can be scientifically evaluated and is one of the major reasons that consumers desire softened water. An existing protocol for evaluating devices to prevent scale formation has also been developed in Germany and provides a basis for the testing done during this study [4].

Water treatment devices can prevent scale formation without the addition of salt. Devices that alter the way ions interact in water without the addition of chemicals are called physical water treatment devices. Most physical water treatment devices work on the principal of scale prevention by the formation of microscopic crystals in water. As water passes through the physical water treatment device, soluble calcium is converted to microscopic calcium carbonate crystals. Scale formation tends to occur on surfaces, particularly on crevices and other irregularities where the formation of calcium carbonate crystals has the lowest formation energy. Microscopic crystals that remain suspended provide a low formation energy surface for crystal growth. As water enters a scale forming environment, suspended microscopic crystals provide a surface for crystal growth and scale prevention can occur. Other physical water treatment devices can use electric fields to either induce the formation of scale on an electrode or to separate ions from water. A device that induces formation of scale on an electrode requires periodic cleaning of the electrode to remove the scale. The device can prevent scale formation by lowering the scale forming potential of a water. Devices that separate ions from water include capacitive deionization and/or electro-deionization. Capacitive deionization technologies have been in development for over 50 years with limited commercial success. These devices can remove all ions from water efficiently and can thereby prevent scale formation by actually softening the water. Deionization technologies produce a brine stream and there can be significant water loss associated with the brine stream.

Other alternatives to ion exchange include devices that add chemicals to water to prevent scale formation. The addition of chemicals to prevent scale formation is well established in industrial and commercial applications. Chelating agents and phosphonates are commonly used to prevent scale formation in cooling towers, heat exchangers, water treatment membranes and numerous other applications where scale formation is a concern. These devices are also being marketed as alternatives to domestic ion-exchange systems. The most common devices either add a chelating agent such as citrate or a phosphonate. Water flows through cartridges that contain a solid material that dissolves into the water. The cartridges must be replaced periodically since the addition of a chemical cannot be indefinitely sustained. While these devices might be effective at preventing scale formation, they were not evaluated in this study since they represent established technologies and they are not sustainable.

The devices chosen for evaluation during this study include physical water treatment devices that do not add chemicals to the water. These devices tend to be the least understood by the engineering community and marketing of the devices often include claims that are not

scientifically sound. Two of the devices chosen for evaluation had passed the German DVGW-512 test for evaluation of a scale preventing technology. These technologies include a template assisted crystallization technology and a scale inducing technology that will be referred to as electrically induced precipitation. The third technology includes an electromagnetic technology that can prevent scale through the formation of microscopic calcium carbonate crystals. One test was also done to simulate the ability of capacitive deionization to prevent scale formation.

Template assisted crystallization is an established technology that is most often used to form nanoparticles or microscopic crystals of uniform size and shape. A template can be placed over a catalytic surface and crystal formation is initiated at holes in the template where the catalytic surface is exposed. Once crystal formation is initiated the crystal grows on the template until the template is filled. Crystals of uniform size and shape are then released from the template and a new crystal can form on the empty template space. While many industrial applications exist for template assisted crystallization, the use of template assisted crystallization in the water industry is relatively new. Template assisted crystallization uses a bed of polysterene beads that contain a template for crystal growth and release. The bed is fluidized when water is flowing through it which increases the surface area of the template and assures good crystal formation. The template assisted crystallization technology used in this study has passed the German DVGW-512 test.

Electrically induced precipitation is a technology that can prevent scale formation by inducing scale formation before water enters a scale forming environment. An electrical field causes the precipitation of calcium carbonate by increasing the local concentration of divalent ions adjacent to an electrode. After a specific quantity of water has passed through, the electrode is cleaned with a wire brush and the scale is flushed as a waste product. The device tested required flushing after treating approximately 3,000 L (800 gallons) of water. The electrically induced precipitation technology used in this study has passed the German DVGW-512 test.

A wide variety of electromagnetic technologies are marketed as physical water treatment devices. Electromagnetic flowmeters use the Hall effect to measure the velocity of fluid flowing in a pipe. A magnetic field is aligned orthogonal to the direction of flow and the induced electrical field is proportional to the flow velocity. Electromagnetic flowmeters require careful use of a square wave to eliminate the effect of Faraday's Law as ions become separated in an electrical field. Elecromagnetic water treatment devices attempt to use the effect of Faraday's Law to create microscopic crystals. Some of the most common devices consist of wires that are wrapped around a pipe and a voltage transformer that controls the level and type of current flowing through the wires. A current flowing through wires wrapped around a pipe will induce a magnetic field aligned either with the direction of flow or against the direction of flow. Such a magnetic field will create a unique electrical field effect that will concentrate cations at the center of the pipe and anions at the wall of the pipe or vice-versa. The divalent cations are subject to twice the force as monovalent ions in a magnetic field. Reversing the field can cause the divalent anions and cations to collide at a high frequency and energy, resulting in the formation of microscopic calcium carbonate crystals [5]. A commercially available device that consists of wires wrapped around a pipe and a voltage transformer was evaluated as part of this study.

1.2 Importance of the Study

The evaluation of alternatives to domestic ion exchange water softeners is important for not only reducing salinity in reclaimed water, but for a variety of other reasons. The ability to treat water without the addition of chemicals, without significant energy use, and without water loss can provide a sustainable solution for the future. Consumers desire "green" products but the products

have to meet the needs of consumers. The results of this study can be used to demonstrate that viable alternative to ion exchange water softeners do exist. Developing an understanding of the mechanisms involved with alternative technologies can provide assurance to the engineering and scientific community that there is a fundamental basis for these technologies. Mechanistic information can also provide insights into the variety of water qualities that may be effectively treated using alternative technologies.

The results of this study can be used by water utilities to promote the use of alternatives to domestic ion exchange systems. Some water utilities already offer incentives or are considering offering incentives to customers that remove their ion exchange water softeners. The ability to convince customers and water utility managers that this is a worthwhile effort should require that customers have access to alternatives. The results of this study can provide the basis for the use of alternatives.

The principal investigator of this study at Arizona State University has become actively involved in an International Association of Plumbing and Mechanical Officials (IAPMO) sub-committee that is tasked with developing an American National Standards Institute (ANSI) standardized test to certify devices as scale preventing. The on-going research was actively discussed and influenced both the product of the committee and the desire to complete the testing protocol after seven years of development.   The sub-committee met on March 5, 2012 in Las Vegas, Nevada, to complete a draft of ANSI Z601. Two different certification laboratories are moving forward with validation of the protocol. Validation of the protocol is anticipated to be completed by mid-2013, after which devices can be certified for scale prevention. Certification will provide confidence in alternative devices by both consumers and the engineering community.

The United States Environmental Protection Agency (USEPA) WaterSense program has considered ion exchange water softeners that are demand based and use less water than timer based ion exchange water softeners as water conserving devices. The WaterSense program does not currently consider alternatives that do not waste any water as conserving devices since there was never any water waste associated with alternative devices. Certification of alternative devices for scale prevention should allow for the USEPA WaterSense program to consider these devices as water conserving since they provide a proven alternative to ion exchange water softeners that do waste water.

1.3 Research Objectives

The primary objective of this research project was to evaluate the alternatives to domestic ion exchange technologies for their ability to prevent scale prevention.   This was accomplished by simulating water use in a house and quantifying scale formation in a simulated water heater.   A secondary objective was to evaluate the alternative technologies with different types of waters. Two different surface waters, including Colorado River water (the most widely used water in the Southwest United States), and a groundwater were tested. Another secondary objective included assessing the technologies using life cycle assessment to determine their impacts on water energy use.

Chapter 2:

LITERATURE REVIEW

2.1 Introduction

Calcium makes up 3.4 percent of the mass of Earth's crust and is primarily found in igneous rocks as calcium silicates and in sedimentary and metamorphic rocks as calcium carbonates. The movement of crustal plates and continental land masses with various upthrusts has brought many of the calcium carbonates accumulated at the bottom of the ocean up to or near the surface as limestone [6]. When acid is present, such as carbon dioxide dissolved in water, calcium is freed from its solid form and dissolves into the water as an ion attracted to water molecules. Hard water is a result of a high concentration of calcium and magnesium ions. Hard water is prevalent in a large area of the United States.

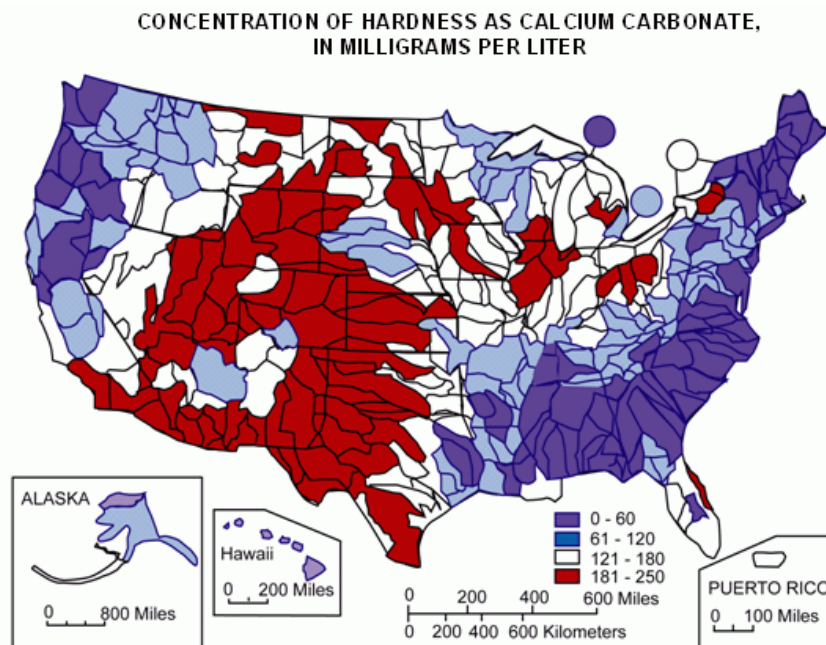FIGURE 1: HARDNESS LEVELS IN THE UNITED STATES

Modified from Briggs and Others, 1977 [2]

The red and white areas in Figure 1 are the regions in which hard water is common. Some of the hardest waters (concentrations of over 1000 mg/L as $CaCO_3$) were found in Arizona and southern California. Hard water is found in the natural water supply of the region including lakes, rivers and groundwater.

