Study of Plasma Treatment of Produced Water from Oil and Gas Exploration

A Thesis
Submitted to the Faculty
of
Drexel University
by
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in partial fulfillment of the
requirements for the degree
of
Doctor of Philosophy
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Dedication

This thesis is dedicated to my mom, Cheryl, who has always encouraged me, and throughout situations of all kind, has always demonstrated great empathy, intellect, class, decency, respect, and genuine love. Among the countless valuable lifelong lessons that I have learned from my mom, there’s the one that I deem most important, and which influences all these lessons and more, and that is: to lead by example.
Acknowledgements

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Abstract

Study of Plasma Treatment of Produced Water from Oil and Gas Exploration

Kamau Wright
Advisors: Dr. Young I. Cho and Dr. Alexander Fridman

Unconventional gas and hydraulic fracturing is helping to increase natural gas production, which is widely viewed in the U.S. as a key asset to bolstering a clean and energy-independent future. Safe and economical management and treatment of water produced during such processes remain of key importance. With the increase of hydrocarbon production and national shale gas production expected to increase threefold and account for nearly half of all natural gas produced by 2035, advanced water treatment and management processes must be investigated, to ensure water conservation and associated economic prudence. The state of the art of produced water treatment technologies is described including the efficacy of plasma to modulate the contents of such aqueous solutions, meeting target parameters and potentially enabling the operation of other treatment technologies. Among other effects, progress is presented on the enhancement of an arc-in-water system to remove bicarbonate ions and prevent the mineral fouling ability of water which causes formation of CaCO$_3$ in heat exchangers and distillation units.

Qualitative and quantitative treatment targets of produced water treatment are discussed. Experimental work is conducted to test theories and identify and reproduce favorable effects useful to treating wastewaters. Plasma arc-in-water systems demonstrated capability of producing bicarbonate-depleted wastewaters, with experiments with gas-field produced waters indicating that generation of H$^+$ ions plays a
greater role in bicarbonate ion removal than local heating. Tests showed abatement of bicarbonate ions from a range of 684–778 mg/L down to zero. Subsequent scaling/fouling tests with waters ranging from 0 to 500 mg/L bicarbonate ions, in the presence of high calcium ion concentrations, showed that scale thickness, as well as mass on a 1-kW heating element was an order of magnitude less for process water containing 100 mg/L bicarbonate ions compared to process water with 500 mg/L of bicarbonate ions. Water with bicarbonate ion concentration approaching zero resulted in prevention of scale.

To enhance this new plasma induced fouling mitigation method, a plasma arc-in-water reactor was re-engineered, using a ground electrode, and two high-voltage electrodes, to stretch the arc discharge in water and increase contact between plasma and water. Results of simultaneous effects were also collected, showing within 5 min, a 4-log reduction in both Sulfate Reducing Bacteria (SRB) and Acid Producing Bacteria (APB), bacteria that are characteristic of oil-field produced waters; as well as oxidation of organics, with degradation of visually observable organics within 3 minutes, and decrease of oil and grease from 40 mg/L to under 10 mg/L within one min. With an arc-in-water system utilizing a stretched arc, simultaneous effects were exhibited on fouling ability of produced water, inactivation of bacteria, and degradation of organics.

Plasma discharges in water represent a unique option in the treatment of produced waters from oil and gas production. While the water softening capabilities of arc-in-water systems present a new method for fouling mitigation and remediation of scale in heat exchangers, the simultaneous effects, including oxidation of organics and
inactivation of bacteria, may allow application of plasma to water, to satisfy treatment targets that allow for the reuse of such waters in oil and gas operations.
1. Introduction

The research contained here is presented to provide a study of high voltage plasma treatment of produced water from oil and gas exploration. Such a study:

- investigates plasma discharges in wastewater from oil and gas exploration
- discusses produced water treatment targets for recycling and re-use
- considers theories of plasma induced modulation of water chemistry properties
- contributes experimental work which helps isolate plasma-in-water mechanisms useful to industrial treatment goals and scalability
- proposes new plasma-induced water softening methods for mitigation of precipitation fouling in heat transfer systems, such as distillation units, which may encounter hard waste waters during treatment processes
- explores technical considerations in plasma treatment of produced water

Benefits and challenges are discussed of plasma arc-in-water systems acting solely or implemented into other more common engineering systems, to treat produced water. Plasma arc-in-water systems can potentially enhance mechanical engineering systems such as distillation units.

1.1 Motivation

Unconventional gas and hydraulic fracturing is helping to increase natural gas production, which is widely viewed in the U.S. as a key asset to bolstering a clean and energy-independent future. With large volumes of oil and gas field wastewaters produced during such processes, safe and economical management and treatment of such produced waters remain of key importance. For example, in the Pennsylvania Marcellus shale, even
with 95% of produced water reuse, approximately 0.15 – 0.3 million gal/day are required to be disposed of by deep well injection [1].

With increasing hydrocarbon production, advanced water management and treatment methods must be developed to help conserve water. A plasma system such as an arc-in-water may offer a unique solution for treating these large volumes of wastewater.

It should be noted that much of this study was conducted under the auspices of Research Partnership to Secure Energy for America (RPSEA), operating as a consortium of premier U.S. energy research universities, industry, and independent research organizations, managing the program under a contract with the U.S. Department of Energy's National Energy Technology Laboratory. Funding for this project (Project number 11122-31) is provided by RPSEA through the “Ultra-Deepwater and Unconventional Natural Gas and Other Petroleum Resources” program authorized by the U.S. Energy Policy Act of 2005. RPSEA (www.rpsea.org) is a nonprofit corporation whose mission is to provide a stewardship role in ensuring the focused research, development and deployment of safe and environmentally responsible technology that can effectively deliver hydrocarbons from domestic resources to the citizens of the United States.

1.2 Objective

Research and experimental work on plasma arc-in-water and its capability to modulate aqueous wastewater solutions such as produced water, may be useful in enhancing or completely replacing some common produced water treatment technologies.
With some investigation of the science involved in plasma treatment of water, as well as further engineering of water-applicable systems, novel processes can be developed.

The objective of this study was to investigate plasma treatment of produced water from oil and gas exploration, for its capability in sole treatment of such waters, or enhancing distillation treatment methods. More specifically, the general scheme of produced water treatment is outlined, quantitative and qualitative target goals are explained, current major technologies are described, and the efficacy of plasma arc-in-water-treatment to contribute to these processes prior to desalination will be discussed.

In this study, a new plasma-based method for bicarbonate removal was tested and bicarbonate ion removal was verified as an effective mechanism for mineral fouling prevention. Re-engineering of effective plasma-in-water reactors was performed to enhance the capabilities of the demonstrated plasma water treatment, both in effect and capability to be scaled up. Toward this goal the feasibility of stretching an arc discharge in produced water was tested.

Results are presented which demonstrate the capability of enhanced arc-in-water systems to treat produced water from oil and gas exploration.

2. Background

2.1 Hydraulic fracturing for oil and gas

Natural gas is considered as a clean energy source because its combustion produces much smaller amounts of harmful emissions (i.e., carbon dioxide, nitrogen oxide and sulfur oxide) [2]. The U.S Energy Information Administration (EIA) reported that the U.S has total 4,829 trillion cubic feet (Tcf) of potentially recoverable dry natural gas [3], with more than 1,744 Tcf from shale formations [4], an amount that is enough to
supply the U.S. for the next 110 years [3, 5, 6]. Less than 1% of the Marcellus shale has been explored to date according to EIA as of 2012 [3]. Shale gas production in the U.S. is expected to increase threefold and will account for nearly half of all natural gas produced by 2035 [3]. This will help the U.S. to move toward an energy independent future, with shale gas extraction through horizontal drilling and hydraulic fracturing in the U.S. becoming a rapidly accelerating field [6].

2.2 Oil and gas field produced waters, properties, and targets

Produced water is water that is trapped in underground formations and brought to the surface during oil and gas exploration and production along with oil or gas [7]; produced water is an oil and gas field wastewater. The wastewater generated during the drilling phase is called flowback water, whereas the water generated during the production phase is called produced water. With global production of this fluid estimated at around 250 million barrels per day compared with around 80 million barrels per day of oil in 2009, the oil to water ratio is around 3:1 [8]. Produced water has been estimated to cost the petroleum industry about $45 billion a year according to Halliburton in 2001 [9].

In oil and gas exploration, hydraulic fracturing, is a process used after a drilled hole is completed [10]. This process utilizes hydraulic fracturing fluid (or frac fluid), which is usually made up of over 98% water and sand, and small percentages of chemical additives [11] to create or restore small fractures in a formation, and effectively stimulate production and extend the life of oil and natural gas wells [10]. This water eventually flows back up through the well head, and is referred to as produced water (or flowback water), containing fracturing fluids, as well as dissolved constituents from underground fluids in the formation.
The aforementioned fracturing fluids typically include a combination of additives that serve as friction reducers, biocides, pH adjusters, scale inhibitors, and gelling agents [12, 13]. Currently, in gas shale plays, the predominant frac fluid being used contains friction-reducing additives (called slickwater), which allow the fracturing fluids and sand, or other solid materials called proppants, to be pumped to the target zone at a higher rate and reduced pressure than if water alone were used [11]. When fracturing gel is used (as opposed to slickwater), proppant support is provided utilizing polymers which swell in water to produce viscous liquid [12], more able to carry, or avoid settling of proppant, than would a less viscous (slickwater) frac fluid [14, 15]. It should be noted that in the U.S., fracturing fluids used over a 4-year period totaled 780 million gallons (~2.9 billion liters) (not including dilution water) [6].

When the produced water flows back through the wellhead, it contains not only fracking additives but also elevated levels of metals, dissolved solids (e.g., brine), organics, and radionuclides that occur naturally in deep underground waters [6, 8].

