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Treatment Technology Validation for Water Softening Technology

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MONTANA TECH OF THE UNIVERSITY OF MONTANA

MT HARD WATER

TASK 3 - TREATMENT TECHNOLOGY VALIDATION FOR WATER SOFTENING TECHNOLOGY

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EXECUTIVE SUMMARY

MT Hard Water of Montana Tech of the University of Montana submits Task 3: Treatment Technology Validation for Water Softening Technology as an entry into the 2012 WERC Environmental Design Contest. Currently, there are several commercially available technologies that treat water hardness. The objective of this project is to develop a strategy to evaluate and validate different water hardness treatment technologies. MT Hard Water (MTHW) has studied several technologies including: electromagnetic water treatment, ion exchange, and reverse osmosis. For validation purposes, an electromagnetic water treatment system (ScaleRID) was selected according to the WERC task description.

Various tests were conducted on the ScaleRID system to determine the validity of its product claims. The main product claims were that ScaleRID 1) prevented scale from forming on pipes, 2) aided in removal of existing scale, and 3) treated hard water causing ions, Ca$^{2+}$ and Mg$^{2+}$. MTHW conducted two beaker tests, five closed loop system tests, an open flow system test, and an evaluation of a currently used reverse osmosis system and ion exchange based water softener. Experiments seemed to suggest that water flow is necessary for CaCO$_3$ to precipitate in both the control and ScaleRID system, however, the size and polymorph of the CaCO$_3$ precipitates in the two systems tested were different. Based on the research conducted by MTHW, the oscillating magnetic field produced by the ScaleRID device may cause CaCO$_3$ to precipitate homogeneously in water. The various closed-loop system tests showed slightly lower Ca$^{2+}$ ion concentrations in the water with treated ScaleRID, but the concentration differences were not significant when compared to the control. Open flow experiments were conducted to determine the effectiveness of the ScaleRID device in treating municipal water with an initial hardness level of 80 mg/L. The results indicated that the Ca$^{2+}$ concentration was cyclic but consistently higher in the control water than in the water treated with the ScaleRID device. This seemed to suggest that ScaleRID was encouraging homogeneous precipitation of calcium compounds. However, the total hardness of water, as measured by titration (EPA method 130.2), in both the control and ScaleRID treated flow did not change. From the experiments carried out for validation, it is MTHW’s understanding that ScaleRID uses time varying magnetic fields on the treated water, which promotes homogeneous precipitation. This leads to a reduction of the overall supersaturation of CaCO$_3$ in solution, and therefore, mitigates potential scale formation.
on pipe surfaces. The formation of precipitates in the water, however, would mean that the EPA method for measuring total hardness would still measure the suspended particulate form of "hardness" in the water. Overall, our experimental results suggested that the ScaleRID device could lower the dissolved portion of hardness in low to moderately hard water.

Other water treatment technologies such as ion exchange and reverse osmosis were also evaluated. Water samples before and after treatment were analyzed to determine the overall effectiveness of these technologies. Total hardness, Ca$^{2+}$ concentration, temperature, pH and other parameters were measured in all samples. The results indicated that both ion exchange and reverse osmosis treatments were effective, immediate and consistent in reducing water hardness by removing dissolved Ca$^{2+}$ ions from the water.

Based on experimental results, MTHW developed an assessment tool that evaluates and validates various water hardness treatment technologies. This method of evaluation employs Ca$^{2+}$ ion concentration, total hardness, pH and conductivity measurements, as well as a microscopic test to examine the nature of the scale or precipitates in the water. The results of these tests represent an overall baseline status of a household’s incoming water hardness. A recommendation of which technology is a best fit for the specific household is then made based on these results. A decision matrix was developed based on existing research and MTHW’s experimental data gathered in the study. MTHW also designed a website which included a web based query tool based on this decision matrix that uses the baseline water condition of the household to recommend the best available treatment technology and approximate associated yearly costs.
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1.0 TASK IDENTIFICATION

1.1 Task Description

Task 3 for the 2012 WERC Environmental Design Contest requested teams to develop a strategy for evaluating the claims of certain water hardness treatment products. The task description given by WERC states:

"Numerous water treatment technologies are marketed to reduce water hardness. While marketing claims are often ambitious, the reality is that some technologies do not live up to the end users' expectations. The purpose of this project is to develop a strategy for evaluating a particular water treatment product."

For bench scale design purposes, MT Hard Water (MTHW) was asked to demonstrate the evaluation strategy using ScaleRID, an electromagnetic water hardness treatment system.

1.2 Background Information

Water hardness is due to multivalent metallic ions, primarily calcium and magnesium. Hard water is generally not harmful to human health; however; it can cause scaling problems in domestic and industrial plumbing systems.