FIGURE 2: MAP OF ARIZONA'S WATER SUPPLY

Obtained from: http://www.crwua.org/coloradoriver/rivermap/index.cfm?action=arizona

Phoenix, Arizona has experienced a constant increase in population for many years. Along with the growing population comes a growing need for fresh water. Changes have been made to the natural flow of rivers to accommodate this growing need for water, and the changes have happened relatively recently (beginning with the construction of Roosevelt Dam in 1912 up to as recently as 1985 with the opening of the Central Arizona Project (CAP) canal that brings water from the Colorado River). The Salt/Verde River system (Salt River Project - SRP) and Colorado River water (CAP) are Arizona's major sources for freshwater and both can be seen on the map in Figure 2. The Salt/Verde River system has several water regulating dams and water from the Colorado River has been diverted to Phoenix. Along with this water delivered to the city comes salt in the form of total dissolved solids (TDS).

A recent study done as part of the Central Arizona Salinity Study concluded that a net of 1.1 million tons of salt is accumulating in the Phoenix Metropolitan Area every year [7]. As the salt levels continue to rise due to increased demand for river water, the addition of salt by homeowners that use ion exchange water softeners only exacerbates the problem. Additional salt added to Phoenix's sewer system by society accounts for an additional 300 to 500 mg/L of total dissolved solids in the wastewater treatment plants [8]. Water in the treatment plants is not desalted and the result is water that is becoming less practical for reclaimed water purposes such as irrigation and aquifer recharge.

While TDS is a measurement of all dissolved solids including all cations and anions, total hardness is a measurement of mainly calcium and magnesium ions present in water. According to the City of Phoenix website, the total hardness average for Phoenix is 235.5 mg/L as calcium carbonate. The U.S. Geological Survey classifies a water with a total hardness of greater than 180 mg/L as calcium carbonate as very hard water [2]. This justifies the use of point-of-use home water softeners in Phoenix and other areas with hard water. As of 2000, about 51% of all new homes in the Phoenix area were being built with ion exchange water softeners and this percentage was expected to rise [8]. Alternatives to ion exchange that do not contribute to the TDS in wastewater are available and, if widely used, could improve the quality of reclaimed water.

The Evaluation of Alternatives to Domestic Ion Exchange Water Softeners study will provide a scientifically based comparison of point-of-use treatment methods that are a salt-free alternative to ion exchange water softeners. These alternative devices use different technologies to condition the water. This literature review provides a background on scale issues and summarizes the existing literature on the alternate technologies tested in this study.

2.2 The Scale Problem

Scale build up from hard water causes a variety of problems in residential households as well as industry. Clogged pipes can result in reduced water pressure, scale deposits on showerheads and other appliances, restricted flow, and reduced product life. Scale causes undesirable aesthetic effects such as soap film on shower tiles and doors, and spots on silverware and glassware. The most costly result of scale build up is the fouling of heating elements in water heaters. Scale reduces the water flow and decreases heat transfer costing the homeowner extra money on their energy bill.

Fouling can be defined as the encrusting, clogging or choking of a surface by a foreign substance. This is essentially what scale does to pipes and appliances in a household setting. The kinetics of the fouling process are typically measured by deterioration of the total heat transfer coefficient or the increase in pressure drop produced by deposition on a heat-transfer surface [9]. Fouling on a heat exchanging surface acts as a thermal insulator. Effects of fouling in heating elements are reduced heat transfer rate, reduced flow, metal overheating, tube rupture, an increase in pressure drop across the exchanger, and decrease in appliance life. It is desirable to reduce the size, maximize efficiency, and extend the life of heat exchangers by the reduction of fouling. Many studies have found different techniques to reduce the tendency of fouling on a heat exchanger [10]. Researchers have tried changing the shape of the heating element tubes, vibration, scale inhibiting chemicals, and catalytic materials to reduce fouling in heat exchangers.
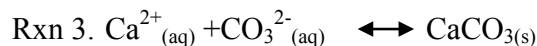
There are numerous possible mechanisms for fouling. Biological fouling includes the growth of algae, fungi, and filamentous bacteria that form slime which sticks to the surface of heat exchangers. Corrosion, which is the oxidation of metals, is caused by dissolved oxygen gradients and acidic solutions. Chemical reaction fouling is the accumulation of tar or coke products onto a heat exchanger as products of a chemical reaction. Polymerization and oxidation are also chemical reactions that produce a film that is very hard to remove [11]. Solidification fouling, also known as particulate fouling, includes the settlement of suspended particles that develops into a sludge on a heat exchanging surface.

The primary focus of this study, is the reduction of scale fouling. Scale precipitation falls into the category of crystallization fouling. Crystallization is the formation of solid salts, oxides, and hydroxides. Supersaturation is the driving force for crystallization, hence the Langelier Saturation

Index predicts the likelihood of a water to form scale. To control or prevent scale fouling, scientists have tried sponge ball circulation devices, enhanced heat exchanger surfaces, and scale inhibiting chemicals such as dispersing and chelating agents [3]. A common practice both in industry and households is to prolong the life of heat exchangers (water heaters) and other appliances by using a water conditioning system as pretreatment. Ion exchange water conditioners remove scale forming minerals and replace them with sodium and chlorine. There are two basic types of ion exchange systems: exchange tank and self regenerating. With exchange tank systems, regeneration is done in a central facility and regenerated tanks are delivered to the home periodically. The impact on wastewater for an exchange tank system as compared to self-regenerating systems can be minimal provided that the central facility uses a brine recovery system. A self-regenerating system works either on a timer or is demand-based and regeneration occurs at the home. The levels of sodium and chlorine in the resulting treated water are not high enough to have a significant effect on the salinity of the wastewater, however, for self-regenerating systems, the regeneration cycle pours a highly concentrated salt solution over the resins and is then discharged into the sewer. This regeneration brine has been found to increase TDS in wastewater [8].

2.3 Scale Formation Process

Scale build-up is a consequence of calcium carbonate ($CaCO_{3(s)}$) precipitation. The precipitation of calcium carbonate is unique from other solids in that its solubility decreases with an increase in temperature. The reason behind this is found in the role that carbon dioxide plays in calcium carbonate formation. In the overall reaction, carbon dioxide falls on the same side of the equation as calcium carbonate. As the temperature rises, the solubility of the carbon dioxide decreases and the gas leaves the system. This reduction in carbon dioxide results in the overall reaction to "go to the right" and produce more calcium carbonate.

$$\text{Rxn 1.} \quad HCO_3^-{}_{(aq)} \longleftrightarrow OH^-{}_{(aq)} + CO_{2(aq)}$$

$$\text{Rxn 2.} \quad OH^-{}_{(aq)} + HCO_3^- \longleftrightarrow CO_3^{2-}{}_{(aq)} + H_2O$$

$$\text{Rxn 3.} \quad Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \longleftrightarrow CaCO_{3(s)}$$

Overall Reaction:

$$Ca^{2+}{}_{(aq)} + 2HCO_3^- \rightarrow CaCO_{3(s)} + H_2O + CO_{2(aq)}$$
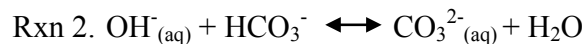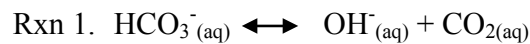
Calcium carbonate tends to attach to surfaces due to the electrostatic attraction between the particles and the metal surface of the heating element. Once the particles have attached to the metal surface they serve as nucleation sites for more particles to attach. The scale can build up to the point where heat transfer is significantly hindered.

2.4 Calcium Carbonate Precipitation

The solubility product, K_{sp}, of calcium carbonate is the product of the carbonate and calcium concentrations. Precipitation is expected when the product of these concentrations exceeds the solubility product because the water is considered supersaturated with calcium carbonate. The maximum recommended temperature in a domestic hot water heater is 60 °C. The DVGW

protocol uses a temperature of 80 °C to accelerate scale formation. Table 1 shows the solubility product for different forms of calcium carbonate calculated at these two temperatures in comparison to the standard temperature of 25 °C.