Water can be classified by amount of Total Dissolved Solids (TDS) in mg/L, as shown in Table 1. Produced water can have excessively high TDS levels, with produced water from the Marcellus shale typically having even higher TDS than other rock formations.
Table 1: Classification of water by the amount of TDS (mg/L) [16].

<table>
<thead>
<tr>
<th>Classification</th>
<th>TDS range (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking water</td>
<td>&lt; 250</td>
</tr>
<tr>
<td>Fresh water</td>
<td>&lt; 1,000</td>
</tr>
<tr>
<td>Brackish water</td>
<td>1000 to 10,000</td>
</tr>
<tr>
<td>Saline water</td>
<td>10,000 to 30,000</td>
</tr>
<tr>
<td>Brine</td>
<td>&gt; 30,000</td>
</tr>
</tbody>
</table>

Figure 1 is a graph reported by Blauch [17] using data from over 100 flowback samples; this graph represents not only a comparison of TDS variations for select formations, but it also shows one of the most prominent unexplained phenomena observed in the Marcellus and other plays, that is the gradual increase in both the concentration of dissolved salts and flowback volume in produced waters during the first year after hydraulic stimulation [17, 18].
Mitchell [19] proposed target goals of various water parameters in both gel frac formulations and slickwater frac formulations as shown in Table 2. Based on his study, gel frac formulations require more stringent treatment than slickwater frac formulations. Slickwater formulations generally allow higher concentrations of water properties, excluding bicarbonate ion concentration, which has a target goal of <400 mg/L for slickwater, very similar to but less than the allowable 500 mg/L for gel frac formulations.
Table 2: Target goals of various water parameters in the treatment of produced water [19].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Target - Gel frac</th>
<th>Target - Slickwater frac</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6 to 8</td>
<td>5 to 7</td>
</tr>
<tr>
<td>Chlorides (mg/L)</td>
<td>&lt; 25,000</td>
<td>&lt; 70,000</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>&lt; 10</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Bicarbonate (mg/L)</td>
<td>&lt; 500</td>
<td>&lt; 400</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>&lt; 100</td>
<td>&lt; 8,000</td>
</tr>
<tr>
<td>Magnesium (mg/L)</td>
<td>&lt; 100</td>
<td>&lt; 1,200</td>
</tr>
<tr>
<td>Sulfates (mg/L)</td>
<td>&lt; 300</td>
<td>&lt; 400</td>
</tr>
<tr>
<td>Total Hardness (mg/L as CaCO₃)</td>
<td>&lt; 250</td>
<td>&lt; 25,000</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>n/a</td>
<td>&lt; 120,000</td>
</tr>
</tbody>
</table>

In addition to the aforementioned dissolved ions and components mentioned, produced water can also contain bacteria. One type of bacteria that can be found in produced water is Sulfate Reducing Bacteria (SRB). SRB breathes sulfate rather than oxygen in a form of anaerobic respiration, obtaining energy by oxidizing organic compounds, while reducing sulfate ions to H₂S.

SRB can cause severe environmental and industrial problems, especially in the oil and gas industry, because this bacteria can produce corrosive, reactive, and toxic sulfide [20]. The corrosion caused by SRB is often referred as microbiologically-influenced corrosion (MIC), which is the officially accepted terminology by NACE (The National Association of Corrosion Engineers) to address this type of corrosion. Abundant
anaerobic bacteria can cause corrosive by-products (e.g., H$_2$S) and biological fouling [21].

2.3 Current treatment methods for produced water

Produced water and flowback waters are conventionally treated through a variety of different physical, chemical, and biological methods. Since there are multiple needs that should be addressed in the treatment of produced water and flowback water, a number of different methodologies are used [8, 22] as shown in Table 3.
Table 3: Various methods for treating produced water, indicating the need for multiple methods [22]

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<tbody>
<tr>
<td>API Separator</td>
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<td>Deep Bed Filter</td>
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<td>Hydroclone</td>
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<tr>
<td>Induced Gas Flotation</td>
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<td>Ultra-filtration</td>
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<td>Sand Filtration</td>
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<td>Aeration &amp; Sedimentation</td>
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✓ = Indicates that the technology is applicable as a potential remedy as indicated by data collected from pilot or commercial scale units.

Note: This figure is adapted from Hayes and Arthur [22]

The targets for reuse and recycling evolve as industry develops and refines its processes, and the requirement for discharge and disposal can also evolve with regulation. For example, the Pennsylvania Department of Environmental Protection announced on January 1, 2011 that all industrial discharges including produced water
would be limited to 500 mg/L TDS. However, there are currently no facilities in Pennsylvania that can treat flowback fluids to this level except with an evaporation and crystallization process [17], which can be cost prohibitive even on a large scale, and result in the production of approximately 400 tons of crystalline salts/day in a 1 million gal/day processing plant, a volume that cannot be accepted by a typical municipal landfill [17].

Due to large concentrations of metal ions (i.e., calcium, magnesium, barium, strontium, iron) together with sulfate and carbonate, the hardness of produced water is extremely high. If hardness control is not properly conducted, scales can impede gas or oil flow, and variations in salinity can compromise well integrity by affecting clay shrinking and swelling within the shale formation. The concentrations of calcium and magnesium ions in produced water are reported to be very high, with the maximum concentration of 51,000 ppm and 4,000 ppm, respectively [8, 23]. Chemical treatment is often used to reduce these mineral ions so that mineral fouling can be prevented or significantly reduced. Hardness can be removed by hydrated lime (Ca(OH)$_2$), and soda ash (Na$_2$CO$_3$) [24].

Membrane filtration is also used for water treatment. Four commonly used membrane technologies include: microfiltration (MF), which removes particles of 50 nm or larger; "ultrafiltration" (UF), which removes particles of roughly 3 nm or larger; "nanofiltration" (NF) removes particles of 1 nm or larger; and reverse osmosis (RO), which removes particles larger than 0.1 nm [25].

MF is for the separation of suspended particles; UF is for the separation of macromolecules, and RO is for the separation of dissolved and ionic components [26].
Membrane technology is being applied intensively in the areas of oil field produced water treatment [27, 28]. The advantages of employing membrane technology for treatment of produced water are numerous: reduced sludge volumes and high quality of permeate [25], relatively small physical and logistical footprint, moderate capital costs, and ease of operation. These features of membrane technology make it a very competitive alternative to conventional technologies such as gravity separators and coalesce plates [29]. However, when frac water runs through a cartridge filter, the filter can only reduce the suspended solids by 15-20%, not an acceptable performance [30].

RO, a purification technology utilizing a semipermeable membrane and pressures larger than the osmotic pressure of seawater, is widely used in the desalination of seawater, where the TDS level is in the range of 30,000-40,000 mg/L [16]. Current technological limitations on the TDS levels in the feed water to an RO membrane are estimated to be 60,000-80,000 mg/L [31]. With feed waters of TDS concentrations in the range of 60,000-80,000 mg/L, resulting in RO rejection rates often greater than 50% [31], it can be expected that for produced waters with even higher TDS, the RO rejection rate will be much higher than 50%. If the RO membrane is operated at a TDS level higher than these threshold levels, precipitation could occur on the surface of the RO membrane, leading to the membrane’s permanent fouling [31]. Since the TDS level of produced water can be as high as 360,000 mg/L [8], the efficacy of RO treatment is greatly limited.

RO is utilized mainly for removal of salinity (i.e., dissolved sodium and chloride), and while high TDS levels in produced waters are mainly due to the high salinity, large amounts of calcium and magnesium ions are also present in produced water, capable of causing the RO membrane to foul, and resulting in further reductions
in efficiency. Hence, a pre-treatment process such as ion exchange, which removes such mineral ions, is often utilized on the feedwater prior to RO to protect the RO membrane from mineral fouling.

Currently the desalination industry is dominated by reverse osmosis (RO) and multistage flash desalination (MSF) processes [32]. Other thermal desalination processes include multiple effect evaporation (MED) and on a limited scale, mechanical vapor compression (MVC). Although the MSF process as well as the MED process consumes a larger amount of energy than the RO process, about 18-50 kWh/m³ for MSF, 15 kWh for MED, and 5 kWh/m³ for RO, the reliable performance of the thermal desalination processes MSF and MED are made highly competitive against the RO process [32, 33].

The use of falling film in either vertical or horizontal tubes and mechanical vapor compression (MVC) distillation are known methods for produced water treatment [34, 35]. The operating temperature of large MVC distillation systems for the desalination of sea water is often at 60-70°C for the prevention or mitigation of mineral fouling [36, 37]; toward the same goal of minimizing fouling, MED operates at low top brine temperatures in this range [32].

It should be noted that inside such evaporative units, mineral ions such as calcium gradually become more concentrated, unless they are removed by a pre-treatment system such as ion exchange or water softening chemicals (i.e., lime, soda ash, etc.). In fact, most commercially available MVC distillation units require near zero calcium, to avoid a calcium fouling problem. The operation of an ion exchange system with feed water containing calcium ions at a maximum concentration of 50,000 mg/L [8] is a technological and economic challenge.
In MVC distillation systems, water vapor is drawn from the evaporation chamber by a compressor, and the vapor is compressed, resulting in an increase in pressure and temperature, allowing the steam and its latent heat to serve as a heat source for the feed water. Having a high capacity compressor allows operation at temperatures below 70°C in a large MVC distillation system, again, helping to prevent the potential for scale formation and corrosion [38]. The MVC distillation process is generally used for small-scale desalination units; ranging from 18 - 550 gpm (1,100 - 18,000 bbl per day) [39].

With some quantitative target goals of produced water treatment explained, and general technologies described, Figure 2 [18], is included here to show a general overview of the industry scheme for managing produced water.