Calcium ions (Ca$^{2+}$), a major constituent of drinking water, originates from the dissociation of calcium chloride or calcium sulfate in water, as shown in Equation 1:

\[
\text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^- \quad \text{CaSO}_4(s) \rightarrow \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq)
\]

Most of the Ca$^{2+}$ ions in water come from limestone (CaCO$_3$), gypsum (CaSO$_4$•2H$_2$O), or other calcium-containing rocks and minerals. Calcium carbonate (CaCO$_3$) is relatively insoluble in water; but solubility increases with increasing carbon dioxide dissolution and decreasing pH. Hard water diminishes the action of soap, due to the interactions between Ca$^{2+}$ and Mg$^{2+}$ ions and soap’s surfactant molecules. The most obvious sign of water hardness is the layer of white film, or scale, left on a surface after exposure to hard water.

Even though water hardness is common in many locations worldwide, there are comparatively few commercially available technologies that address water hardness removal. However, with many manufacturers marketing water hardness treatments, choosing a specific product or
technology can be a challenge. Therefore, it becomes necessary to compare and evaluate
different water hardness treatment technologies and products.¹

The objective of this task is to develop a strategy for evaluating a specific water hardness
removal technology. To demonstrate MTHW’s evaluation strategy, the team was required to
verify the proposed protocol on the commercially available ScaleRID system, which claims to
use time varying electromagnetic fields to “change the form of water hardness chemicals”,³
hence reducing scale formation.

2.0 WATER HARDNESS TREATMENT TECHNOLOGIES

2.1 Definition of Hardness

There are two methods for expressing water hardness: total hardness and calcium hardness. Total
hardness is a measurement in both Ca²⁺ and Mg²⁺ ions that are dissolved and suspended in water.
On average, magnesium hardness represents about one third of the total hardness.³ As a result,
water hardness is often expressed as calcium hardness, which is a measurement of hardness
related to calcium. Hardness levels are recorded in parts per million (ppm), milligrams per liter
(mg/l), or grains per gallon (gpg). Discrepancies exist in categorizing and standardizing the
concentration levels of CaCO₃ that gives rise to total hardness. Table 1 depicts two commonly
used water hardness scales.⁴

Table 1. Water Hardness Standards⁴

<table>
<thead>
<tr>
<th>Hardness Levels</th>
<th>Sanitary Engineers (mg/L as CaCO₃)</th>
<th>Water Conditioning Industry (mg/L as CaCO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft Water</td>
<td>0 – 75</td>
<td>0 – 50</td>
</tr>
<tr>
<td>Somewhat Hard Water</td>
<td>76 – 150</td>
<td>51 – 100</td>
</tr>
<tr>
<td>Hard Water</td>
<td>151 – 300</td>
<td>101 – 150</td>
</tr>
<tr>
<td>Very Hard Water</td>
<td>&gt; 301</td>
<td>&gt; 151</td>
</tr>
</tbody>
</table>

Currently, the Environmental Protection Agency’s (EPA) approved method for testing water
hardness is Method 130.2.⁵ This method uses Ethylenediamine Tetraacetate (EDTA) to titrate a
sample solution. Ca²⁺ and Mg²⁺ ions in the sample are sequestered upon the addition of a buffer
solution disodium ethylenediamine tetraacetate (Na₂EDTA). The end point of the reaction is
detected by means of Eriochrome Black T indicator. This method effectively measures both
dissolved and suspended Ca²⁺/Mg²⁺ and CaCO₃ concentration respectively.⁵ The concentration
of dissolved Ca$^{2+}$ ions can also be measured by using a calcium ion selective probe that measures the voltage differences across a Ca$^{2+}$ selective membrane.\(^5\)

### 2.2 Hardness Removal Technologies

Commonly used hardness removal technologies in a residential setting are ion exchange (IE), reverse osmosis (RO), and magnetic water treatment. This section discusses each water treatment technology.

#### 2.2.1 Ion Exchange

Ion Exchange water softeners are the most common type of household water treatment systems. This technology removes Ca$^{2+}$ and Mg$^{2+}$ ions from solution so that carbonates will not precipitate and scale onto pipe surfaces. Sodium ions replace Ca$^{2+}$ and Mg$^{2+}$ ions in the water. Figure 1 shows a schematic of the process. Ion exchange is a simple, effective, and safe solution to hard water remediation. However, cumulative operating costs and increased sodium concentrations in the water are drawbacks to the technology.\(^5\)

#### 2.2.2 Reverse Osmosis

Reverse osmosis (RO) is a water purification process that involves applying pressure to reverse the natural flow of water through a membrane, forcing the water to move against a chemical concentration gradient. The porous semi-permeable membrane allows water to pass through, but blocks the passage of larger molecules and ions. The end result is water with a lower ionic content. This technology effectively removes Ca$^{2+}$ and Mg$^{2+}$ ions from water to reduce total hardness. However, high Ca$^{2+}$ and Mg$^{2+}$ ion concentrations can decrease the efficiency and life of the membrane by hardening the membrane. RO requires high water pressure to operate, making it an expensive technology for households.\(^8\)
2.2.3 Magnetic Water Treatment

Magnetic water treatment is a unique, non-chemical approach to treating water hardness. There are two types of magnetic water treatment technologies: 1) electromagnetic water treatment technology (EMT) and 2) permanent magnets. Both types of magnetic water treatments claim to prevent scale deposition on pipe surfaces. For the purpose of evaluation, WERC requested that MTHW evaluate ScaleRID, a type of EMT.