TABLE 1: SOLUBILITY PRODUCTS FOR DIFFERENT FORMS OF CALCIUM CARBONATE [9]

Form	Structure	-log Ks (solubility constant)			Temperature Law (T in K, t in °C)
		25 °C	60 °C	80 °C	
amorphous		6.40	6.91	7.33	-log Ks = 6.1987 + 0.005336t + 0.0001096t^2
ikaite	monoclinic	6.62	6.02	5.74	-log Ks = 1696/T + 0.9336
vaterite	hexagonal	7.91	8.28	8.54	-log Ks = +172.1295+0.077993T - 3074.688/T - 71.595logT
aragonite	orthorhombic	8.34	8.64	8.88	-log Ks = +171.9773 + 0.077993T - 2903.293/T - 71.595logT
calcite	rhomboedric	8.48	8.76	8.99	-log Ks = +171.9065 + 0.077993T - 2839.319/T - 71.595logT

The different forms of calcium carbonate include different crystalline shapes and polymorphs as follows:

- Vaterite (polycrystalline spheres)
- Calcite (rhomboeder) ← Scale
- Aragonite (needles) ← Less prone to form hard scale
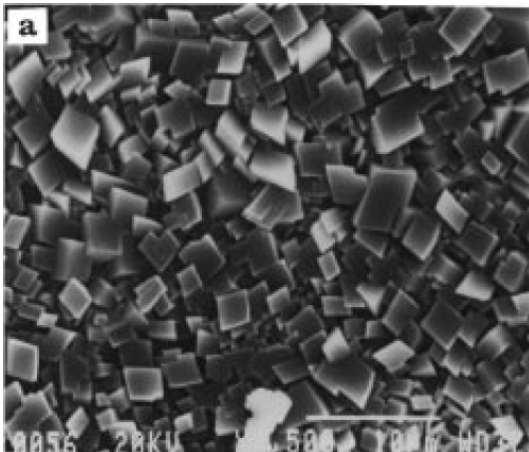
FIGURE 3: SEM MICROGRAPH OF CALCIUM CARBONATE PRECIPITATED AS CALCITE [12]
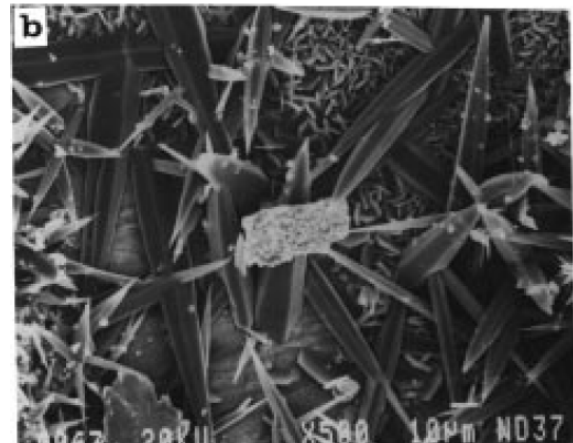
FIGURE 4: SEM MICROGRAPH OF CALCIUM CARBONATE PRECIPITATED AS ARAGONITE [12]

In order of decreasing solubility, the polymorphs of calcium carbonate are amorphous, ikaite, vaterite, aragonite, and calcite. The more hydrated forms are more soluble and give higher values of the solubility product. The forms with lower solubility are more stable crystalline structures

and correspond with a lower solubility product. Calcite is the most common form of calcium carbonate and is typically what causes scale formation.

In a study published in Science in 2008 [13], a carbonate containing solution was titrated with a calcium solution to study pre-nucleation and nucleation of calcium carbonate. The study consistently found that calcium immediately formed pre-nucleate calcium carbonate clusters at extremely undersaturated conditions. The formation of pre-nucleate clusters was verified by measuring free calcium ions with an ion selective electrode. These pre-nucleate clusters continued to form until the total calcium concentration was 3-4 times the saturation value at which time precipitation occurred and the system came to equilibrium as predicted by the solubility product relationship. The pre-nucleate clusters were determined to range from 4-12 nm in size.

2.5 Langelier Saturation Index and Calcium Carbonate Precipitation Potential

The Langelier Saturation Index is a helpful tool to identify whether a water chemistry is undersaturated, neutral, or supersaturated with respect to calcium. The three water qualities evaluated are Scottsdale groundwater, City of Tempe tap water (Salt/Verde water), and CAP (Colorado River) canal water. The Langelier Saturation indexes for all three of these water qualities were calculated for both temperatures being considered for the study. All are greater than zero, indicating a calcium supersaturation, so consequently, all three water chemistries will precipitate scale. The City of Tempe tap water has the lowest degree of supersaturation while the Scottsdale groundwater had the highest degree of supersaturation.

Langelier Saturation Index (LSI) [14]:

$$LSI = pH - pH_s$$

Where $pH_s = -log\left(\frac{K_a * \gamma_{Ca^{2+}} * [Ca^{2+}] * \gamma_{HCO_3^-} * [HCO_3^-]}{\gamma_{H^+} * K_{sp}}\right)$

Indications:

LSI < 0: Water is undersaturated with respect to calcium carbonate. Undersaturated water has a tendency to remove existing calcium carbonate protective coatings in pipelines and equipment.

LSI = 0: Water is considered to be neutral. Neither scale-forming nor scale removing.

LSI > 0: Water is supersaturated with respect to calcium carbonate ($CaCO_3$) and scale forming may occur.

The Calcium Carbonate Precipitation Potential (CCPP) is an estimate of the quantity of $CaCO_3$ that will precipitate or dissolve as a water equilibrates [14]. Two principles are applied to calculate equilibrium concentrations. The first principle is that the total acidity does not change as $CaCO_3$ precipitates or dissolves. The second principle is that the total alkalinity minus the calcium concentration is a constant as precipitation or dissolution occurs. Therefore the CCPP can be calculated as the original calcium concentration minus the equilibrium calcium concentration. The results are usually expressed in mg/l as $CaCO_3$. Positive values of 4 to 10 mg/l as $CaCO_3$ suggests a well conditioned water that is close to equilibrium but is not corrosive.

2.6 Electrical Double Layer

The electrical double layer is the excess opposite electrical charge on two sides of an interface (i.e. solid and solution.) The electric state of a surface depends on the spatial distribution of free (electronic or ionic) charges in its neighborhood [15]. One layer is envisioned as a fixed layer attached to the particle while the other is diffusely distributed in the water in close proximity to the particle. This double layer can keep colloidal precipitate particles from coming into contact with each other for further coagulation.

Some water conditioning processes, such as magnetization, work due to the reducing effect of the double layer. If the double layer is compressed, particles in water will come together as a result of Brownian motion and remain attached due to van der Waals forces of attraction [16]. When the double layer is reduced, more suspended coagulation can occur, resulting in a light sludge that is easily wiped off of the surface.

2.7 Methods to Reduce Scale

Scale can be reduced by physically removing scale forming minerals such as calcium and magnesium from the water or by altering these particles so they precipitate in the bulk liquid rather than on metal surfaces. Water is considered softened when the calcium and magnesium are removed and conditioned when the potential to form scale is reduced while calcium and magnesium may still be present in the water. There are a variety of devices on the market that use one of these mechanisms to condition water. Four alternative water conditioners were tested during this study.

2.7.1 Electrically Induced Precipitation

DEVICE: BIOSTAT2000
A commercially available electrically induced precipitation device is shown in Figure 5.

FIGURE 5: JUDO BIOSTAT2000

Obtained from http://www.watertiger.net/judo/biostat.htm

Summary:
Electrically induced precipitation is a physical water treatment process which utilizes an electric field to precipitate dissolved scale forming particles in the bulk fluid. Precipitate forms on an electrode that must be cleaned periodically. The device tested in this study required cleaning after treating 3,000 liters (800 gallons) of water. Microscopic particles also remain suspended in the water and can serve as suspended nucleation sites. As the water enters a more scale forming environment, the calcium carbonate can react with suspended nucleation sites instead of surfaces and scale formation can be prevented. The particles formed may settle on the surface of heating elements as a soft sludge rather than as a chemically precipitating scale.

Tijing [17] found that treating water with an electrical field increased the number of suspended particles by 540 percent. This is a good indication that the electric field aids the bulk precipitation mechanism of dissolved solids. Cho [18] concluded that the electric field produced by the device does not produce enough overall energy to dissociate the bicarbonate ions, but the local electrostatic effect from the pipewall roughness does. Once bicarbonate dissociates at the pipe walls and produces calcium carbonate particles, those particles serve as seeds for particulate fouling inside a heat exchanger. Particulate fouling produces a soft sludge on the surface of the heating element, easily removable by the shear force of the water.

2.7.2 Magnetic Water Treatment

DEVICE: AQUA REX

FIGURE 6: AQUA REX DEVICE

Obtained from http://www.aqua-rex.com/PDFs_Docs/spec_guide_jan2010_reduced.pdf

Summary:
Magnetic water treatment is a physical treatment in which the water is subjected to a magnetic field to alter calcium carbonate adhesion properties. A magnetic device installation is shown in Figure 6. Some companies offer permanent magnets as a form of treatment by attaching the permanent magnet to the pipe. Most devices use a series of wires wrapped around a pipe, illustrated in Figure 7. A voltage transformer controls the current through the wire, which induces a magnetic field within the pipe. By controlling the current, the magnetic field induced by the current can be reversed. The magnetic field is oriented with the direction of flow or against the direction of flow. The field will cause cations to move to the center of the pipe and anions to the

wall of the pipe or vice-versa. Reversing the field will cause the cations and anions to move toward one another and increase the collision frequency and energy.
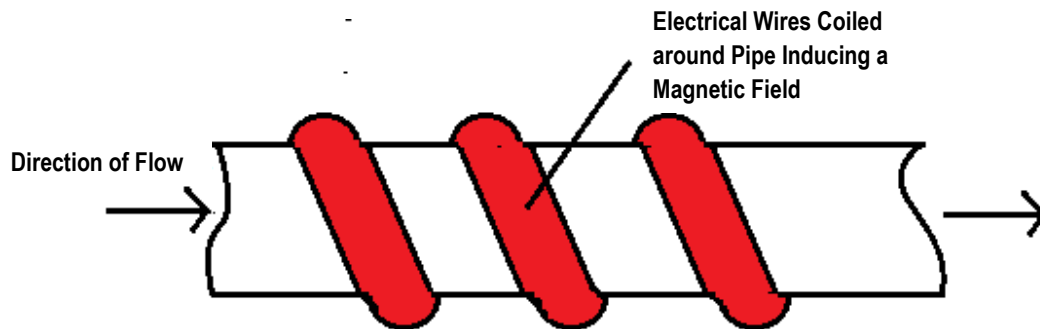

FIGURE 7: MAGNETIC WATER TREATMENT SCHEMATIC

Smith [19] found that a permanent magnet could reduce scale by an average of 34 percent [19]. Their test results ranged from a 17 percent reduction to 70 percent reduction of scale formation in heated storage tanks. There was a visible difference in the heating elements and their bases. Scale had visibly formed on the untreated case while the treated water left no visible scale on the heating element and base. There is evidence that the magnetic field causes the calcium carbonate present in water to form as aragonite rather than calcite. Aragonite has a different structure and a larger specific gravity than calcite and is less prone to form hard scale. Coey and Cass [20] examined the ratio of aragonite to total calcium carbonate in magnetically treated and untreated water. They found that in untreated water the ratio was 7 percent while in treated water the ratio grew to 54 percent. This effect lasted longer than 200 hours after exposure to the magnetic field. Busch and Busch [21] tested two other possible mechanisms: formation of $CaCO_3$ seed crystals in regions of high alkalinity and heterogeneous nucleation of calcium carbonate by iron corrosion products. However, their experimental results indicated that these mechanisms had a very small impact on particulate precipitation. The conclusion they drew from their work was that magnetohydrodynamic forces were most effective in a continuous flow regime.   The electrical field that causes separation of cations and anions will increase as the flow velocity increases.