![Diagram of current practices for treatment of flow back water](image)

**Figure 2**: Diagram of current practices for treatment of flow back water [18]
The qualitative targets of produced water treatment illustrated in Figure 2, depend on the end use of the water, whether partial treatment will suffice as in the case of re-use, or whether more extensive treatment is required.

With the general scheme of produced water treatment outlined, quantitative and qualitative target goals explained, and current major technologies described, the efficacy of plasma arc-in-water-treatment to contribute to these processes prior to desalination is now discussed. Research and experimental work on plasma arc-in-water systems may be useful in enhancing or completely replacing some of the commonly used produced water treatment technologies. The potential for plasma and plasma arc-in-water systems is discussed in the next section.

2.4 Plasma and plasma arc in water: technical considerations

The term “plasma” is used in this thesis to denote electrical plasma (as opposed to blood plasma). This “plasma” is a state of matter, defined as an ionized gas containing balanced charges of ions and electrons [40], and although all particles do not need to be ionized (i.e. ratio of density of major charged species to that of neutral gas for conventional applications is typically, $10^{-7}–10^{-4}$), this plasma is capable of conducting electricity, and responding to applied electromagnetic fields [41]. While plasma occurs naturally on Earth (e.g. lightning), its man-made generation in laboratories is usually achieved by means of electrical “discharges”, with the term “discharge” representing any flow of electric current through ionized gas, and any process of ionization of the gas by an applied electric field [42]. To form such a plasma, while the required electrical field
for breakdown of gas varies depending on the type of gas and the pressure, it is approximately 30 [kV/cm] for atmospheric-pressure air.

Applications of plasma to water for the purpose of controllably modulating the contents of aqueous solutions, is a growing area of interest.

Results in literature have demonstrated the capabilities of electrical discharges to produce active plasma species including physical effects such as electric field, shockwaves, cavitation, and light emissions, e.g., UV, as well as chemicals including hydroxyl radicals (OH), molecular oxygen (O), hydrogen peroxide (H₂O₂), ozone (O₃) with the addition of air or oxygen at the high voltage electrode, hydroperoxyl (HO₂), and other species [43, 44] dependent on the type of discharge, the carrier gas, and the method of plasma application, i.e., to gas phase or to liquid phase. These effects have shown capabilities in the treatment of water and liquids potentially contained within water including rapid and efficient degrading of many organic compounds such as: benzene, toluene, ethylbenzene, xylenes (BTEX), phenols [45], organic dyes (e.g. methylene blue) and many others [43, 44]. Plasma induced oxidation of inorganic ions in water has also been studied [43] including oxidation of iodide ions [46]. Studies with plasma have also demonstrated destruction and inactivation of bacteria [47-49], viruses [50], and fungi (e.g., yeast) [51].

The effects already shown present some potential uses in the treatment of oil and gas field wastewater. Newer capabilities will also be reviewed and presented in this study, including the ability to remove water hardness caused by bicarbonate ions.

As plasma treatment methods are developed for potential industrial implementation in the treatment of waste waters such as produced waters, technical
specifications that should be considered, include: type of discharge; configuration of applied discharge; energy input; excitation source parameters; carrier gas; liquid properties, concentrations, and adverse or enhanced effect on treatment; electrode configuration and potential degradation; target goals for effluent water; water volume and scalability of reactors; reliability of systems over time; safety in operation of high voltage systems; and potential for implementation of plasma systems with other technologies.

It should be noted that plasma discharges can be applied to water in a few categorical ways, including methods of “direct” liquid phase discharges, i.e., without a gas medium. This method of application of plasma to water is not discussed nor utilized in the experimental work in this thesis. Instead, the plasma arc-in-water discharges utilized in the present studies are fundamentally discharges in gas which are then applied to water. Briefly, to give some insight into the nature of “direct” liquid phase discharges, liquids in general have been used for high pulsed power applications and high voltage insulation [52, 53], with deionized degassed water, commonly used in pulse forming lines to generate high pulse power (Power > 1 terawatt; pulse < 100 ns) [54], because water is usually a much more effective dielectric, i.e., electrical insulator, than most gases, including air, and can sustain a high electric stress until a breakdown threshold is reached [52]. This phenomenon in pulsed power applications also applies to mechanisms of generating plasma discharges when two electrodes are both completely submerged under water, i.e. direct liquid phase discharges. Other categorical methods for bringing plasma in contact with water are described here.

In classifying discharges in and in contact with liquids, Bruggeman offered the following: (1) direct liquid phase discharges, (2) discharges in the gas phase with liquid
electrode(s), (3) discharges in bubbles in liquids [55]. A fourth classification is included to represent discharges in the gas phase with non-liquid electrodes, e.g., when a gas phase discharge is propelled by gas flow toward water [56] or when liquid is sprayed through the gas phase discharge such as has been demonstrated with gliding arc systems [48, 57-60].

With the general nature of application of plasma discharges to water explained, and potential benefits of plasma water treatment described, a plasma-in-water system will be studied for its potential use in treating produced water, and/or enhancing technologies used to treat produced water, i.e., a distillation unit. Plasma-in-water considerations are presented in the next sections.

2.4.1 Plasma Gliding Arc Discharge (GAD) and its use in water treatment

While the viability of a specific type of plasma discharge is closely tied to the specific use and conditions, the attributes of the pulsed arc including generation of high radical density, and large energy pulse (1 kJ/pulse) coupled with believed scalability in treating large volumes [61], can make this discharge potentially desirable for application to wastewater treatment. Such effects must be studied for capabilities to modulate contents of industrial waters and abilities to meet target goals, and/or enable other technologies to better meet target goals set by industry.

The Gliding Arc Discharge (GAD) has existed for more than 100 years [41], in the form of a discharge across two vertical flat plates oriented with one of each of their edges facing the other plate, and each plate having a shape such that the distance between these facing edges increases along the axial direction, i.e., the gap between the plates is diverging, a system commonly referred to as a Jacob’s ladder. Studies in the past two
decades [41, 62-64] have resulted in the elucidation of the non-equilibrium nature of such a discharge, and development and enhancement resulting in 3-D versions such as the “plasmatron”[65], with a version of this device used in the present study [66, 67].

The GAD has been generated in a few ways but still based on similar principles, and operating at atmospheric pressure or higher [63]. A GAD can be defined as an auto-oscillating periodic discharge between at least two diverging or non-diverging electrodes propelled by a gaseous flow [41], resulting in a high degree of non-equilibrium to sustain a selective chemical process [61, 63]

For a GAD, the column of plasma increases in length as it transitions from a quasi-thermal to non-thermal regime, and this cycle repeats. Upon initiating (i.e., ignition as an arc) at the shortest distance between electrodes, the arc channel moves with, and is convectively cooled by room temperature gas flow [61, 63] during a quasi-equilibrium phase (e.g. gas temperature, $T_o \sim 10,000$ K). The arc length increases together with voltage, and the power increases to a maximum power, $P_{\text{max}}$ provided by the power supply, reaching a critical value at which heat losses from the plasma column exceeds the energy supplied by the source [41]. At this point, the arc column is no longer in quasi-equilibrium [41]. Instead it quickly transitions into non-equilibrium phase, in which the gas temperature of the plasma cools (e.g., down to 1000 K - 2000 K), while the conductivity of the plasma is sustained by high electron temperatures, $T_e = 1$ eV (about 11,000 K) [41, 63]. Then, after the decay of the non-equilibrium discharge, there is a new breakdown at the shortest distance between electrodes and the cycle repeats [41, 63].

Within the past two decades, work by various researchers [41, 63, 68-70] has resulted in development and enhancements of gliding arcs from 2-D to 3-D gliding arc
systems more ideal for high volume plasma processes [71]. These include radially gliding arcs, cylindrical electrode systems [69, 70], and systems with tangential upstream gas injection to produce a vortex that elongates the plasma and keeps the arc anode root in constant rotation to minimize electrode erosion [72]. Further enhancements in gas flow include tornado using reverse vortex flow resulting in increased residence time, more uniform treatment for gases, and thermal insulation of reactor walls, while retaining the advantage of the 2-D GAD to provide desirable degrees of non-equilibrium and avoid electrode erosion [71].

While such systems are not made to be completely filled with water (for various reasons including some explanations of difficulties of breakdown in water presented before), work in development of reactors suitable for water treatment are ongoing, and some studies have included work with humid air [73], or water sprayed through the discharge [48, 57, 59, 60], or small amounts of water relative to gas flow injected through the discharge inside the reactor body of such systems [61], or 2D GAD with aqueous solution as a cathode [74].

Whereas the use of thermal plasma for chemical applications can lead to overheating of the reaction media when energy is uniformly consumed by the reagents, a GAD can offer a degree of nonequilibrium more well adapted for the purposes of plasma chemistry, by offering selectivity and associated efficiency [63]. Useful benefits of thermal plasma including large electron densities, currents, and power, can converge with those of non-thermal plasmas, i.e., low gas temperature [55]. Hence the use of a gliding arc discharge, can potentially provide desirable plasma attributes for altering the chemical contents of aqueous solutions.
Plasma gliding arcs have been studied for ability to oxidize organic compounds, especially hydrocarbons, including reforming [70] and partial oxidation of methane [75], fuel conversion [76], general production of hydrogen and hydrogen-rich gases from a variety of hydrocarbon fuels (including gasoline [77], natural gas, and diesel fuel [69]), as well as degradation of organic pollutants such as phenol in aqueous solutions [58] and organic dyes such as reactive blue 137 [57], and with some studies within the past decade discussing application of gliding arc to water including ability to inactivate bacteria in water [47, 48, 78, 79], usually E. Coli amongst other types of bacteria. Treatment of oil and gas–field specific bacteria should be demonstrated, as bacteria can have different requirements for inactivation.