ScaleRID, manufactured by EdenPURE® (7800 Whipple Ave. NW, Canton, OH 44767-00010), creates an electromagnetic field that treats water hardness and scaling. ScaleRID is designed as a residential electromagnetic water treatment device that consists of a solenoid coil and a wall mountable control module. The control module continually sends pulsed fields through the coil (Figure 2) creating an oscillating magnetic field, which promotes homogeneous precipitation. This causes the precipitates to stay in suspension, reducing the chance of scale build-up but not changing the total hardness of the water.9

Most permanent magnet devices are a sequence of magnets, arranged so that the water passes alternately through non-magnetized and magnetized regions. This alternating sequence of magnets is supposedly more effective than one long magnetized region. Although magnets treatment appears to be effective in some cases, the parameters of water composition, magnetic field strength, treatment geometry, and flow rate that lead to satisfactory performance have never been clearly defined.10

3.0 BASIC PRINCIPLE FOR SCALERID OPERATION

The purpose of this task was to evaluate the claims of ScaleRID. To do so, a basic understanding of how ScaleRID works was required. The ScaleRID technology claims to 1) prevent scale from forming on pipes, 2) remove existing scale, and 3) treat hard water causing ions, Ca^{2+} and Mg^{2+}. The time frame for these results after installation is given as two to four weeks, but once the
water is stagnant in a tank for two to three days, the suspended precipitates are said to slowly dissolve back into the solution.\textsuperscript{9}

ScaleRID descaling technology is based on the Lorentz forces, which describes the resulting force between particles after a magnetic field is applied.\textsuperscript{11} The Lorentz force equation is:

\begin{equation}
F = q[E + (v \times B)]
\end{equation}

where $F$ is the force applied on the particles in newtons, $q$ is the electric charge of the particle in coulombs, $E$ is the electric field in volts per meter, $v$ is the instantaneous velocity of the particle in meter per second, and $B$ is the magnetic field in Tesla. In the equation, the symbol "\times" is a vector cross product. The Lorentz forces, resulting from magnetic fields, could alter the trajectories of ions in the water leading to a more chaotic local environment, resulting in increased probability of ionic interactions. Water in residential pipes is constantly subject to changing flow rate, which in turn influences the instantaneous velocity of the ions. The ScaleRID device claims to vary the electromagnetic field applied to the water flow to account for changes in the ions' velocities.\textsuperscript{11}

The electromagnet wave output of the ScaleRID system was recorded in Montana Tech Electrical Engineering laboratory using an oscilloscope. The results indicated that the electronics embedded in the ScaleRID box generate various frequencies to create an electromagnetic field using MOSFET (metal oxidized semi-conductor field effect transistor) technology which amplified the frequencies of the electromagnetic field.\textsuperscript{11} These oscillating electromagnetic waves are thought to have the effect of increasing the randomness of the velocity gradient of the targeted ions, as given by the Lorentz force. This force could artificially increase the interaction potential, or activity of these ions in solution leading to the claimed effect of increasing ionic interaction. This could lead to an increased homogenous nucleation rate of compounds in the water, increasing the rate of precipitation in the flowing water. This, in turn, would lower the supersaturation of scale forming ions in solution, hence, lowering the probability of scale formation on the surface of pipes.\textsuperscript{9} Scale formation on the pipe surface is known as a heterogeneous precipitation process and is energetically favored over homogenous nucleation and growth.\textsuperscript{12} Based on this theoretical assessment, the ScaleRID device claims to increase the homogeneous nucleation rate of CaCO$_3$ in the water by providing this energetic difference in the
form of an oscillating magnetic field.\textsuperscript{11} The added energy that overcomes this nucleation energy barrier in solution, could lead to spontaneous precipitation of nano-equilibrium phases of CaCO$_3$. The Gibbs Free Energy equation for the homogeneous nucleation of a spherical particle in a liquid is given by:

$\Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma$

(Equation 3)

where $\Delta G$ is the total Gibbs Free Energy, $r$ is the radius of the particle, $\Delta G_v$ is the Gibbs Free Energy for the volume, and $\gamma$ is the surface energy term.\textsuperscript{13} Equation 3 can be used to derive an expression for activation energy for homogenous nucleation, of a critical particle size, or $\Delta G^*_{\text{hom}}$:

$\Delta G^*_{\text{hom}} = \frac{16 \pi \gamma^3}{3 \Delta G_v^2}$

(Equation 4)

Similarly, the activation energy for heterogeneous nucleation on a flat surface is given by:

$\Delta G^*_{\text{het}} = \left(\frac{16 \pi \gamma_{SL}^3}{3 \Delta G_v^2}\right) S(\theta)$

(Equation 5)

where $S(\theta)$ is a function of the wetting angle between the interface of the scale and liquid vector and the interface of the scale and the surface vector, and $\gamma_{SL}$ is the scale-liquid interface vector.\textsuperscript{13} The variation of homogeneous and heterogeneous nucleation energy as a function of particle radius is shown in Figure 3. A heterogeneous nucleation event needs to overcome a smaller $\Delta G^*$, hence precipitation is always more likely on a surface (for example, on the inside of a pipe) as opposed to in solution.