When magnetic systems have been successful, the most apparent result is the formation of aragonite resulting in "soft" scale formation instead of calcite which readily forms scale [22]. The mechanism by which this occurs has not been clearly identified and many different variables may affect the performance of this system. In some cases, the electronic current induced by the magnetic device can increase corrosion in iron containing pipe, adding Fe^{+2} to the water and this is known to inhibit calcite formation. Both dissolved oxygen and silica concentrations have also been shown to affect calcite formation [23,24].

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2.7.3 Capacitive Deionization

DEVICE: AQUA EWP

A commercially available capacitive deionization (CDI) system is shown in Figure 8.

FIGURE 8: AQUA EWP SYSTEM

Obtained from http://www.aquaewp.com/pdf/EWPWH2009Mailer.pdf

Summary:

Capacitive deionization (CDI) is an electro-chemical water treatment process in which ions in the water adsorb to charged electrodes that have a high surface area. The regeneration and backwashing phases of CDI technology are illustrated in Figures 9 and 10.
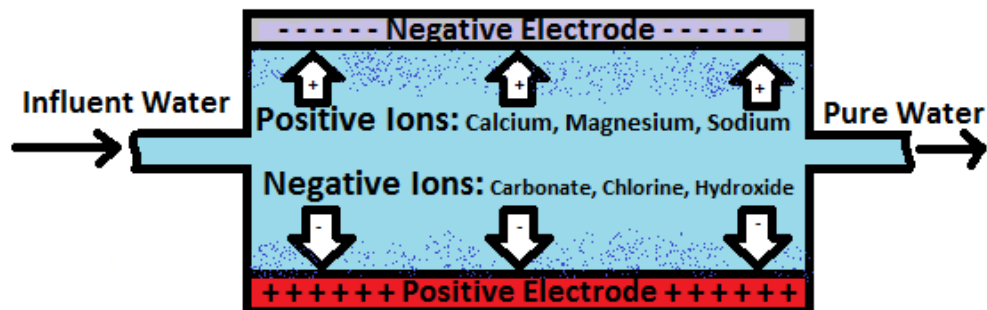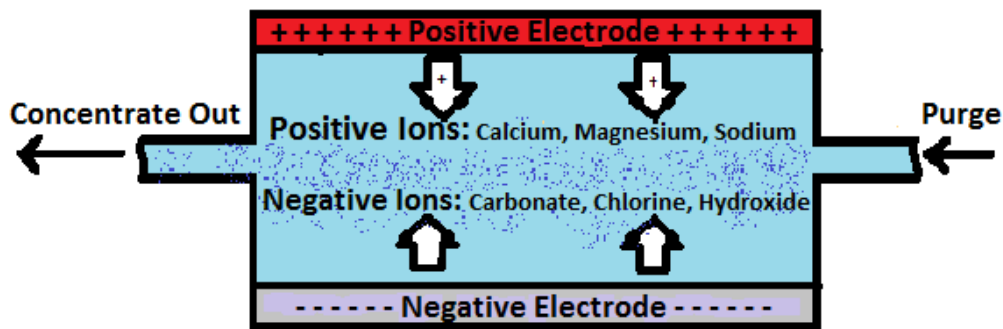

FIGURE 9: CDI REGENERATION

FIGURE 10: CDI BACKWASH

The theory behind this technology has been developed, yet the main concerns related to the feasibility of commercial technology development are: development of an electrode material that is suitable for the process; arrangement of the various components within the basic cell unit; turning the process into a continuous or semi-continuous process; and energy recovery [25]. Carbon is the most popular electrode material due to its high surface area and a lot of research has been done with carbon aerogels for CDI, supercapacitors, and other separation processes in which electroadsorption is involved. A few different designs of CDI devices have been developed and they all include a forward flow adsorption/regeneration process and a backward flow cleaning and recharging process (the charge on the electrodes is reversed and the excess ions are backwashed, then the cell is recharged by an external power supply). Some include energy recovery: as the cells regenerate they can release their residual electrical energy to an external accumulator for future use.

2.7.4 Template Assisted Crystallization

DEVICE: NEXT SCALESTOP

Figure 11 shows some commercially available units that employ the template assisted crystallization method of scale reduction.

FIGURE 11: NEXT SCALESTOP SYSTEM FROM NEXT SCALESTOP PRESENTATION

Summary:
Template assisted crystallization utilizes polymeric beads with tiny nucleation sites to convert dissolved hardness into microscopic crystals. Once these crystals are formed and released from the beads, they are insoluble particles that will not form scale on surfaces [26]. This process is illustrated in Figure 12.
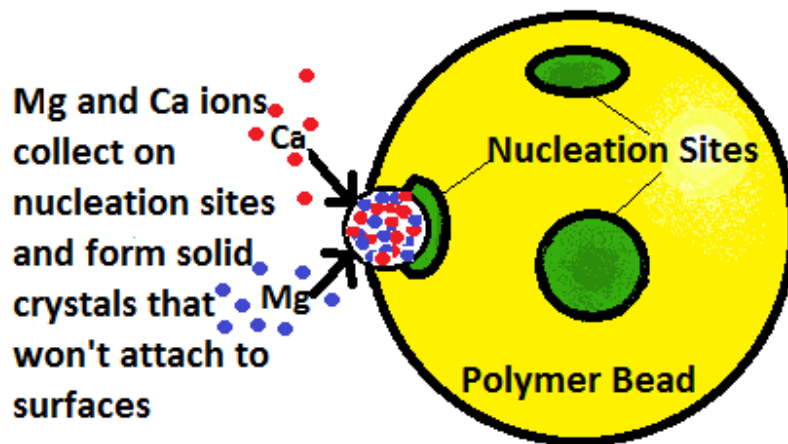
FIGURE 12: TEMPLATE ASSISTED CRYSTALLIZATION POLYMERIC BEAD

Recent research has been conducted on surface assembling molecules to control the morphology of crystals and produce specialized materials for industrial applications. Many studies have involved the use of templates to control crystal growth for the production of various inorganic nanostructured materials [27]. Morphology, microstructure, complexity, and length scales of the nanostructured materials can be controlled by using template assisted crystallization. However, the use of template assisted crystallization for water treatment and the formation of calcium carbonate crystals has only recently been done. Colfen, 2003 used template assisted crystallization to form specific structures of calcium carbonate crystals [28]. This study found that the use of polymeric templates resulted in the formation of typical calcite rhomboeders.

No studies were found in the literature that used template assisted crystallization for the purpose of reducing scale formation. This is a relatively new technology for water conditioning purposes.

2.7.5 Ion-Exchange

DEVICE: Morton System Saver Model MSD34C

The ion exchange unit used for testing in this study is shown in Figure 13.

FIGURE 13: MORTON SYSTEM SAVER

Summary:

Ion exchange water softening utilizes plastic resin beads saturated in a sodium chloride solution, or brine, to remove calcium and magnesium ions from the water. The calcium and magnesium ions essentially trade places with the sodium ions and the water is softened. The resin beads work in a regenerative process in which approximately 4,000 gallons of water are treated before the beads are regenerated by a high sodium chloride brine. The brine used in self-regenerating systems such as the one used in this study and shown in Figure 13 is then washed down the drain and the softening process begins again.

The problem with these systems is that salinity is added to the wastewater when the brine used for regeneration is washed down the drain. The wastewater treatment plants do not treat for salt and the water is less effective for reuse purposes [3].

2.8 Summary

Scale accumulation is a common problem in areas with hard water such as the Southwest United States. Homeowners can often see the results of scale fouling on their appliances and in their electric bills for water heating. Scale is formed on surfaces when the temperature of the water is high. Scale usually forms as calcite or aragonite depending on the water chemistry. Aragonite may be relatively easy to remove from surfaces, whereas calcite is more likely to produce a hard scale on metal surfaces. The Langelier Saturation Index (LSI) is a tool used to find the scaling potential of water based on water quality parameters such as pH, calcium concentration and alkalinity. The three water qualities that were tested all have a LSI greater than zero, indicating a supersaturation of calcium carbonate and a likelihood of calcium scale formation. The electrical double layer also plays a role in the probability of scale formation. If reduced, the scale forming minerals can coagulate together then precipitate out of the water as solid particles. The devices that were tested work using one of these mechanisms: 1) precipitate forms within the matrix, resulting in solids that settle into a sludge easily removed by the velocity of the water, or 2) scale

forming minerals are collected on a surface and removed using a backwash. The first mechanism allows minerals to stay in the water in a form that will not produce scale, while the second partially removes the minerals. A summary of the devices, their associated technologies, and the possible mechanisms at work, is presented in Table 2.

TABLE 2: SUMMARY OF WATER CONDITIONING DEVICES AND TECHNOLOGIES

Device	Technology	Mechanism
Judo Biostat 2000	Electrically Induced Precipitation	1
Aqua-Rex	Magnetic Water Treatment	1
Aqua EWP	Capacitive Deionization	2
Next ScaleStop	Template Assisted Crystallization	1
Morton System Saver	Ion Exchange	2

Much more research has been performed on some of the alternative water conditioning procedures than others. No research has been done, however, to compare no-salt methods directly to ion exchange and untreated water. Due to the effects of salt accumulation in wastewater in Phoenix and other areas with hard water, it is desirable to find an alternative form of water conditioning pretreatment that will not add salt to wastewater but will perform similarly to ion exchange water softening. This project provides a direct comparison of water conditioning methods.