With some investigation of the science involved in plasma treatment of water, as well as further engineering of a water-applicable systems, the efficacy and scalability of plasma water treatment and plasma enhancement of other treatment methods, e.g., distillation, can be demonstrated, including capability to modulate aqueous wastewater solutions such as produced water.

2.4.2 Carrier gas for plasma system

Various carrier gases and combinations therein can be used for forming and propelling plasma, resulting in a range of effects, but it is offered that air is utilized as it is the most accessible of gases, for implementation into industrial water treatment systems. The use of other gases in plasma studies in laboratory investigations do however allow for isolation of gas dependent effects and is utilized in the present study to elucidate mechanisms involved in modulation of water properties. The effect of the carrier gas used is dependent on the discharge. Some brief observations about plasma
carrier gases include: the observation of air and nitrogen-containing gases to cause decreases in pH of liquids [51]., and the observation that oxygen gas injection (which can lead to production of O₃, and other O-based active species, and boost OH production) has been widely demonstrated to be best for degradation of organic compounds followed by air, argon, and then nitrogen [44].

2.4.3 pH of aqueous solution being plasma-treated

It has been reported that acidification of liquid due to air plasma is usually observed [55] and furthermore that discharges with nitrogen and oxygen containing gases together can cause steep decreases in pH, due to nitrate and nitric products such as NO₂, HNO₂, and HNO₃ dissolving in water [44]. Some effect of pH on a plasma discharge itself have also been reported [80]. In experiments with metal pin to liquid plane with liquid as a cathode and HCL added to solution, for an atmospheric glow discharge, it was found that in the range below pH 3, a decrease in pH resulted in a decrease in discharge voltage, a phenomenon which was attributed to hydronium ions playing a role in the secondary electron emission process of the cathode [80]. It has been suggested that the role of ions in solution and subsequent conductivity be taken into consideration in such observations [55].

2.4.4 Bacteria in water

Various plasma disinfection studies have been conducted, mainly of which involved inactivation of E. coli. A bacteria that is characteristic of some produced waters is sulfate-reducing bacteria (SRB) which breathes and reduces sulfate ions to H₂S, and can cause severe environmental and industrial problems upon production of corrosive, reactive, and toxic sulfide [20]. In a study conducted by Ma et al. [20], dielectric barrier
discharge (DBD) plasma was used to inactivate Desulfovibrio (D. bastinii, a common SRB) in liquid, with various carrier gases tested (e.g., oxygen, air, nitrogen, and argon), and the effects of other parameters monitored and investigated including pH, temperature, production of hydrogen peroxide and ozone, with results showing germicidal efficiency of oxygen plasma was superior to those from others gases with 100% SRB killed in less than 4-min plasma exposure. It was found that plasma reactive species including hydroxyl radicals, oxygen radicals, N atoms, NO, and NO₂ had profound effects on plasma inactivation of SRB, determining that pH and temperature played less of a role than the interaction of ozone, H₂O₂, pulsed electric field, and UV photons [20].

### 2.4.5 Organics, oil and grease

Various plasma studies have demonstrated capability to degrade organics such as phenol and phenolic compounds [44]. For example, Sunka et al., in chemical experiments to demonstrate the chemical activity of the corona discharge in an aqueous solution with conductivity of 0.11 mS/cm (1 mmol/L of NaCl), showed relatively linear phenol degradation of 1 mmol/L of phenol using 600 kJ of energy to decrease phenol concentration by 0.2 mmol/L (~18 mg/L) [54]. Jiang in a recent review presented a wide range of comparison of results with multiple discharges and electrode systems including a best energy efficiency from a gliding arc discharge, degrading phenol at an energy cost of 0.08 kWh/g and 91% removal efficiency, with a dc arc showing 0.12 kWh/g at 100% removal efficiency; and pulsed DC electrical discharge (i.e. a corona-like discharge) showing 0.34 kWh/g at 38% removal efficiency [44].
While plasmas have demonstrated capability to degrade organics, and this should be able to be demonstrated in treatment of produced water, some organics have also been shown to have an effect on plasma mechanisms as well. For example, for very turbid water containing suspended solids such as dissolved hydrocarbons, the effect of UV to inactivate bacteria in water, can be reduced as UV cannot propagate through the suspended solids as easy [52].

2.4.6 Conductivity (and associated TDS and salinity)

While conductivity, salinity, and TDS are all different, with some laboratory and field procedures utilizing conductivity based measurements and meters to assess the aforementioned, these are grouped together here for the purposes of discussing produced waters, as most of the dissolved solids are due to dissolved salts such as NaCl. While caution should be used with this assumption, for produced waters at high solids concentrations, trends in TDS, conductivity and salinity tend to coincide.

For direct liquid phase discharges, conductivity of liquid has been shown to affect various plasma parameters, including: discharge current, electron density, discharge length, and generation of acoustic waves [54] with effect on breakdown voltage or lack thereof debated in literature [55] but potentially influenced by electrode configuration, voltage pulse duration, and voltage polarity [55, 81, 82]. Sunka et al. discussed the effect of electrical conductivity on partial electrical discharges [54] i.e., discharges connecting only one metal electrode. In this case, the current is transferred by slow ions in the liquid phase as generally free electrons are absent in water or quickly solvated within 1 ps [55, 83].
2.4.7 Electrode degradation and subsequent effect on solution

With the large electric fields required to generate plasma, and even larger electric fields of $10^6$ V/cm required to form discharges directly in water, sharp tip electrodes have been used to help enhance the electric fields given the inverse relationship between electric field and radius of curvature of a needle-shaped electrode. However, problems encountered with sharp needle electrodes ($r_c = 0.05$ mm) include that they are quickly eroded (with an estimate that at 100 W their lifetime is 10 – 20 minutes); and furthermore a plasma discharge from a single needle occupies only a very limited volume [54]. Furthermore, depending on orientation, electrode materials can have an effect on the aqueous solution to be treated. For example, it was reported that the use of platinum and tungsten as high voltage electrodes decreased the yield of H$_2$O$_2$ produced by a pulsed corona in water, but were able to increase the efficiency of plasma chemical removal of organic compounds from water due to catalytic effects [44]. Hence the balance between reliability, energy cost, and ability to treat large volumes are all influenced by electrode selection.

2.4.8 Electrode orientation- high voltage polarity on water

While plasma systems with discharges formed in gas and then subsequently brought into contact with water are a feasible way to design plasma water treatment systems, development of reactors which utilize liquid water electrodes is also a viable option for the treatment of produced water, especially considering the high conductivity of such waters. Although such a discharge is technically still a gas discharge, other effects can be noticed. For example, for discharges with liquid electrodes, the current is transported through the water by ions, which have a smaller mobility than electrons in
metals [55, 84]. Since water has a smaller secondary electron emission coefficient (2-3 orders of magnitude smaller than most metals) this can result in differences, e.g., diffuse atmospheric pressure glow in air is possible, while with metal electrodes, instability can be experienced revealed by radial constriction [55, 84], i.e., a glow more narrow than the tube containing it [85, 86]. This process can initiate a process of thermalisation [84, 87], leading to arc or spark.

Studies have been conducted and are mentioned in a review paper by Bruggeman [55] and references therein, on plasma with liquid electrode(s) with mainly dc exited discharges with characteristics similar to micro glow discharges between metal electrodes. Such apparatuses have included: metal pin to liquid plane with water as a cathode [88] or as an anode [89]; other discharges such as gliding arc with water cathode [74]; or use of two liquid electrodes [90-93]. Additional observations of liquid electrodes which have been reported include the following: (1) if high frequency or pulsed excitation is not used, and dc or low frequency ac is used, such discharges generated with liquid electrodes can be more volumetric in atmospheric pressure air; (2) thermionic emission from an electrolytic cathode is unlikely as it requires temperatures exceeding 2000K, which is well above the critical temperature of water (650 K); (3) a “cathode voltage drop” can be associated with a water electrode in the range of 400 – 800 V, higher than the voltage drop at a metal electrode [55].

Bruggeman in experiments with a metal pin-liquid plane apparatus consisting of a cone shaped stainless steel metal electrode above a liquid reservoir cathode, determined that the plasma had constricted contact points, filamentary in nature near the water surface, with the contact points dancing over the water surface [88]. He also determined
that cathode voltage drop was not affected by pH of solution at constant conductivity of the electrolyte solution, while it was smaller for water than electrolyte solutions, and acidification of water was always observed (with air as a carrier gas) [88].

### 2.4.9 Water volume and scalability

The ability to treat large volumes and/or large flow rates and potential scalability to meet industrial requirements is key to the development of plasma systems. For example, with the partial corona discharges in water occupying limited volume, using the same power supply consisting of a variable voltage 0 - 40 kV DC source, a low inductance storage capacitor of 10 nf and a rotating spark gap switch, Sunka et al. made a case for overcoming limitations of needle-plate corona discharges, by using metal electrodes coated by thin porous ceramic layers to make for multichannel corona-like discharges, capable of producing larger volume plasmas that can handle large average power and over longer durations of time (since they don’t experience the same electrode degradation as a sharp electrode) [54].

### 2.4.10 Viability of implementation of plasma into other treatment processes

Some examples of implementation of plasma systems into water treatment processes include implementation of plasma systems into biodegradation, chemical oxidation, and advanced oxidation processes (AOPs) for the destruction of toxic compounds; plasma pre-treatment can convert initially recalcitrant organic compounds or biologically undegradable effluents into more biodegradable intermediates, which would then be treated in a biological oxidation process with a considerably lower cost [44].
2.4.11 Potential for plasma and vapor compression distillation

While plasma can be used to treat produced water for reuse, it is possible that a plasma GAD can pretreat water so that it can be processed in a distillation unit without fouling. A general scheme of current practices for managing produced water includes treatment for reuse, and more extensive treatment including desalination [18]. It should be noted that while RO and supporting technologies are the dominant technology for such desalination, treatment can be complicated by the need to treat high TDS waters, as occurs in Marcellus produced waters, making distillation a potential option, for final treatment, of course if water softening can be executed in an economical way. Plasma treatment with an arc discharge may provide an alternative method for softening produced water before it is treated with distillation. Such a method may exhibit potential benefits over chemical or electrochemical methods.