If the claims proposed by the manufacturers of ScaleRID are true and indeed increase the homogeneous nucleation rate of CaCO$_3$ in the flowing water, then there should be fine non-equilibrium CaCO$_3$ precipitates in the flowing water. In a continuous flow system, these fine particles would be discharged along with the flow and decrease the chances of scale formation.

\textbf{Figure 3. Activation Energies for Heterogeneous and Homogeneous Nucleation} \textsuperscript{13}
The lowered supersaturation of Ca\(^{2+}\) and CO\(_3\)^{2-} with respect to CaCO\(_3\) should theoretically also increase the dissolution of existing scale on the pipes. Even though this treatment can be potentially regarded as a beneficial way to remediate hard water, it poses a problem with conventionally measuring hardness in the flow system. As the fine CaCO\(_3\) particles are still present in the water, carrying out titration on a grab sample will reveal no changes in the measured hardness of the water, even though the concentration of Ca\(^{2+}\) and CO\(_3\)^{2-} ions in solution would have been lowered. However, these claims based on nucleation and growth theory could be tested by measuring the changes to the Ca\(^{2+}\) concentration in the flow system using a Ca\(^{2+}\) selective ion probe.

Other findings suggest that a magnetic field increases the nucleation rate of homogeneous CaCO\(_3\), and is pH and flow dependent. Also, they suggest the change in the morphology of CaCO\(_3\) precipitate from calcite to aragonite and that the nucleation time is approximately 15 minutes.\(^{12}\)

Based on this understanding and the main claims listed in the ScaleRID product brochure, a series of tests were conducted to study these phenomena. First, MTHW carried out tests to verify if ScaleRID would lead to precipitation of fine non-equilibrium precipitates, compared to a control system without ScaleRID. Next, MTHW considered several continuous flow systems and monitored hardness and Ca\(^{2+}\) variation as a function of time.

4.0 BENCH SCALE SUMMARIES

MTHW conducted several tests, of which five tests are discussed here: 1) beaker test, 2) closed loop system, 3) open flow system, 4) evaluation of an ion exchange system, and 5) evaluation of a reverse osmosis system.

4.1 Beaker Test

As water may become stagnant in household pipes from time to time, MTHW conducted an experiment to determine if flow was required for ScaleRID to induce hardness reduction. A test was conducted using a beaker with the ScaleRID coil wrapped around the base and another beaker without the coil (Figure 4). The water used was a mixture of sodium carbonate (Na\(_2\)CO\(_3\)) and calcium chloride (CaCl\(_2\)) dissolved in deionized water to yield 80 ppm of CaCO\(_3\). The
beakers were sealed to minimize carbon dioxide dissolution. The temperature, pH, conductivity, and total hardness of the samples were measured at two hours, six hours, one day, and two days after the initial testing. MTHW also added microscope slides to the beakers to sample any precipitates that formed.

![Figure 4. Beaker Test with Static Water](image)

![Figure 5. Beaker Test with Flowing Water](image)

The beaker test with static water did not produce results that agree with the manufacturer’s claim that the water hardness should stay constant. The exact experiment was conducted again with the addition of a peristaltic pump using one eighth inch plastic polygon tubing (Figure 5). Samples were analyzed at two hours, six hours, one day, and two days.

The results from the beaker tests are presented in Figure 6. The beaker test with flowing water indicated that flow played an important role in stabilizing water hardness when treated with ScaleRID. With flowing water, the water hardness in the control beaker decreased rapidly while the ScaleRID beaker indicated no change in hardness. With static water, there was little difference in hardness between the two systems.
In the beaker test with flowing water, both beakers produced precipitation, however, the location of the precipitation was different. In the control system, precipitation was observed on the bottom and sides of the beaker. In the ScaleRID system, precipitation was observed in the water itself, making the water considerably more turbid than the control. The size and shape of the precipitates were further analyzed using a scanning electron microscope (SEM). Micrographs from both tests confirmed that the presence of ScaleRID caused a change in the size and morphology of the CaCO₃ precipitation. Figure 8 shows the precipitates that formed in the beaker with and without ScaleRID. The morphology of the precipitates in the control (Figure 7A) was indicative of the rhombohedral calcite type crystal precipitates (15-20 μm in size) that formed on the slide and continued to build on top of previous layers, which seemed comparable to the classical scaling phenomenon. On the slides from the ScaleRID experiment (Figure 7B), the precipitates were much smaller in size (~50 nm) and appear to be the vaterite polymorph of CaCO₃ or a form of amorphous CaCO₃. These precipitates were easily wiped off, but those on the control slide required a sharp edge to scrape off. Both experiments indicated that water exposed to the ScaleRID device was indeed giving rise to finer precipitates that were likely formed in solution due to homogeneous nucleation and growth, as opposed to scaling on the control slide surface from heterogeneous nucleation and growth.
4.2 Closed Loop System

The beaker tests suggested that ScaleRID enhanced precipitation in the water. Based on these results, a closed loop flow reactor was designed that allowed for an increased flow rate. Increasing the size of the system enabled testing the operational limits of ScaleRID. In these experiments, flow rate, starting hardness, and ionic strength of the water were varied.