Chapter 3:

EXPERIMENT AND TESTING PROCEDURE

The testing procedure was based on the German Technical and Scientific Association for Gas and Water protocol to determine if a water treatment device can prevent scale formation.

3.1 DVGW-W512 Protocol

The experiment was set up based on the German standard protocol DVGW Article W512, "Verification of a Water Treatment Device for the Reduction of Scale Formation." The schematic that is specific to the DVGW-W512 protocol is shown in Figure 14. The protocol uses four test rigs that all receive the same synthetic water. Two of the test rigs include a scale prevention treatment device and two of the test rigs are controls. Only one test rig is shown on the schematic.   Since the test rig is designed to evaluate scale reduction devices that might be used for industrial applications, the ability to recycle water through the water conditioning device and the water heater is included. The basic protocol includes testing for a 20-day time period at a temperature of 80 $^{\circ}$C. A 10-L tank is used with a heating element that has a watt density less than 5 W/cm^2, which is typical of energy efficient electric water heaters used in Europe. The flow through the rigs is turned on and off by a controller at specific intervals each day. There is an 8-hour rest period each day to simulate no water use during the night.
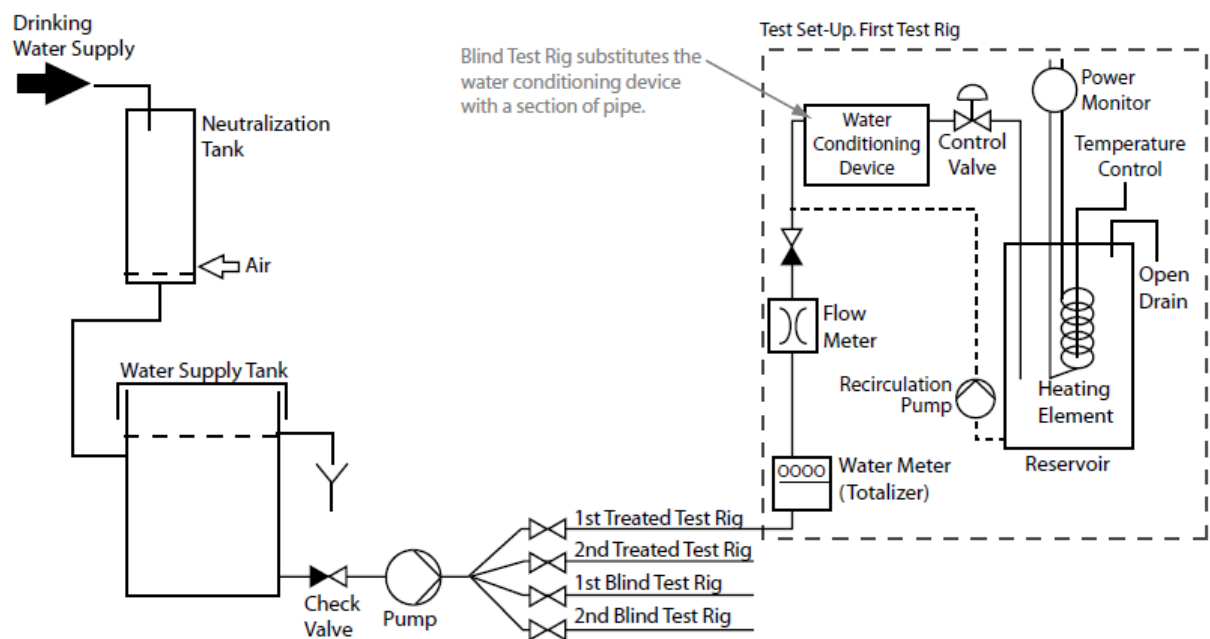

FIGURE 14: DVGW-W512 SCHEMATIC

3.2 Experimental Set-Up and Testing Procedure

The experimental system used in this study was based on the DVGW-W512 protocol. The main components were a water supply tank, a pump, treatment lines, the treatment device, a check

valve, a water heater, and an open drain. A timer was used to control the flows and periodically turn water on and off during the day. An 8 hour rest period with no flow through the system occurred each evening.

Two systems in parallel were constructed to run two tests at a time. The system used in this experiment is similar to the DVGW-W512 protocol, and the schematic is shown in Figure 15.
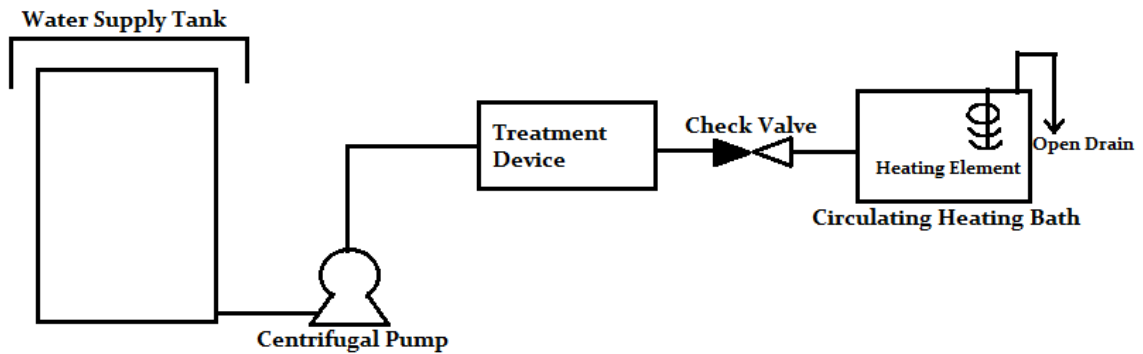

FIGURE 15: TESTING APPARATUS SCHEMATIC

The capacity of the water supply tank was 350 gallons, and it was refilled once during the experiment for a total of 700 gallons used for each test. Testing consisted of water intermittently being pumped though the system at 1 gpm throughout the day to simulate the turning on and off of faucets in a home setting. A total of 700 gallons were pumped through the system over a period of 21 days. The flow rate from the centrifugal pump was 1 gpm. For the controls with no water treatment, the water treatment device was simply removed or bypassed. Piping was installed using PVC pipe with ¾-inch nominal inside diameter. The circulating heating bath capacity was 14 liters. The circulating heating bath was set at either 60 °C or 80 °C with an inner pump that constantly circulated the water inside to maintain an even temperature. Water was allowed to flow out of the heating bath and into an open drain on the floor during refilling cycles. The wattage of the heating element was 1200W and it has a surface area of 738 cm^2, giving it a total watt density of 1.6 W/cm^2. All devices were installed according to the manufacturer's instructions.

3.3 Methods

The 350-gallon storage tanks were cleaned between testing with different water qualities using a 10 ppm solution of chlorine and then rinsed with the next water to be tested. The tanks were filled with 350 gallons of the water being tested and then refilled after 10.5 days of testing to complete the 700-gallon requirement. Water was periodically sampled to monitor water quality parameters.

After 21 days of testing, the accumulated scale on the heating elements and baths was removed from the areas shown in Figure 16.
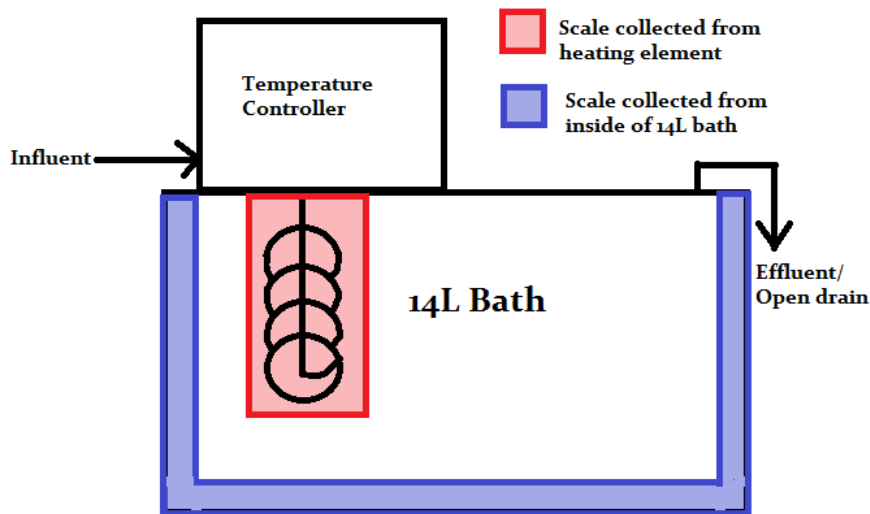
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FIGURE 16: AREAS OF SCALE COLLECTION

Solid scale was removed from the heating element by scraping with a stainless steel tool, combined with any loose scale from the bath, and weighed. A 10-mg sample of the solid scale was dissolved using hydrochloric acid (HCl) and diluted in 100-mL of deionized water. The pH was raised to approximately pH 7 using potassium hydroxide. The solution was then tested for calcium and hardness content using the EDTA method and this percentage of calcium content was applied to the total weight of scale collected. The remaining scale in the bath and on the heating element was dissolved using a 1N HCl solution. The solution was also neutralized with potassium hydroxide and then measured for calcium and hardness content using the EDTA method. The total scale formed during each test was determined by summing the total mass of scale collected with the calculated mass of scale that was dissolved in acid. The mass was calculated using the calcium and hardness content of the 10-mg solid sample dissolved in acid.

3.4 Water Qualities

Three typical water qualities found in the Southwest United States were tested for all devices except the capacitive deionization device which was only tested using Salt/Verde River water. This is because the efficiency of this device in terms of ion removal is well established. Some of the differences in water quality for these three water sources are listed in Table 3.