2.5 Chapter conclusions

Wastewater treatment, such as that of oil and gas field produced water requires modulation and abatement of various water chemistry properties, based on the targets set for end-use goals including recycling and reuse. With qualitative and quantitative treatment targets discussed, potential uses of plasma discharges in water elucidated, technical specifications considered, and the general state-of-the-art in plasma treatment of oil and gas field wastewaters established, investigation of plasma treatment of produced water from oil and gas exploration is proposed. Plasma alone, or implemented into other common methods can potentially offer economical treatment of wastewaters. Experimental work is needed to test theories and identify and reproduce favorable effects
which can be useful to treating wastewaters and treating them on increasing industrial scales.
3.0 New fouling prevention method with plasma arc in produced water*

3.1 Introduction

A new plasma-based method is introduced here, for the purpose of preventing mineral fouling in produced water. While this study demonstrates a new fouling prevention method, applicable to waters of various compositions, it is also the first known study which brings plasma discharges directly in contact with produced water from hydraulic fracturing. A study was conducted with an objective of removing bicarbonate ions (HCO$_3^-$) using a gliding arc discharge (GAD), and to quantify the scaling ability of water. For the first part of the study, a “plasmatron” was used to generate a gliding arc discharge in water. Multiple tests were conducted, with six conducted for 10 min and the others conducted for longer periods up to an hour to assess the effect of the GAD on bicarbonate ions.

The system works by utilizing a plasma arc discharge to modulate the concentration of bicarbonate ions (HCO$_3^-$) in produced water to levels as low as zero, as a method of water softening. This water softening method serves to prevent the fouling ability of these waters when they come into contact with heat transfer surfaces. Even in the presence of excessively high Ca$^{2+}$ ions in water, the decrease of bicarbonate ions was demonstrated to prevent the ability to cause a significant CaCO$_3$ fouling problem.

The present study had two objectives, including to test a new plasma-based method for bicarbonate ion removal in produced water from unconventional gas exploration, and to verify bicarbonate ion removal as a mechanism for mineral fouling

* It should be noted that much of the work by the author, presented in this Chapter 3 was published in the referenced paper, reference # [66]. Wright, K., H. Kim, D. Cho, A. Rabinovich, A. Fridman, and Y. Cho, New fouling prevention method using a plasma gliding arc for produced water treatment. Desalination, 2014. 345: p. 64-71
prevention. Toward these objectives, the study employed dual hypotheses: (1) gliding arc plasma can reduce bicarbonate ion concentration of produced water to negligible levels, and (2) water without bicarbonate ion content is unable to cause mineral fouling in the form of calcium carbonate scale even in the presence of extremely high concentrations of calcium ions as is often found in produced water [66].

During this study, the plasma arc treatment was able to reduce the bicarbonate ion concentration from a range of 684–778 ppm down to zero. Upon conducting heat transfer fouling tests with water samples, containing a fixed concentration of calcium ions at 5,000 ppm, and varied bicarbonate ion concentrations from 0 to 500 ppm, the weight of mineral scale accumulated on the heating element over time was determined for comparison. The results of the heat transfer fouling tests showed that no scale was formed over the entire 30 h duration of the test, for the water without bicarbonate ions.

This study serves as a proof-of-concept that plasma is capable of reducing the concentration of bicarbonate ions in produced water to a level where CaCO₃ fouling can be prevented on a heat transfer surface [66]. The plasma gliding arc in water represents a new method of fouling prevention that unlike traditional water softening methods, does not require the manual addition of chemicals (i.e., lime, soda ash) to water.

With widespread optimism toward the increase in natural gas production, spurred by hydraulic fracturing of shale formations, environmental concerns have arisen ranging from seismic effects, to aggressive consumption of water, to more importantly, possible pollution of local water resources by produced and flowback waters.

In addressing the concerns about water and its associated conservation, new methods for treating and managing this water are of interest. The method presented in
this study is for the main purpose of treating such waters in a manner that may enable partial treatment for further reuse, or to enable and enhance the capabilities of current technologies to treat such produced waters fully, to levels that permit them to be discharged. One such possible enhancement is the potential to prevent mineral fouling in heat transfer surfaces such as those of distillation units, when waters with significant hardness are processed for treatment.

As described in Chapter 2.3 of the Background of this thesis, and highlighted in Table 3 which references Hayes and Arthur [22], there is currently no single modality of technology which can achieve all treatment targets of produced water, and furthermore, in most cases, each modality achieves that of only a single treatment target. With conventional treatment of produced water relying on a range of physical, chemical, and biological methods, a review by Ahmadun et al. [8], indicated a variety of conventional methods including: water-softening by application of lime soda; various forms of filtration (such as sand, cartridge, multi-media, or membrane filtration); chemical precipitation; organic-clay adsorbers; air strippers; activated carbon; chemical oxidation; UV disinfection; chemical biocides; steam stripping, acidification, evaporation, settling ponds, clarifiers, ion exchange, and reverse osmosis. One example of the stark nature of limited capabilities of these technologies is UV disinfection, which can destroy bacteria but is not able to address any of the other treatment targets.

With the current study indicating the potential of high voltage plasma-induced water softening and subsequent prevention of mineral fouling, the nature of water hardness and the traditional technologies for removing such hardness must first be described. Water hardness consists of temporary (bicarbonate) hardness and permanent
(i.e., calcium) hardness [16]. In many industries, chemical precipitation of water hardness is performed with hydroxide added to water in the form of lime, i.e., CaO or Ca(OH)$_2$, as a common practice utilized for the removal of temporary hardness [16, 24, 94, 95]. This method of lime-softening of water is an effective chemical means for preventing fouling. However, a major drawback of this chemical additive process is that it increases the solid content of CaCO$_3$ sludge, and by effect increases the overall cost of disposal to landfarms or landfills, which is an important environmental and economic driver in produced water treatment [8].

The present study focuses on the ability of a plasma GAD to remove bicarbonate ions as a means of softening produced water, and preventing the ability of this water to cause mineral fouling in heat transfer systems. The high voltage plasma utilized in this study is an ionized gas with highly localized temperature increases near the arc of the GAD [52]. General attributes of a plasma GAD were described in more detail in section 2.4.1 of the Background of this thesis, and detail of the system used in this study will be described in the experimental section of this chapter.

In regard to the general composition of produced water, oil field produced waters have been reported to contain large amounts of bicarbonate ions and even larger concentrations of calcium ions, with respective concentrations in the range of 77–3,990 mg/L for bicarbonate ions, and a maximum of 25,000 mg/L for calcium ions [8]. Hence, abatement of bicarbonate ions in produced water can be a more prudent task than removal of calcium ions therein.

Although the present study focuses on a novel capability of the GAD to prevent mineral fouling in produced water, it has been well reported in literature, the ability of the
GAD to effect various targets contained in gas and liquid phases including oxidizing organic compounds, degrading organic pollutants in aqueous solutions, inactivation of E. Coli and other types of bacteria in water, as well as other uses previously outlined in Chapter 2.4.1, and not repeated here. GAD systems are well-suited to alter the chemistry of aqueous solutions, due to their geometry and ability to distribute plasma in water. A 3-Dimensional GAD, referred to as a “plasmatron” is utilized in this study. The general geometry of the version of this device which is used in this study has been reported in previous studies by Drexel University researchers including the author of this thesis [61, 96], but a rough schematic of the device will be shown in the experimental section, Section 3.5 of this thesis in Figure 3 along with the orientation of this device with respect to the plasma water reactor developed specifically for this study as shown in Figure 4.

It should be noted that water softening capabilities with a plasma spark in water were previously reported [97, 98] and attributed to a local heating effect which allowed the discharge to precipitate CaCO₃ at a plasma-liquid interface in cooling tower water (containing much lower calcium and bicarbonate ion concentrations than typically would be observed in produced waters). This water softening method was shown to protect a heat exchanger from scale deposition and mitigate associated mineral fouling problems in waters containing calcium and bicarbonate ions. The plasma induced precipitation of CaCO₃ produced a filterable particle that could be removed [97]. Given the high local temperatures and quasi-thermal nature of a GAD, it is considered possible that this discharge can also generate such a mechanism of water softening, however it should be noted that while this mechanism has the potential of removing both calcium and bicarbonate ions simultaneously, it would require a molar ratio of 2:1 of bicarbonate ions
to calcium ions, to facilitate precipitation. Given the large concentrations of calcium ions in produced water, in general, bicarbonate ions would be a limiting reactant.

With the synergistic effects of a gliding arc discharge in water, it is possible that a combination of mechanisms contribute to water softening and removal of bicarbonate ions. For example, one mechanism that could contribute to such an effect is the ability of a gliding arc discharge to produce $H^+$ ions in water under certain conditions, a phenomenon previously reported [61, 96], and having the effect of decreasing pH of solutions; such an effect could play a role in bicarbonate ion removal, as $H^+$ ions can react with bicarbonate ions, converting them to $H_2O$ and $CO_2$ (gas) [16].