The closed loop system included a 10 Liter polyethylene tank with an outlet near the bottom of the tank and an inlet near the top of the tank. Garden hose was used to connect the tank to an 18 inch recycled copper pipe and to a centrifugal pump that delivered water back into the tank (Figure 8). The copper pipe was chosen because it is a common material used in residential water systems. A recycled pipe was chosen by visually inspecting the amount of scale already in the pipe. The control system was a replicate of the experimental system with the exception of the
ScaleRID system. A 20 μm filter was added between the pump and the tank in some experiments in order to capture precipitates from the water.

A total of five experiments were carried out using sample water that contained 1) 100 ppm CaCO₃, 2) 150 ppm CaCO₃, 3) water with constituents as provided by WERC (which contained about 1600 ppm CaCO₃), 4) a local well water source with 260 ppm CaCO₃, and 5) a continuous test. Variation in concentration of water hardness allowed MTHW to test the effectiveness of ScaleRID at different initial hardness levels. The tests were conducted for 7-16 days. Again, microscope slides were added to reservoirs to sample any precipitates that formed.

4.2.1 Closed Loop System Experiment: 100 ppm Test

In this experiment, the closed loop system maintained a stable temperature within the 24-27°C range and a stable pH (8.5±0.5). The test was carried out for 16 days with samples being collected daily, to test the claim that ScaleRID will cause changes to the water hardness after 2-4 weeks. It was observed that the experiment with ScaleRID, as in the beaker tests, maintained a higher total hardness while the total hardness in the control decreased rapidly (Figure 9).

![Closed Loop System- 100 ppm CaCO₃](image)

Figure 9. Experimental Results in the Closed Loop System: 100 ppm CaCO₃

The SEM images of the scale formed on the slide in this experiment are shown in Figure 11. The ScaleRID slide revealed fine vaterite-like crystal formations that seem to have settled on the slide (Figure 10A). The precipitates in the control experiments (Figure 10B) were calcite crystals that grew off the surface of the slide. The higher magnification provides evidence for the scaling.
4.2.2 Closed Loop System Experiment: 150 ppm Test

After completing the first test, the hardness level was increased to 150 ppm, which is considered to be "hard water" by professionals. This test was conducted for a total of 4 weeks. The longer duration accounted for any changes that were not seen in the previous test.

Only two samples were taken for this experiment: an initial sample and a sample at four weeks. Overall, there was a decrease in total hardness. However, due to the small sample size, the results collected from this experiment were inconclusive.

4.2.3 Closed Loop System Experiment: WERC Water Test

The third test conducted in the closed loop system was at the salt concentration levels provided by WERC in an update to the task statement. This water contained hardness levels that were significantly higher than the water used before. The water contained magnesium sulfate (MgSO₄), sodium sulfate (Na₂SO₄), sodium bicarbonate (NaHCO₃), and calcium chloride (CaCl₂). The test was conducted for one week. A calcium ion-selective probe was used to measure the Ca²⁺ concentrations in the water. Also, a 20 μm filter was added to each system. The results of this experiment are given in Figure 11.
The total hardness for the experiment with ScaleRID was higher than that in the control. The ScaleRID system also had lower overall Ca\(^{2+}\) concentrations that decreased with time, which was consistent with what was expected. The filter added into the bench scale collected particles that were easily visible to the naked eye and fell off when the filter was removed for examination. The collection of these fine particles supported the theory of homogenous nucleation. This experiment indicated that at this initial hardness the ScaleRID device did not decrease appreciably even after several days.

4.2.4 Closed Loop System Experiment: Well Water Test

After testing the water composition suggested by WERC, MTHW decided to use water from a well in Whitehall, MT, which is known for its hard water. This was the most realistic test water because it was from a typical residential setting. Initial tests showed that this water contained 260 mg/l CaCO\(_3\), which is considered to be hard water by the water conditioning industry (Table 1). Well water was chosen to examine how the ScaleRID would work in a realistic non-controlled setting. Results from this test are shown in Figure 12.
The total hardness was constant at 260 mg/l of CaCO$_3$ for both systems. The Ca$^{2+}$ concentrations were much more variable than the total hardness, but both systems followed the same fluctuations proving that precipitation in water with a high ionic strength was a very dynamic process. In general, the Ca$^{2+}$ concentration was slightly lower in the ScaleRID than in the control, but again, ScaleRID did not decrease the hardness for the period tested.

4.2.5 Closed Loop System Experiment: Continuous Test

To understand the instantaneous changes that the ScaleRID device might be causing, continuous tests were conducted for 10 minutes to 45 minutes. The continuous tests examined the small instantaneous changes in Ca$^{2+}$ and total hardness in the system with and without ScaleRID. Samples were taken every 15 seconds using a calcium selective probe over a 40 minute time period. The calcium probe was calibrated prior to use and left in the solution the entire 40 minutes. Different combinations of turning the ScaleRID on and off and turning the water flow on and off were used to see the difference in Ca$^{2+}$ concentration.