TABLE 3: WATER QUALITIES TESTED

Parameter	TDS (mg/l)	Hardness (mg/l as $CaCO_3$)
Salt River Water (Tempe Tap Water)	479	180
Central Arizona Project (CAP) Canal Water	666	150-250
Scottsdale Groundwater	1200	450-500
Santa Clara Valley Water District (SCVWD) Groundwater	420	210

Each water quality has a unique make up of total dissolved solids and hardness levels.

Chapter 4:

RESULTS AND DISCUSSION

4.1 Scaling Potential

The scaling potential of each water quality can be measured using the Langelier Saturation Index (LSI) or Calcium Carbonate Precipitation Potential (CCPP). The characteristics associated with the values obtained from these methods are listed in Table 4.

TABLE 4: LSI AND CCPP STANDARDS

LSI or CCPP	
< 0	Undersaturated with $CaCO_3$ (will dissolve $CaCO_3$)
0	At equilibium with CaCO3
> 0	Oversaturated with CaCO3 (will precipitate CaCO3)

The LSI measures the difference between the pH of the water and the saturation pH. The saturation pH is dependent on various water quality parameters including alkalinity and calcium concentration. The CCPP represents the amount of calcium carbonate that will precipitate or dissolve from the solution as it comes to equilibrium with solid $CaCO_3$. The LSI and CCPP of the water qualities used in this experiment are summarized in Table 5.

TABLE 5: SCALING POTENTIAL FOR WATER QUALITIES TESTED

	LSI	CCPP
Salt River Water (Tempe Tap Water)	+0.2	20
Central Arizona Project (CAP) Canal Water	+0.5	50
Scottsdale Groundwater	+0.8	80
Santa Clara Valley Water District (SCVWD) Groundwater	+0.4	40

Testing was initially done with Tempe tap water at a temperature of 80 ^{o}C. All technologies were evaluated with Tempe tap water at 80 ^{o}C including ion exchange and capacitive deionization. All other testing was only done with the three alternative devices since the expected efficacy of the ion exchange and capacitive deionization was established. The next set of tests was done with Tempe tap water at a temperature of 60 ^{o}C to simulate the maximum temperature expected in a domestic hot water heater. Testing with Colorado River water (CAP) and Scottsdale groundwater was then completed at 80 ^{o}C.

4.2 Measured Scale

All devices were successful at reducing scale at varying efficiencies. The total calcium scale collected for each test is listed in Table 6. Note that the increasing scaling potential of the waters as predicted by the Langelier Index is consistent with the results for the no treatment controls. The CAP water has approximately 1.5 times the scale formed as the Tempe tap water and the Scottsdale groundwater has approximately 2.25 times the scale formed.

TABLE 6: TOTAL CALCIUM SCALE COLLECTED

SCALE TOTALS (g Ca)

Treatment Type	Tempe 80 °C	Tempe 60 °C	CAP 80 °C	Scottsdale GW 80 °C
No Treatment	13.36	9.97	20.0	29.75
TAC	0.48	0.33	0.65	3.2
EIP	6.72	5.56	9.84	15.4
MAG	7.56	5.28	10.23	16.7
CDI	0.56	NT*	NT*	NT*
IX	0.79	NT*	NT*	NT*

* NT = Not Tested

Since the total scale formed in the no treatment controls was significantly different for each water tested, the results for each water were normalized to the no treatment controls to show the relative reduction in scale formation. These comparisons are summarized in Table 7 and illustrated in Figure 17.

TABLE 7: NORMALIZED SCALE COMPARISONS

NORMALIZED SCALE TOTALS

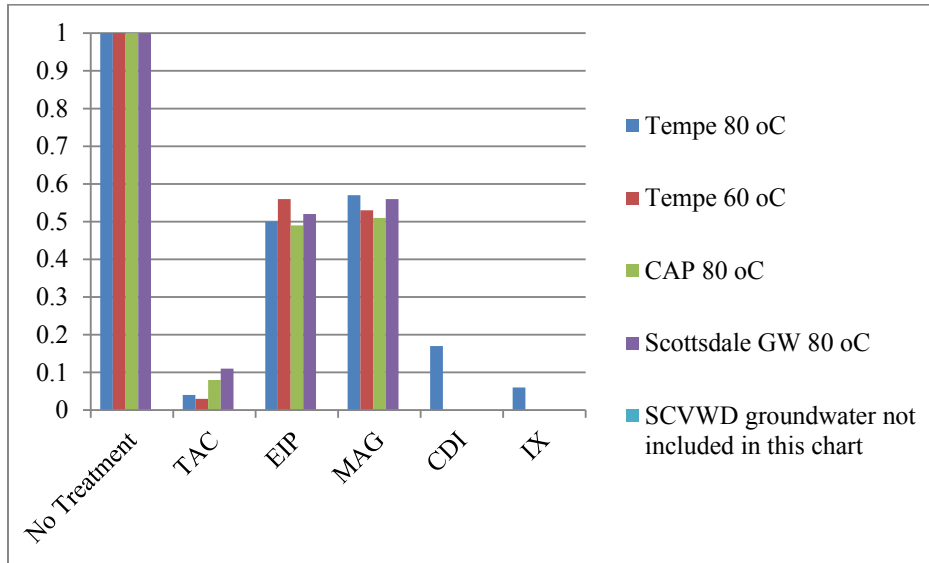| Treatment Type	Tempe 80 °C	Tempe 60 °C	CAP 80 °C	Scottsdale GW 80 °C
No Treatment	1.00	1.00	1.00	1.00
TAC	0.04	0.03	0.08	0.11
EIP	0.50	0.56	0.49	0.52
MAG	0.57	0.53	0.51	0.56
CDI	0.17	NT*	NT*	NT*
IX	0.06	NT*	NT*	NT*

* NT = Not Tested

FIGURE 17: NORMALIZED SCALE GRAPHICAL COMPARISON

4.3 Discussion

These results show that the template assisted crystallization device was the most efficient device for reducing scale with greater than 88 percent scale reduction. Both the electrically induced precipitation device and the electromagnetic device consistently reduced scale formation by approximately 50 percent. Both of these devices also resulted in a different type of scale that is referred to as a soft scale. The scale was easily removed from the heating elements and minimal acid was required to remove the scale. Although there was a reduction in the mass of scale produced, the soft scale appears to be more than the no treatment controls since the scale was less dense. Some soft scale was also apparent with the Template Assisted Crystallization treatment with the Scottsdale groundwater. The quantity of scale with the other Template Assisted Crystallization tests was not significant enough to assess. Acid was required to remove a significant portion of the scale in the no treatment controls. It is important to note that some no-salt alternatives do not remove hardness while ion exchange and capacitive deionization do remove hardness. The other alternative methods reduce scale formation by altering the dissolved scale in the water. It has been proposed that alternative treatment induces the formation of aragonite which is a softer scale than calcite. The scale formed on the heating elements was tested using X-ray diffraction to identify the structure of the calcium carbonate formed. The results from the X-ray diffraction of the scale formed with Tempe tap water at 80 ^{o}C is shown in Figure 18.
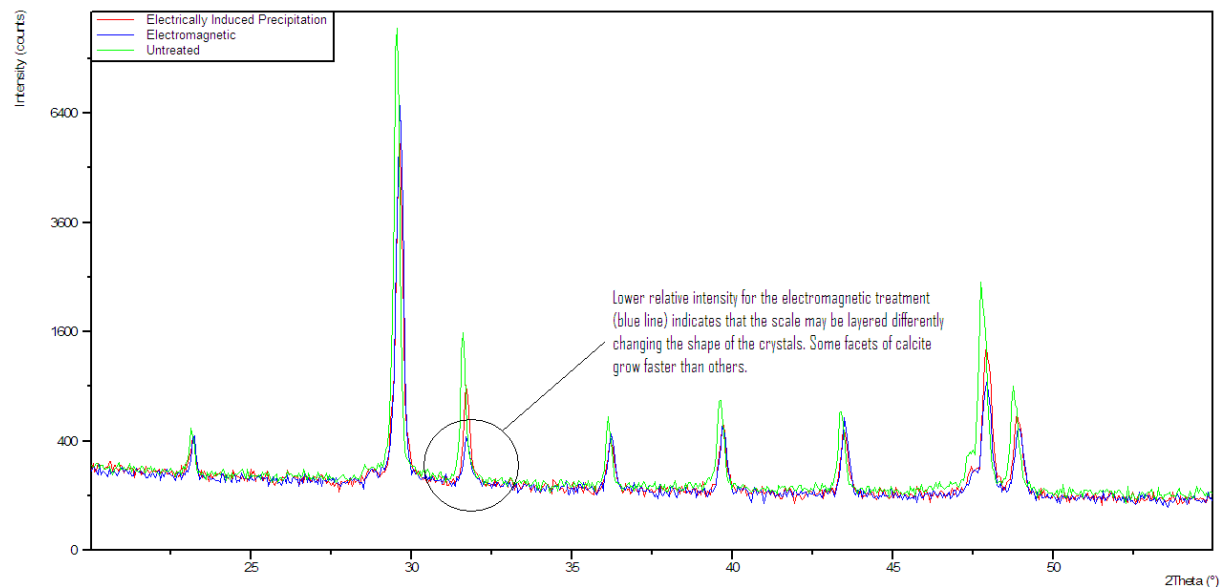
WateReuse Research Foundation

FIGURE 18: X-RAY DIFFRACTION RESULTS

The peaks for all calcium carbonate formed in all cases correspond to calcite. The analysis revealed that calcite was the main constituent after all treatment methods (>90 percent). There was a difference in the relative intensities for the scale formed with EIP treatment and MAG treatment and the difference was most pronounced for the MAG treatment. The difference intensities indicate a difference of how the scale was layered in the sample. Calcite has the lowest solubility product of all forms of calcium carbonate which explains the higher likelihood of the formation of calcite, a hard scale, as opposed to aragonite, a softer scale. The results also demonstrate that a scale that behaves as a soft scale can be composed of primarily calcite. This could be from the formation of suspended nucleates that deposit on the heating element resulting in a different layering as compared to scale that forms by nucleation directly on the element. The XRD results for both the Tempe tap water (60 ^{o}C) and the CAP water. Aragonite was the primary form of $CaCO_3$ formed with Scottsdale groundwater and the XRD results also provided some evidence for a difference in layering between the no treatment control and the other tests. The no treatment control formed a hard scale with aragonite and a soft aragonite scale formed with all three treatment devices.