With removal of temporary hardness using plasma discharges not previously reported in scientific literature (until Wright et al. [66]), it was necessary to demonstrate the efficacy of such plasma-induced prevention of calcium carbonate scaling and its use in treatment of produced water. Toward this goal, this study was conducted in two parts with two separate objectives but with the overall purpose of the study, to investigate the feasibility of a new method of plasma-induced prevention of scaling in produced water through the removal of bicarbonate ions. The objective of the first part of the study was to test a plasma-assisted method for bicarbonate removal in produced water. The objective of the second part of the study was to verify bicarbonate removal as a mechanism for scale prevention. A diagram of the anatomy of the study is shown in Table 4.

To meet the first objective, the removal of bicarbonate content and associated softening of produced water samples from hydraulic fracturing was to be demonstrated by application of a plasma GAD to water samples.
To meet the second objective, high concentrations of calcium ions and bicarbonate ions were added to distilled water or municipal water to bring the concentration of bicarbonate ions to a range of zero to 500 ppm, and the concentration of calcium ions to a very high amount in the range of 5,000 ppm. A 1-kw heater was submerged in this water, and with the power to the heater on for 30 hours, scale (or the lack thereof) was observed along the heater surface. Hence this set-up allowed for the effect of bicarbonate removal to be verified as a mechanism for CaCO₃ fouling prevention, by providing an apparatus to compare and contrast the potential buildup of scale.

Table 4: Flow sheet with study design and methods [66].

| Study Objectives | (1) To test a plasma-assisted method for bicarbonate removal in produced water, and (2) To verify bicarbonate removal as a mechanism for CaCO₃ fouling prevention (in the presence of high calcium concentration) by quantifying the degree of fouling that can |
Gliding arc plasma can reduce bicarbonate ion concentration in produced water samples to negligible levels.

Water samples without bicarbonate ions are unable to cause fouling in the form of calcium carbonate scale.

Plasma treatment test using gliding arc discharge plasma.

Fouling test using boiler with heating element.

Produced water from hydraulically fractured gas wells

Municipal or distilled water with calcium added (5000 mg/L) and varying amounts of bicarbonate ions.

- Bicarbonate ion concentration (mg/L) after 10 min plasma treatment.
- Time (min) of bicarbonate removal to zero

Scale mass [g] and thickness [mm].

This test set-up was valuable to demonstrating a new method using plasma GAD for pretreatment of complex waste waters which many times can have very high calcium ion concentration, contributing to the water hardness, and have a requirement to be softened to prevent potential scale in heat transfer systems. This setup allows for the quantification of the amount of scale potentially prevented when utilizing a strategy of decreasing bicarbonate ion concentration as a method of mineral fouling mitigation in the presence of high calcium ion concentration.
3.2 Experimental set-up and procedure for new fouling prevention method

The general experimental method described here was published [66]. For the first part of this study, the experimental set-up used was a plasma-water reactor consisting of a cylindrical vessel for water, a plasma GAD generator configured for reverse tornado flow, and supporting equipment including the following: a compressed air line to supply the carrier gas to the GAD generator, which was also connected to a high voltage power supply; a peristaltic pump was utilized to load water from a 1-L reservoir, into the reactor; for safety, the top of the reactor was located underneath a laboratory snorkel ventilation unit for extraction of gas or vapor from the system to outside of the laboratory. A general schematic of the plasma GAD generating device, referred to as a “plasmatron”, is shown in Figure 3; it should be noted that this figure is adapted from those reported in previous studies by Drexel University researchers including the author of this thesis [61, 96].
Figure 3: General schematic of “plasmatron”, device used to generate gliding arc discharge; [61, 96].

The produced water samples to be tested in this plasma-water reactor were samples from hydraulic fracturing for shale gas in an area of the Marcellus shale rock formation (Springville, PA). The general composition of this water was as follows: TDS of 36,000–38,000, pH of 7.1–7.71, sodium concentration of 10,600–11,300 mg/L,
calcium ion concentration of 940 mg/L–1010 mg/L, potassium concentration of 1870–2080 mg/L, and bicarbonate ion concentration of 685–778 mg/L [66].

The tests were initiated by opening the compressed gas line to a set flow rate, usually 1 SCFM, prior to the reactor being filled with any water sample. Then, 700 mL of produced water was isolated in a 1-L beaker, and 50 mL of this sample was extracted with a syringe in preparation for baseline assessments including alkalinity and pH. The peristaltic pump was used to load the remaining 650 mL volume of produced water into the plasma-water reactor, and during testing this pump was used to recirculate this water at a flow rate of 50–200 mL/min. Plasma power was then turned on and the power supply parameters were recorded, including current and voltage.

A general schematic of the “plasmatron” oriented for use in the plasma-water reactor is shown in Figure 4; it should be noted that this figure is adapted from those reported in previous studies by Drexel University researchers including the author of this thesis [61, 96].

Plasma power was turned off after 10 min to end the plasma treatment tests and 50 mL of this treated water was sampled for laboratory assessment including bicarbonate ion concentration. These tests were repeated six times. Six additional tests were also conducted using this procedure except that treatment was continued beyond 10 min, with 50 mL of treated water sampled every 10 min, until the bicarbonate ion concentration was reduced to zero, for up to 1 h.
Figure 4: General schematic of “plasmatron” oriented for use in plasma-water reactor; [61, 96].

The extracted water samples were assessed to determine the time required to achieve bicarbonate removal (i.e., time to zero bicarbonate). The method of determination of bicarbonate ions relied on the common assumption that alkalinity was due almost entirely to hydroxides, carbonates, or bicarbonates, and more specifically given the measured range of pH for the produced water samples tested here, the alkalinity was due completely to bicarbonate ions [16, 99].

The second part of this study (the fouling test portion) utilized municipal water or distilled water (exact water utilized for each test will be specified), with bicarbonate and
calcium ions manually added. This was done to verify that bicarbonate removal may be
able to serve as a mechanism for scale prevention, and to experimentally quantify how
effective this mechanism could be. It was not possible to use produced water for this
scaling/fouling component of this study, as the volume of produced water that would
have been required to conduct such tests, was not available. Instead, a desired
composition of fouling test water was obtained by mixing appropriate proportions of
sodium bicarbonate (NaHCO$_3$) and calcium chloride (CaCl$_2$). Three 30-h fouling tests
were conducted, with tests (a) and (b) utilizing municipal water (Camden, NJ), and
fouling test (c) prepared using distilled water as the solvent, to ensure that there was
almost no bicarbonate ions in this sample. Each of these water samples was prepared by
adding Anhydrous CaCl$_2$ powder (96%, extra pure, Acros Organics) to 38 L of water
inside the reservoir tank with gentle stirring (done by hand using a stainless steel rod),
and allowing the CaCl$_2$ to dissolve in water for 10 min (following laboratory hardening
procedures utilized previously at Drexel University) [97]. Additionally, for fouling test
(a) only, bicarbonate ion concentration of the reservoir tank water was increased by
slowly adding (over the course of 10 min) anhydrous NaHCO$_3$ powder (USP/FCC, Fisher
Chemical) to the reservoir, while gently stirring with a long metal rod, and allowing this
solution to dissolve over the course of 5 min.

With preparation of makeup water complete, for the given test (a, b, or c), makeup
water was gravity fed from a 38-L water reservoir tank through a floating ball valve, into
stainless steel boiler to fill this vessel to a predetermined level marked on its sidewall,
representing a 3.8-L volume, at which point the floating ball valve would automatically
restrict flow of water from the reservoir to the vessel. This mechanism was utilized
continuously over the 30 h duration of the test, as makeup water replaced vaporized water to maintain a constant water level inside the boiler, housing a 1-kW heating element, operated at maximum power, used to vaporize water. The heater power was capable of being gradually varied and turned on and off with the use of a variable transformer connected to a standard AC 120 V power source, but it was operated at maximum power for all tests. Water vaporized by this heater was continuously disposed of through a laboratory snorkel ventilation unit. A cut-off valve installed between the reservoir tank and the ball valve, allowed flow could to be closed off and cleaning of the test apparatus to be facilitated upon completion of each test.

It should be noted that the fouling test began at the moment the heating element was turned on (time, t = 0). A schematic diagram of this fouling test facility is shown in Figure 5.
With the cylindrical cartridge-type heating element used to collect scale, it was necessary to clearly define the dimensions of this element prior to fouling tests. The dimensions included an outside diameter = 15.65 mm and length = 154 mm. The total weight, and diameter at eight points along the axial direction (each spaced 22 mm apart from 0 to 154 mm), were assessed and used for baseline data before testing started, and would be reassessed upon completion of fouling tests to assess any scale or the lack thereof that had formed. With this element installed in the boiler vessel through a port in
the sidewall of the vessel, it should be noted that the element has unheated sections at both ends, approximately 10 mm at the free end and 25 mm at the fixed end.

During each fouling test, at 6-h intervals, from $t = 0$ h to $t = 30$ h, the water level and associated volume of water in the reservoir tank was monitored, and using a 50–mL syringe, a total water sample volume of 200 mL was extracted from the middle of the water volume in the boiler so that water chemistry analysis could be conducted, including alkalinity, calcium hardness, total dissolved solids, salinity, conductivity, and pH. These assessments of water could be initiated simultaneously over the duration of each 30-h fouling test, and they were always completed within 20 h after completion of the fouling tests. Since the completion of each extracted sample always occurred after the fouling tests were complete, the description of the test methods utilized will be described at the end of this section on the experimental procedure.