In one such test, the ScaleRID device was turned on for the first ten minutes, and then turned off and on periodically every ten minutes until the end of the experiment. The initial Ca$^{2+}$ reading was 95.0 mg/l and went up to 101.7 mg/l by the end of the 40 minute test. It was expected that for the first ten minutes the Ca$^{2+}$ readings should have slowly been decreasing, due to the ScaleRID device being on. The next ten minutes should have displayed a flat or upward trend, followed by another decrease in Ca$^{2+}$ ions when the ScaleRID was turned back on. Instead, there
was a slow up trend in the Ca\textsuperscript{2+} ions throughout the entire experiment, showing no changes when the ScaleRID was turned on or off. Thus, the results of this experiment suggest that the ScaleRID device is ineffective at these hardness concentrations and required a longer period of time to observe reductions in Ca\textsuperscript{2+} concentrations. The results of this experiment are shown in Appendix B.

4.3 Open Flow System

Because water in a house is not recycled but used continuously, a continuous flow experiment using Montana Tech’s S&E laboratory tap water was conducted. Initial tests of this water showed 80 mg/l of CaCO\textsubscript{3}, and there was visible scale on the faucets and tubing connected to the faucets. Also, the copper piping in this laboratory has not been replaced since the building was remolded in the 1980\textsuperscript{15}. ScaleRID was installed below the sink as per the installation methods listed in the manual (Figure 13A). A 15 foot hose was clamped onto the faucet and delivered the discharge into a different sink (Figure 13B). The sample was taken from a beaker that was placed at the end of the hose (Figure 13C). The experiment was carried out for two weeks and water samples were analyzed throughout this time. Control samples were taken from a sink that was connected to a different plumbing system from the same water source. Flow rates were also varied for certain days.

The total hardness did not change in either system, and no noticeable difference in the Ca\textsuperscript{2+} concentration was observed upon changing the flow rate. The Ca\textsuperscript{2+} concentration was again cyclic and generally higher in the control than that in the ScaleRID (Figure 14).
4.4 Evaluation of Additional Water Softening Technologies

4.4.1 Evaluation of Ion Exchange System

MTHW evaluated the hardness removal performance of an ion exchange based water softener system currently employed in a household using well water. Water, directly from the well and after the treatment system, was sampled. The total hardness, Ca\(^{2+}\) ion concentration, conductivity, pH, and temperature were measured for each sample. The results were used to compare ion exchange water softening technology to ScaleRID and other systems and to develop the test protocol for evaluating different water hardness treatment technologies.

There was a significant decrease in total hardness for samples after the water softener treatment: the hardness of water before the treatment was 260 mg/L, whereas the hardness of water after the treatment was 0.667 mg/L. The Ca\(^{2+}\) concentration also dropped significantly after the water softener treatment, decreasing from 171.2 mg/L to 1.9 mg/L. Other parameters were very similar. The results are shown in Table 2.

Table 2. Complete Results of Water Softener Test

<table>
<thead>
<tr>
<th></th>
<th>Total Hardness (mg/l)</th>
<th>Temperature (°C)</th>
<th>Conductivity (µs)</th>
<th>pH</th>
<th>Calcium (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Treatment</td>
<td>0.67</td>
<td>24</td>
<td>551</td>
<td>6.87</td>
<td>171.2</td>
</tr>
<tr>
<td>After Treatment</td>
<td>260</td>
<td>24</td>
<td>571</td>
<td>6.99</td>
<td>1.9</td>
</tr>
</tbody>
</table>
4.4.2 Evaluation of Reverse Osmosis System

MTHW also evaluated the hardness removal performance of a reverse osmosis system currently employed in a household using municipal water. Samples of tap water before and after the RO system were taken and evaluated for total hardness, Ca\(^{2+}\) concentration, pH, temperature, and conductivity.

The hardness of tap water before the RO treatment was 80 mg/L, whereas the hardness of water after the RO treatment was 60 mg/L. The Ca\(^{2+}\) concentration of the tap water was 70.8 mg/L, which is higher when compared to that of the water sample after RO treatment (50.4 mg/L). The conductivity, pH, and temperature of the two samples were very similar. The complete results are listed in the Table 3:

<table>
<thead>
<tr>
<th></th>
<th>Total Hardness (mg/l)</th>
<th>Temperature (°C)</th>
<th>Conductivity (μs)</th>
<th>pH</th>
<th>Calcium (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Water</td>
<td>80</td>
<td>24</td>
<td>144</td>
<td>7.48</td>
<td>70.8</td>
</tr>
<tr>
<td>RO Water (Treated)</td>
<td>60</td>
<td>23</td>
<td>142</td>
<td>7.40</td>
<td>50.4</td>
</tr>
</tbody>
</table>