To further explore the layering and structure of the scale formed, Scanning Electron Microscopy (SEM) images were taken of the scale. Images of the heating coils after testing with Tempe tap water at 80 ^{o}C are presented in Figure 19. The images clearly demonstrate the efficacy of template assisted crystallization. For both the electromagnetic and electrically induced precipitation, there are clean spots on the heating coils where "soft" scale was easily brushed away. The insets on the images are SEM images of the scale formed during testing. Consistent with the XRD results, the SEM images appear to be calcite. Similar results are observed for Tempe tap water at 60 ^{o}C (Figure 20) and Colorado River water (Figure 21). The calcite in the no treatment scale appears to have a uniform structure that would be consistent with scale formation directly on the heating coil. The calcite in the electromagnetic and electrically induced precipitation tends to vary in both size and orientation, which would be consistent with calcite formation in solution coupled with calcite formation on the heating coils. Images from Scottsdale groundwater tests are shown in Figure 22. The large quantity of scale formed on the no treatment control is obvious. The appearance of the scale was clearly different and this was

verified by scanning electron microscopy and XRD. The SEM image is clearly aragonite and not calcite. The reason for the difference in the crystalline form of calcium has not been determined. The high scaling potential of the Scottsdale groundwater was most likely the reason aragonite was formed instead of calcite. As listed in Table 1, the solubility product for aragonite is lower than calcite so a higher scaling potential is necessary for the formation of aragonite.
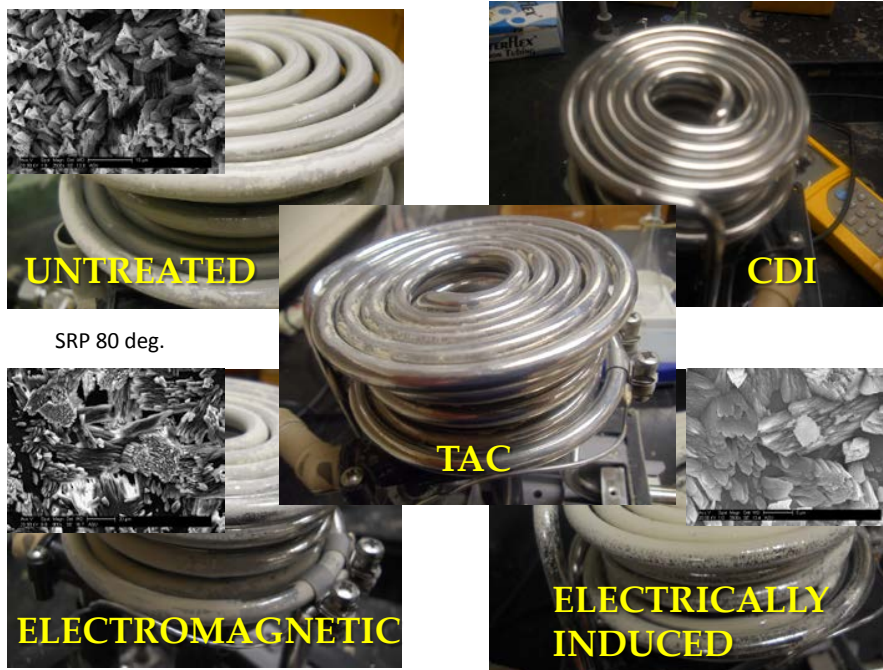

FIGURE 19: TEMPE TAP WATER (80 °C) SCALE ON ELEMENTS AND THROUGH SEM
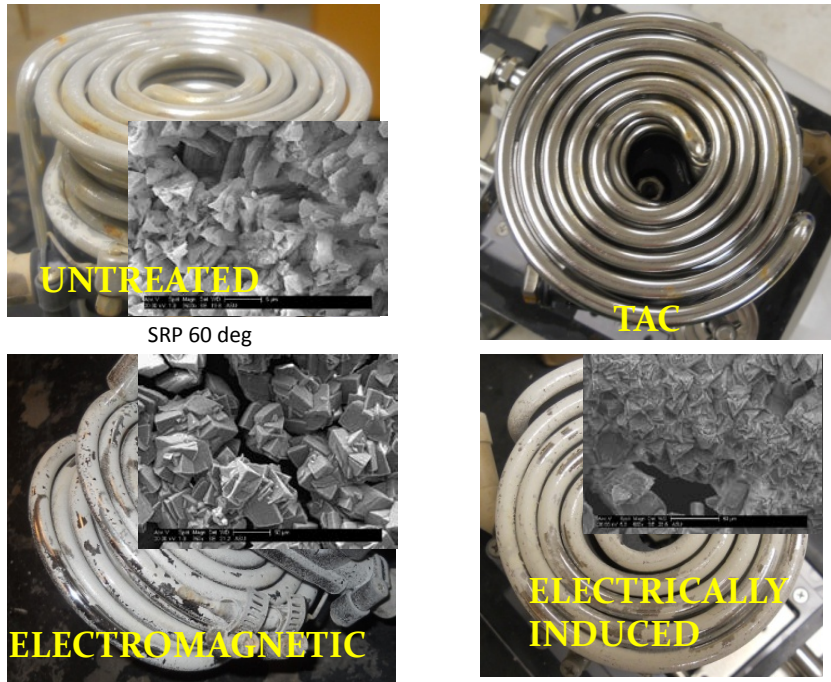
FIGURE 20: TEMPE TAP WATER (60 °C) SCALE ON ELEMENT AND THROUGH SEM
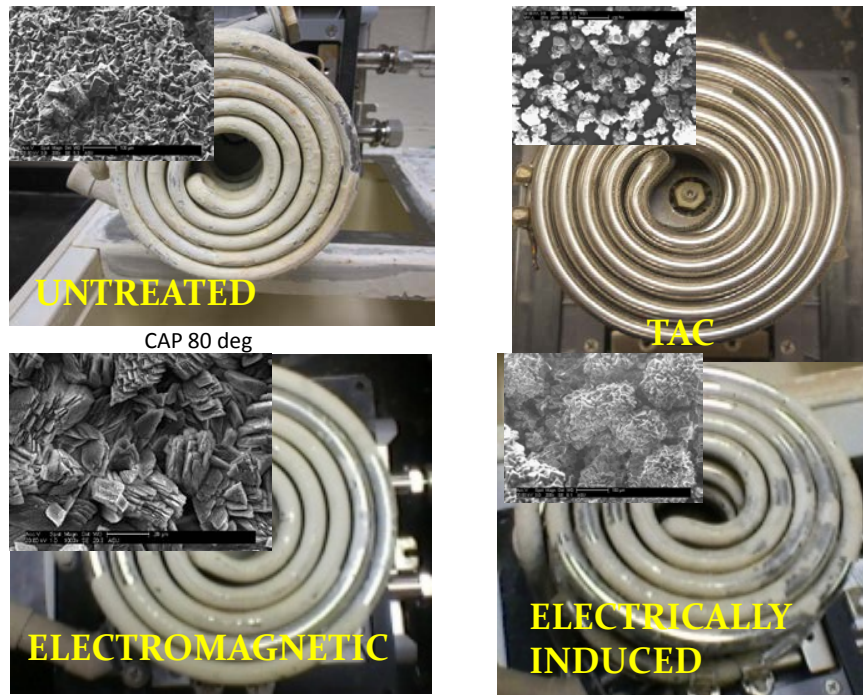

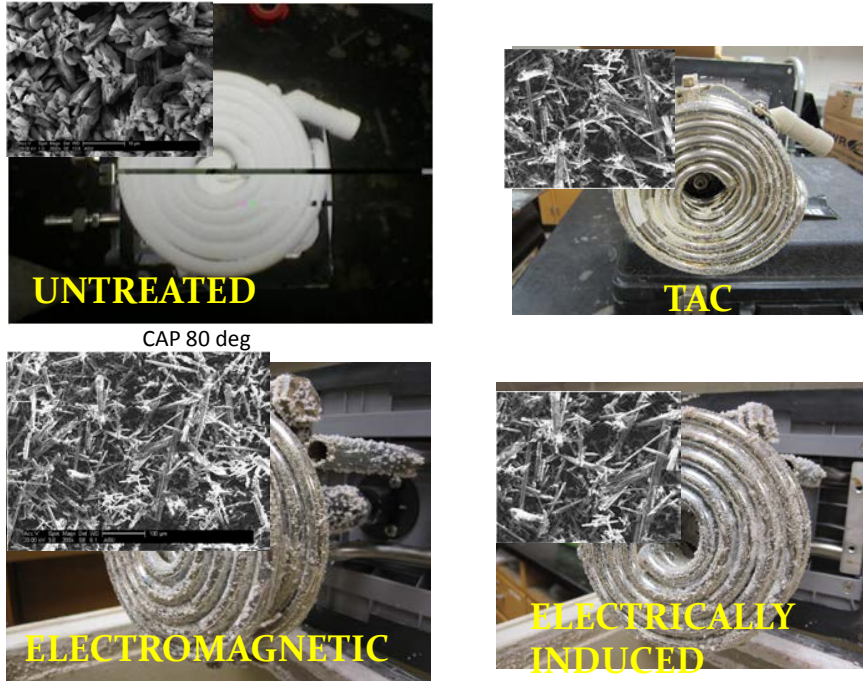FIGURE 21: COLORADO RIVER WATER (80 °C) SCALE ON ELEMENTS AND THROUGH SEM

FIGURE 22: SCOTTSDALE GROUNDWATER (80 °C)) SCALE ON ELEMENT AND THROUGH SEM

4.4 Life-Cycle Costs

Commercially available water conditioning systems were reviewed and classified under one of the following alternative technologies: electrically induced precipitation, electromagnetic water treatment, capacitive deionization, and template assisted crystallization. Systems were classified based on the primary treatment step, i.e., the technology which either removes the hardness or conditions the water such that production of scale is reduced. Systems were chosen based on availability solely, with no attention given to effectiveness or system quality.