Fouling tests were complete upon the heater power being turned off (at $t = 30$ h) using the variable transformer. Upon completion of these tests this procedure was followed: additional water was prevented from flowing from the reservoir tank to the vessel by closing the cut-off valve; a peristaltic pump was used to pump water out of the boiler at a low flow rate to minimize any physical disturbances to the heating element and any scale that may have been formed; tubing between the reservoir tank and floating ball valve was disconnected, so the system could be cleaned prior to the next test; the heating element was left inside the waterless boiler for 30 min to allow it to cool to room temperature before it was handled at its edges and removed from the boiler; upon careful removal from the boiler, the heating element was placed on a white sheet of paper located on the laboratory bench and allowed to dry for 1 h; then, a digital photograph was taken.
of the heating element; the diameter of the potentially scaled heating element was measured at 8 equidistant points along the axial direction using a digital caliper (Cen-Tech model, Harbor Freight Tools, Calabasas, CA); a laboratory balance (Model VB-302A, Virtual Measurements & Control, Santa Rosa, CA) was used to measure the amount of accumulated scale. Subsequently, the thickness and mass of the scale layer on the heating element was determined by calculating the change in diameter and mass of the heating element from time, $t = 0$ to $t = 30$ h.

Upon completion of this assessment of the scaled heating element, a razor blade was used to remove small pieces of the scale, approximately 1 cm x 1 cm in size. To ascertain the nature of the solubility of the scale, an individual piece from each test case was placed inside separate beakers filled with 200 mL of distilled water for a duration of 24 hours. This was done as a method of validating the test procedure, by determining if the scale was indeed a relatively insoluble compound such as CaCO$_3$, or if it was a soluble salt such as NaCl (which could have formed if the water inside the boiler was oversaturated with such a salt, although water assessments should also show that this would not occur, given the solubility of NaCl in water at room temperature is very high, just under 360,000 mg/L [100]).

With fouling tests completed and assessments of the scale almost completed (still wanted to wait to see if scale would dissolve in water), water assessments of the samples extracted from the boiler at 6-h samples still had to be assessed. Toward this goal, various types of equipment and assessment techniques were utilized to assess samples, and this assessment was always conducted after samples reached room temperature but within 20 h of the end of each fouling test. A procedure similar to EPA 160.1 Total Dissolved
Solids (TDS) Test Method [101], was utilized to assess TDS. Briefly, the TDS procedure included filtration of a water sample, and an evaporation component, in which the mass of a porcelain evaporating dish was measured using a precision laboratory balance (Sartorius GP603S, Data Weighing Systems, Elk Grove, IL), before filling the dish with a 100-mL sample, and then heating it using a laboratory hot plate (model Cimarec 3, Thermolyne, Dubuque, IA), to evaporate the liquid until solid particles were left inside; upon re-measuring the weight of the now residue-containing dish, and dividing by the volume of water that was evaporated, the amount of solids per unit volume of water in (mg/L) could be quantified. It should be noted that the volume of liquid utilized is different than required by the actual procedure, and the heating of the porcelain dish and subsequent drying of the residue requires the use of a steam bath and drying oven, respectively. Mass measurements for this TDS assessment method were performed using a precision laboratory balance (Sartorius GP603S, Data Weighing Systems, Elk Grove, IL).

Other water assessments relied on meters and chemical test kits. The conductivity and pH were assessed using a MP521 Type pH/Electric Conductivity meter provided by SANXIN (Shanghai, China). Water hardness and alkalinity were assessed using chemical test kits, HI 3842 Hardness Range (400 – 3,000 mg/L) from Hanna Instruments (Woonsocket, RI) and Carbonate Hardness/Alkalinity from Salifert (Duiven, Netherlands), respectively. Again, these assessments often began while the fouling tests were being completed, but were always completed within 20 h of the completion of each fouling test.
3.3 Results of new fouling prevention method

3.3.1 Plasma-induced modulation of bicarbonate ions in produced water

Results of the plasma component of this study are shown in Table 5. The baseline concentration of bicarbonate ions in produced water samples used in the present study ranged from 685 to 778 mg/L. Upon application of plasma GAD to produced water samples, decreases in concentration of bicarbonate ions were observed for all 12 tests, within 10 min of treatment time. This phenomenon was observed for the first six tests, and while tests 1-6 were only conducted for 10 min, tests 7 – 12 were allowed to continue running passed 10 min, to investigate whether or not complete removal of bicarbonate ion content was possible. Toward this goal, samples were collected every 10 min for a total of 1 h of treatment for those tests.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Bicarbonate ion concentration at baseline (mg/L)</th>
<th>Bicarbonate ion concentration after 10-min plasma treatment (mg/L)</th>
<th>Voltage (kV)</th>
<th>Current (A)</th>
<th>Time to zero bicarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>699</td>
<td>467</td>
<td>2.1</td>
<td>0.1</td>
<td>n/a</td>
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<tr>
<td>2</td>
<td>685</td>
<td>475</td>
<td>2.1</td>
<td>0.1</td>
<td>n/a</td>
</tr>
<tr>
<td>3</td>
<td>778</td>
<td>560</td>
<td>2.1</td>
<td>0.1</td>
<td>n/a</td>
</tr>
<tr>
<td>4</td>
<td>745</td>
<td>370</td>
<td>2.0</td>
<td>0.1</td>
<td>n/a</td>
</tr>
<tr>
<td>5</td>
<td>685</td>
<td>458</td>
<td>2.0</td>
<td>0.1</td>
<td>n/a</td>
</tr>
<tr>
<td>6</td>
<td>685</td>
<td>203</td>
<td>1.0</td>
<td>0.2</td>
<td>n/a</td>
</tr>
<tr>
<td>7</td>
<td>760</td>
<td>364</td>
<td>2.0</td>
<td>0.1</td>
<td>50 min</td>
</tr>
<tr>
<td>8</td>
<td>747</td>
<td>347</td>
<td>2.0</td>
<td>0.1</td>
<td>30 min</td>
</tr>
<tr>
<td>9</td>
<td>684</td>
<td>317</td>
<td>2.0</td>
<td>0.1</td>
<td>30 min</td>
</tr>
<tr>
<td>10</td>
<td>752</td>
<td>472</td>
<td>2.0</td>
<td>0.1</td>
<td>30 min</td>
</tr>
<tr>
<td>11</td>
<td>685</td>
<td>292</td>
<td>2.0</td>
<td>0.1</td>
<td>30 min</td>
</tr>
<tr>
<td>12</td>
<td>685</td>
<td>83</td>
<td>2.0</td>
<td>0.1</td>
<td>20 min</td>
</tr>
</tbody>
</table>
Complete removal from 760 ppm to zero bicarbonate was observed within 50 min for Plasma Test 7. Complete removal from 747 mg/L, 684 mg/L, 752 mg/L and 685 mg/L to zero was observed for plasma tests 8 – 11, respectively. The best test was plasma test 12, in which complete abatement of bicarbonate ions from 685 mg/L to zero was observed within 20 minutes. This was a treatment time more than twice as fast as exhibited for test 7. For all test cases, the plasma GAD was able to decisively reduce bicarbonate ions in water and despite extremely high calcium ion concentrations.

3.3.2 Assessment of scalability of water with bicarbonate ions varied

With the results of the plasma treatment component of this study, it is expected that if this treated water were to come into contact with heated surfaces, as would happen in a heat exchanger or distillation unit, mineral fouling due to CaCO$_3$ should not occur. Results of the fouling test component of this study are utilized to demonstrate the benefits, even in the presence of high calcium concentration, of supplying bicarbonate-depleted water into heat transfer systems. Fouling tests using waters with high calcium concentration and bicarbonate ion concentration ranging from 0 to approximately 500 ppm can demonstrate the scaling ability of such waters, and the effectiveness of the plasma-induced fouling prevention methodology. Table 6 indicates the baseline conditions for each of the three fouling tests, with the calcium ion concentration in the range of 5000 mg/L for all tests, and the bicarbonate ion concentration varied from 7 mg/L to 445 mg/L.

It should be noted that for the water prepared for fouling test (b), the bicarbonate ion concentration was 118 ppm, reflecting the bicarbonate ion concentration of municipal tap water, since no NaHCO$_3$ was added to this sample. For fouling test (c), although
distilled water was used as the solvent for preparation of the solution, a small amount of bicarbonate ions was still present (i.e. 7 mg/L). In regard to the other water properties, there were small variations in pH between the three water samples. Salinity and electric conductivity were both relatively high in all three water samples due to the addition of CaCl₂.

Table 6: Initial conditions for each fouling test, including amount of chemicals added to achieve desired compositions of samples, and measured properties of water after preparing sample [66]

<table>
<thead>
<tr>
<th>Chemicals added to achieve initial conditions</th>
<th>Test (a)</th>
<th>Test (b)</th>
<th>Test (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CaCl₂ (g)</strong></td>
<td>530</td>
<td>530</td>
<td>530</td>
</tr>
<tr>
<td><strong>NaHCO₃ (g)</strong></td>
<td>53</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Water (L)</strong></td>
<td>38 [tap water]</td>
<td>38 [tap water]</td>
<td>38 [distilled water]</td>
</tr>
<tr>
<td><strong>Measured Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ca²⁺ (mg/L)</strong></td>
<td>4800</td>
<td>5200</td>
<td>5200</td>
</tr>
<tr>
<td><strong>HCO₃⁻ (mg/L)</strong></td>
<td>445</td>
<td>118</td>
<td>7</td>
</tr>
<tr>
<td><strong>TDS (mg/L)</strong></td>
<td>18,600</td>
<td>15,800</td>
<td>12,000</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>6.73</td>
<td>7.22</td>
<td>21.9</td>
</tr>
<tr>
<td><strong>Conductivity (mS/cm)</strong></td>
<td>23.0</td>
<td>22.8</td>
<td>21.9</td>
</tr>
<tr>
<td><strong>Salinity (mg/L)</strong></td>
<td>15,000</td>
<td>15,000</td>
<td>15,000</td>
</tr>
</tbody>
</table>
For each of the three fouling tests conducted with the varied levels of bicarbonate ion concentration, before and after photographs are shown in Figure 6, of the heating element. The figure indicates eight demarcated points along the axial direction of the heating element, at which change in diameters was quantified, to determine the thickness of any scale that had formed.
Digital Photographs of heating element for three fouling tests