5.0 EXPERIMENTAL FINDINGS AND DISCUSSION

The results from the experiments seem to suggest that ScaleRID would work in a small window of operational conditions (flow rate and starting hardness concentration). The different morphologies of scale formation indicated that ScaleRID does change the size and crystal polymorph of CaCO\(_3\) precipitates. However, the formation is dependent on factors like pH, flow rate and starting hardness levels. This supports the claims that ScaleRID prevents new scale from forming on pipes and treats water hardness by “changing the form of Ca\(^{2+}\) ions”\(^{10}\) The experimental data also indicated the device was not effective for initial hardness greater than 80 ppm. ScaleRID seems to be most effective on pipes that have preexisting scale: only minimal changes in Ca\(^{2+}\) concentration in water flowing through a new pipe can be observed. Preexisting scale seemed to increase the efficiency of ScaleRID; however, the results could not support the claim that preexisting scale would be removed. ScaleRID did not affect the total hardness, suggesting that it was not a hardness removal technology but rather a scale reduction technology.
5.1 Formalization of Test Protocols

After the experimental results were analyzed, the following test protocol was developed to evaluate the effectiveness of a water hardness treatment technology. This protocol includes examining initial conditions, total hardness, Ca\(^{2+}\) concentration, and visual observation. Appendix A contains a field data sheet and a detailed procedure for the protocol. The results of these tests represent an overall status of the household’s water hardness. Based on these results, a recommendation will be generated as to which water treatment technology is potential fit for that specific household.

5.1.1 Initial Conditions

The initial condition test includes measuring pH, temperature, conductivity, and flow rate. These tests will provide a basic understanding of the effect of current water treatment.

5.1.2 Calcium Ion Concentration

Measuring the amount of dissolved calcium in the solution will be carried out using a calcium ion-selective electrode. This probe is a reliable water hardness indicator since water hardness is largely caused by calcium. The probe measures the amount of Ca\(^{2+}\) dissolved in the water, not the amount of calcium in a solid phase. This test would effectively evaluate the performance of EMT technologies.

5.1.3 Total Hardness

Total hardness is measured using a titration kit and is the measure of both dissolved and solid hardness in the water. This titration kit accounts for both magnesium and calcium, which will then be compared to the calcium reading from the ion selective probe. Samples that are 20°C or colder should be titrated slower allowing for sufficient time for color change to occur.

5.1.4 Visual Observation

The visual test may use a light microscope with high magnification objectives lenses or a SEM to obtain high resolution photos of the scale captured on sampling slides.
5.2 Decision Matrix

A decision matrix was developed based on existing research and MTHW's experimental data gathered in the study. For each available water hardness treatment, MTHW researched water usage, and operating conditions such as flow rate, pH, temperature, pressure, and hardness treatment efficiency. All the parameters were entered into a spreadsheet. MTHW consolidated the spreadsheet and used it as a decision matrix to recommend the best available treatment technology (Appendix C).

5.3 Smart Query-based Water Hardness Removal Evaluator (SQWRE)

For the purpose of evaluation, MTHW created a simple web based tool called SQWRE, to evaluate existing water hardness treatment technologies or to recommend which type of technology would be best suited for a specific household condition. Appendix D further discusses the query parameters and design.

6.0 CONCLUSION

The experimental results suggested that ScaleRID potentially meets two out of the three claims in its brochure under specific conditions; 1) to prevent scale from forming on pipes, 2) to treat hard water causing ions, Ca$^{2+}$ and Mg$^{2+}$, while maintaining the ions in the water. However, the results did not conclusively support the third claim: ScaleRID removes preexisting scale. ScaleRID seemed to have a small window of viable operability; it seemed to be most effective in treating water with low to moderate starting hardness levels, steady flow rate, stable pH (7-8) and temperature conditions. These specific conditions may not, however, exist in real world scenarios. The results also seemed to suggest that the ScaleRID works best if applied to pipes with preexisting scale. The ion-exchange results proved that this technology performs over a wide range of hardness, normal pH and temperature conditions, and on scaled or new pipes. The RO evaluation showed that it might be more cost effective in households with other water quality issues than just hardness.
7.0 RECOMMENDATIONS

Based on the experimental results that led to the decision making of the test protocol, recommendations as to which hardness treatment technology applies best to one’s conditions are provided by MT Hard Water. The degree of the problem is first assessed and reviewed based on the initial conditions, Ca$^{2+}$ ion concentration, total hardness, and visual observations of existing scale. A recommendation is then calculated from a web query system based on the following criteria: water hardness reduction, scale reduction, efficiency, and total cost of the system. MTHW designed a website to systemize this evaluation. The website, http://www.mthardwater.com/, contains a technology decision tool that automatically calculates which water treatment technology might work best for a household. This site also shows the yearly costs associated with that particular technology, and lists the next best system if that cost does not meet an individual’s budget.

8.0 SAFETY AND LEGAL REQUIREMENTS

In accordance to OSHA 1910.303, all equipment should be inspected and free of any damaged parts or potential hazards likely to cause physical harm before each use. Also, under OSHA 1910.147, it is required to use lock out/tag out procedures if, for some reason, an individual intends to access the pump motor or power cord connection.

Proper protective procedures will be enforced. Workers will also be required to wear general lab safety PPE including chemical splash goggle, chemical-resistant nitrile glove, and chemical-resistant lab coats.