Life-cycle costs for the commercially available systems were tabulated based on a 10-year life assumption. A 10-year life was chosen based on a review of warranty periods for the available systems. Capital costs and operation and maintenance (O&M) costs were tabulated based on quotes from manufacturers/vendors and average energy usage and water waste for each alternative technology. Where available, energy usage and water waste rates as quoted by the manufacturer/vendor of a given system were utilized. Other system specific O&M costs including chemical and filter media replacement were included per manufacturer/vendor quotes.

The 10-year life-cycle cost was calculated as Present Value and is expressed in present day [2012] dollars. Annual O&M costs are totaled for a given system, and the annual payments are calculated as a present day sum, which is added to the capital cost to determine the life-cycle cost. Annual payments are discounted at 3 percent to calculate the Present Value. Assumptions regarding O&M cost items including energy usage, water waste, filter replacement and chemical usage which can be based on feed concentrations and production volume are as follows:

- Devices using electrical power are active 24 hours a day, 365 days a year.
- All systems are analyzed for usage at a single-family residence with a daily water usage of 300 gallons per day (gpd).
- Feed water hardness is assumed to be 150 grains per gallon (gpg).
- If a product line for a given system exists, the basic model is analyzed with no add-ons or additional features.

System life cycle costs for each technology were averaged to determine an approximate cost for each alternative. A minimum of three commercially available systems were averaged for each technology, with the exception of capacitive deionization. While capacitive deionization is classified as a commercially available technology, no vendor data were readily available for use. Costs for capacitive deionization are based on the general technology rather than a specific make and model.

Results

The costs for the commercially available water conditioning systems reviewed are summarized in Table 8. The breakdown between capital costs and 10-year O&M costs for each technology is shown graphically in Figure 23.

TABLE 8: ANNUAL O&M, CAPITAL, AND 10-YEAR LIFE CYCLE COSTS BY
TECHNOLOGY AND VENDOR

Treatment Technology	System ID	Total Annual O&M Costs	Capital Cost	10-year Life Cycle Cost
Electrically Induced Precipitation	EIP 1	$236	$3,000	$5,522
	EIP 2	$184	$4,150	$5,716
	EIP 3	$88	$850	$1,597
	EIP 4	$266	$1,500	$3,768
	Averages	$194	$2,375	**$4,151**
Magnetic water Treatment	MWT 1	$7	$500	$560
	MWT 2	$4	$500	$537
	MWT 3	$7	$750	$810
	MWT 4	$31	$1,299	$1,561
	MWT 5	$7	$750	$810
	Averages	$11	$760	**$855**
Capacitive Deionization*	CDI 1	$102	$4,000	**$4,873**
Template Assisted Crystallization	TAC 1	$80	$1,750	$2,432
	TAC 2	$0	$795	$795
	TAC 3	$0	$750	$750
	Averages	$27	$1,098	**$1,326**
Ion Exchange	IEX 1	$168	$1,700	$3,130
	IEX 2	$168	$949	$2,379
	IEX 3	$168	$3,495	$4,925
	Averages	$168	$2,048	**$3,478**

*Capital and O&M costs for CDI units were not readily available. Costs are based on a technical evaluation done by the Advanced Water Technology Center (AQWATEC) at the Colorado School of Mines. Unit costs of $4,000 (capital system cost), 4 kwh/kgal, and 20% waste are used.

Average Capital and O&M Costs Breakdown
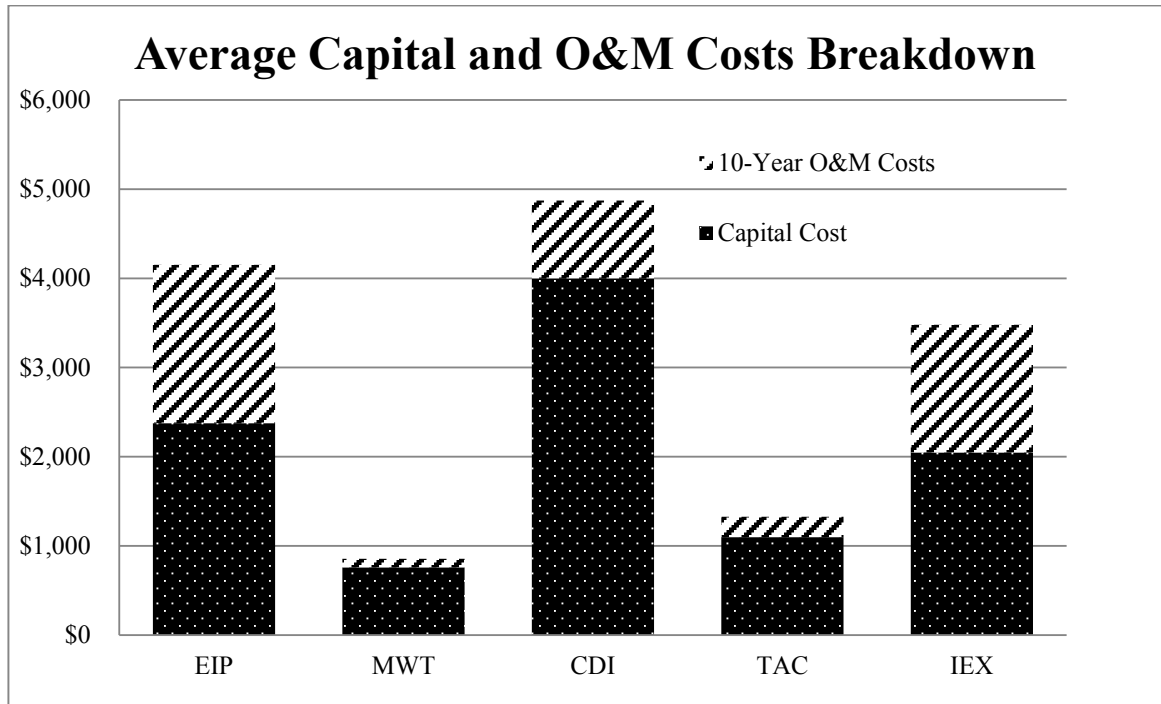
FIGURE 23: AVERAGE LIFE CYCLE COSTS WITH O&M AND CAPITAL COST BREAKDOWN

Based on the data presented in Table 8 and Figure 23, the highest 10-year life-cycle cost of the alternatives reviewed is for CDI, and MWT is the lowest. It should be noted that CDI is not currently as readily available to homeowners as other technologies, and the capital cost may decrease as competition is introduced.

Chapter 5:

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The results of this study show that scale can potentially be reduced in home water heaters with physical water treatment devices. Similar scale reduction was observed at two different temperatures and with different water qualities. The ability of the devices to perform with different water qualities is critical since different water chemistries can alter the type of scale that is formed.

The water conditioning devices included in this study were capable of reducing scale by 46 to 99 percent as compared to the untreated case. Both the electromagnetic and electrically induced precipitation devices reduced scale formation by approximately 50 percent. Template assisted crystallization reduced scale formation by greater than 88 percent. Both capacitive deionization and ion exchange are known to remove scale forming minerals and they effectively reduced scale formation as expected.

The primary component of the scale was calcium carbonate. For both Tempe tap water and Colorado River water, the calcium carbonate formed scale as calcite. Both the electromagnetic and electrically induced precipitation devices resulted in the formation of a soft scale that was easily removed. The calcite in the soft scales was variable in size and orientation which could be from deposition of calcite particles formed in suspension. The calcite in the no treatment controls was more uniform in orientation, which is consistent with scale formation directly on the heating elements. The same trend was also observed when aragonite was formed with the Scottsdale groundwater.

5.2 Recommendations

A more rapid testing procedure would be desirable to evaluate water conditioning devices. Research is currently being done to determine if a calcium ion selective electrode might be suitable for a rapid test. If a device is converting soluble calcium into pre-nucleate calcium carbonate clusters, the free calcium concentration should decrease.

A more rapid test could also lead to a method to monitor the performance of a physical water treatment device. There is currently no method to assess whether a physical water treatment device is working other than observing scale formation.

The development of an ANSI protocol to certify devices as preventing scale formation will greatly increase the reputation of alternative treatment devices. The protocol will be similar to the testing completed during this research study. One important difference is the protocol will allow a manufacturer to choose a watt density for the heating elements. This is necessary to certify a device for different types of hot water heaters including electric, gas-fired and tankless hot water heaters. The testing of devices that add a chemical to the water will have to extend over the expected useful life of the device which results in tests that could last 6 months or longer. This again points to the need for a more rapid test that could provide similar assurance for certification.

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ABBREVIATIONS

ANSI	American National Standards Institute
aq	Aqueous
CAP	Central Arizona Project
CASS	Central Arizona Salinity Study
CCPP	Calcium Carbonate Precipitation Potential
CDI	Capacitive Deionization
DVGW	Deutscher Verein des Gas und Wasserfaches [German Gas and Water Corporation]
EDTA	Ethylenediaminetetraacetic Acid
EIP	Electrically Induced Precipitation
GW	Groundwater
HCI	Hydrochloric Acid
IAPMO	International Association of Plumbing and Mechanical Officials
IX	Ion Exchange
Ksp	Solubility Product
LSI	Langelier Saturation Index
MAG	Magnetic
NT	Not Tested
O&M	Operations and Maintenance
PAC	Project Advisory Committee
RAC	Research Advisory Committee
Rxn	Reaction
SEM	Scanning Electron Microscopy
SRP	Salt River Project
TAC	Template Assisted Crystalization
TDS	Total Dissolved Solids
USEPA	United States Environmental Protection Agency
XRD	X-Ray Diffraction