MT Hard Water is not responsible or liable for any personal injuries or damages to equipment resulting from improper use of water treatment technologies. This team does also not condone the practice of performing the protocol mentioned in this report.
9.0 REFERENCES


Appendix A- Full Scale Test Protocol

The following test protocol and field data sheet explain the steps needed in order to evaluate a water hardness treatment technology.
1. **Initial Conditions Test**

   1.1. Samples will be collected in a triple rinsed container before and after any water treatment technology (if any).
   1.2. Remove 150 ml of water from the water softener bypass.
   1.3. Test the temperature in Celsius. Record.
   1.4. After calibrating the pH meter, measure the pH of the solution. Record.
   1.5. After calibrating the conductivity meter, measure conductivity. Record.
   1.6. Record the time it takes to fill a 1 gallon bucket.
   1.7. Calculate flowrate. Record.
   1.8. Repeat steps 1-7 using water from the faucet.
   1.9. Calculate difference. Record.

2. **Calcium ion concentration**

   2.1. Calibrate calcium probe

      2.1.1. Rinse probe off with DI water.
      2.1.2. Immerse Probe into high standard of 1000 mg/l. Make sure the probe is not touching the bottom of the bottle and that the reference contacts are fully immersed.
      2.1.3. Allow the probe to soak in the high standard for 30 minutes.
      2.1.4. Enter the concentration value.
      2.1.5. Wait for the voltage reading to stabilize.
      2.1.6. Press the “keep” button.
      2.1.7. Thoroughly rinse probe off with DI water and blot with lab wipe.
      2.1.8. Immerse probe into low standard of 10 mg/l making sure the probe is not touching the bottom of the bottle and that the reference contacts are fully immersed.
      2.1.9. Repeat steps 1.3 to 1.5.
      2.1.10. Rinse Probe with DI water.

   2.2. Place calcium probe into the water from the initial conditions test.
   2.3. Run until the standard deviation is below 1.0.
Water Hardness Evaluation

Procedure

2.4. Record the reading the average calcium concentration.
2.5. Repeat steps 2 and 3 using water from the faucet that has been treated with the water softening treatment.
2.6. Calculate difference. Record.

3. Total Hardness Test

3.1. Fill the small hardness measuring test tube with water from initial conditions test.
3.2. Place water into the larger hardness mixing vial.
3.3. Add 3 drops of buffer solution, Hardness 1, and swirl to mix.
3.4. Add 1 drop of ManVer Hardness Indicator Solution, Hardness 2 and swirl to mix.
3.5. Add EDTA Titrant drop by drop into mixing bottle. Swirl the bottle as each drop is added and count each drop. Continue until the sample turns from pink to blue.
3.6. Multiply the number of EDTA Titrant drops by 20 to get the hardness concentration in [mg/l]. Record.
3.7. Repeat steps 1-6 using water from the faucet that has been treated with the water softening treatment.
3.8. Calculate difference. Record.

4. Visual Test

4.1. Place about 5 drops of water from initial test onto test slide.
4.2. Allow slide to dry exposed to the air.
4.3. Place slide in petri dish for transportation back to lab.
4.4. Gently wash slides in DI water and then 50% ethanol.
4.5. Dry samples.
4.6. Using double-sided tape transfer samples onto an aluminum stub and then sputter coated with gold.
4.7. Repeat steps 1-6 using water from the faucet that has been treated by the water softening treatment.
Name: 
Address: 
Date and time: 
Current treatment? (Yes/No) 
Model: 
What is the water source? (Well/Municipal) 
History of high metals? (Yes/No) 
History of microbes? (Yes/No) 
Visible scale on faucets? (Yes/No) 
Adequate water pressure? (Yes/No) 

<table>
<thead>
<tr>
<th>Before Water Treatment</th>
<th>After Water Treatment</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductivity (μS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Hardness (mg/l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺ (mg/l)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: 

A-4
Task 3: Montana Tech
Appendix B

Continuous Test

Time (sec)

Calcium (mg/l)

B-1
Task 3: Montana Tech
Appendix D- Website Design

There are many commercially available water treatment technologies in the market today. It is necessary to choose the technology that best fits one's water conditions. Based on the water hardness test protocol that MT Hard Water has developed, a website that makes product recommendations has been established. This website, http://www.mthardwater.com/, allows a customer who wishes to solve water hardness problems to enter his/her current conditions such as temperature, pH, water pressure, current hardness, cost, and etc. into a decision tool. The decision tool will then automatically rank the parameters and make a recommendation to the customer on which technology is the best based on the customer's inputs. This site also shows the yearly costs associated with that particular technology, and lists the next best technology if that cost does not meet the customer’s budget. In addition to the decision tool, the website contains facts about water hardness, MT Hard Water's testing method and protocol, biographies of the MT Hard Water team members, and contact information.

After the data on the limits and effectiveness of each treatment technology was collected, a table was assembled with the upper and lower bounds for each hard water decision criterion. The entry form in the decision allows the user to enter their particular water quality information. When the user hits the submit button, the form passes those parameters to a database query application that selects all the technologies that meet those criteria. The decision tool then displays the results of that query in order from lowest to highest yearly cost of operation.