<table>
<thead>
<tr>
<th></th>
<th>a) Tests with bicarbonate ions at 500 mg/L</th>
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<tbody>
<tr>
<td>Before</td>
<td><img src="image1" alt="Before image" /></td>
</tr>
<tr>
<td>After</td>
<td><img src="image2" alt="After image" /></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>b) Tests with bicarbonate ions at 100 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td><img src="image3" alt="Before image" /></td>
</tr>
<tr>
<td>After</td>
<td><img src="image4" alt="After image" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>c) Tests with bicarbonate ions at 0 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td><img src="image5" alt="Before image" /></td>
</tr>
<tr>
<td>After</td>
<td><img src="image6" alt="After image" /></td>
</tr>
</tbody>
</table>

Figure 6: Digital photographs of heating element before and after fouling test for each of the three test cases; Note: Unheated sections of heating element are demarcated with an “X” [66]

A quantitative comparison of the thickness in scale along the heating element, for each of the three fouling test cases is indicated in Figure 7. For fouling test (a), which contained the 500 mg/L of bicarbonate ions in the presence of 5,000 mg/L of calcium ions, the average scale thickness as quantified by averaging the thickness between
positions 2 – 6, was 1.85 ± 0.09 mm. This is in comparison to fouling test (b), for which between positions 2-6, the average scale thickness was an order of magnitude less, at 0.17 ± 0.05. For fouling test (c) the thickness of scale approached zero.

In addition to average scale thickness, Table 7 indicates the masses of the accumulated scale for the three test cases. While the heating element used in test case (a) had the largest accumulation of scale (as expected), for fouling test (c) the mass of scale approached zero.
Table 7: Mass and average thickness of scale accumulated along heating element for three test cases

<table>
<thead>
<tr>
<th>Test</th>
<th>HCO$^3$- (mg/L)</th>
<th>Average scale thickness (mm)</th>
<th>Mass of scale (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>500</td>
<td>1.85 ± 0.09</td>
<td>9.97</td>
</tr>
<tr>
<td>(b)</td>
<td>100</td>
<td>0.17 ± 0.05</td>
<td>0.97</td>
</tr>
<tr>
<td>(c)</td>
<td>0</td>
<td>0.02 ± 0.02</td>
<td>−0.01</td>
</tr>
</tbody>
</table>

While assessments of the heating elements provided insight into the scaling ability of the various test waters, assessment of the test waters are provided in Figures 8 - 12. Results in Figure 8 show volume of water in make-up tank over time, and water properties inside the boiler including, TDS, electric conductivity, and salinity.

Figure 8: Fouling test - Total water volume in tank over time for 3 tests (a, b, and c).
As the heating element inside the boiler, provided constant thermal energy during the fouling tests, water was vaporized, and makeup water from the reservoir tank was continuously supplied to the boiler, with Figure showing a linear decrease in water volume of the reservoir tank from 38 L to near 12 L over the duration of the 30 h, for each test. This resulted in most ions in the boiler becoming more and more concentrated with a liner increase in conductivity, TDS, and salinity observed for all three test cases. It should be noted that the conductivity and TDS for all test cases reached a level of 110 mS/cm and 95,000 ppm, which are values within the order of magnitude of those found in produced waters.

Figure 9: Fouling test – Salinity in boiler over time for 3 tests (a, b, and c).
Figure 10: Fouling test - TDS in boiler over time for 3 tests (a, b, and c).

Figure 11: Fouling test - Electric conductivity in boiler over time for 3 tests (a, b, and c).
Figure 12 shows the results of assessments of bicarbonate ions over time for all three fouling test cases. For tests (a) and (b), the bicarbonate ion concentrations significantly dropped in the first 6 h. Heating during these tests dissociated bicarbonate ions into CO$_2$ and OH$^-$, initiating the process of formation of CaCO$_3$ scale on the heating element [95]. For these tests, after $t = 6$ h, although the bicarbonate ion concentrations were below 50 mg/L, as they were replenished by the make-up water from the reservoir tank, the CaCO$_3$ particles suspended in water continued to adhere to the surface of the heating element, increasing the scale thickness on the heating element over time.

Figure 12: Fouling test - Bicarbonate ion concentration in boiler over time for 3 tests (a, b, and c).
Figure 13 shows the results of assessments of pH over time for all three fouling test cases. Fouling tests (a) and (b) seem to follow similar trends, with pH decreasing slightly for both tests, by 0.25 and 0.34, respectively. This corresponded to the loss of bicarbonate ions due to heating, and is in contrast to the pH of water for test (c) which stayed relatively constant as there were no bicarbonate ions to lose.

Figure 14 shows the results of assessments of calcium over time for all three fouling test cases. While bicarbonate ion concentration decreased for tests (a), and (b), calcium ion concentration which was much higher than bicarbonate ion concentration, increased almost linearly for all tests.
3.4 Discussion of new fouling prevention method

The study presented in this chapter, explored the potential for a robust strategy utilizing electrical plasma to remove carbonate hardness from water, by decreasing bicarbonate ion concentration while allowing very high concentrations of calcium ions to remain. Such a system has potential for use in produced water treatment and enhancement of desalination systems. Application of the aforementioned methodology can be useful in treating complex waste waters, which upon undergoing thermal processes such as distillation, can result in fouling crystallization problems having a negative impact on fluid processing equipment [38, 102]. Hence, the impact or scope of the present study is that it has identified a new method for fouling mitigation, while
identifying a new application for plasma discharges in water. The scope of the present study is illustrated in the diagram in Figure 15.

Figure 15: Scope of the study presented in this chapter

Plasma water treatment tests showed abatement of bicarbonate from as high as 760 mg/L to as low as zero, while fouling tests indicated that a decrease from 500 mg/L to 100 mg/L of bicarbonate in produced water could decrease CaCO₃ scale on a 1-kW heating element by a factor of 10.
The results of plasma treatment tests, as shown in Table 5 indicate that the time to decrease bicarbonate concentration to zero, ranged from 50 min for test 7 to 20 min for test 12. It is hypothesized that this discrepancy can be attributed to different mixing conditions and factors that were not accounted for during these experiments that may have served to increase the surface contact area between plasma and water. A study of such phenomenon could be useful, as it demonstrates that it is not only the bringing of plasma into contact with water to test hypotheses and explore solutions, but the engineering of plasma systems that can provide enhancements that show the true viability of such systems.

Energy cost calculations for all tests are shown in Appendix A. Given the application of the 200–W plasma GAD system to 650 mL of produced water over 10 minutes, Plasma treatment test 12 (see Table 1) experienced the best energy cost for bicarbonate removal:

\[
Energy\ cost = \frac{(0.2 kWh) \times \left(\frac{1}{5} \text{hours}\right)}{(685 \frac{mg}{L} - 83 \frac{mg}{L}) \times \left(\frac{1 g}{1000 mg}\right) \times (0.65 L)} \times \frac{0.39 g}{0.033 kWh} = 0.085 \frac{kWh}{g}
\]

On a basis of energy per units of concentration, this corresponds to 0.307 kJ/ppm of bicarbonate to be removed per liter of water, hence to bring 1 liter of bicarbonate from 10 ppm to 0 ppm using the present system would require 3.07 kJ of energy. An energy cost comparison of this value, with that of conventional methods is outside the scope of this study, as the conventional method of removing temporary hardness is accomplished with the addition of a chemical, lime (CaO) [8, 22]. Consideration of cost would have to
take into account various financial costs of the chemicals themselves and the process utilized, which includes account of the concomitant increase in cost due to the chemical approach resulting in an increase in the overall mass of solids of which will ultimately need to be disposed [8].

For the fouling component of this study, it was shown that given extremely high calcium ion concentrations, i.e. 5,000 mg/L, and a bicarbonate level as low as 7 ppm, the thickness of CaCO₃ scale formed on a 1-kW heating element was under 0.03 mm, as compared to a 1.85 mm thick layer for test case (c) where initial bicarbonate concentration was 445 ppm. While the fouling component of the study was conducted for the purpose of mechanistically showing the implications of plasma treatment on produced water, they also provide trend-line data that is valuable and capable of being expounded on, to better understand and compare implications of water quality on precipitation fouling in heat transfer systems. Figure 16 combines the data on CaCO₃ scale generated during the present study over the range if initial bicarbonate concentrations, 0 to 500 mg/L.
The mass of the scale reported in this figure is quantified on a per unit area basis. The conditions of the present study which should be noted which resulted in this data include: a boiler vessel containing a 1-kW heater with a heated surface area of 56 cm² was used to evaporate 26 L of water of initial calcium ion content of 5,000 mg/L, and bicarbonate varied for each test. If additional data were to be generated, the power of the heating element should be precisely measured to ensure accurate comparison. Comment on the heating element power is provided in Appendix B.

While it is well known that CaCO₃ scale is caused by the presence of bicarbonate and calcium ions in water, to date, strategies for preventing formation of scale often emphasize removing hardness by reducing calcium content such as through the addition of soda ash (Na₂CO₃), ion exchange, reverse osmosis, or even electrochemical processes...
[8, 95, 103]. In produced water, the calcium concentration is often very high [8], such that removal in many cases can be impractical, given other options. Accordingly, removal of bicarbonate from such waters, provides an alternative strategy for the purpose of water softening.

The effect of bicarbonate removal is clearly seen when the 1-kW heater is assessed after testing (and drying). The digital photographs, associated calculations of the change in diameter along the length of the heating element, and the change in mass, all provide qualitative and quantitative data which indicates the potential effect of plasma generation of bicarbonate-depleted produced water.

Once the amount of scale that had formed was determined, reaffirmation of the nature of the scale was obtained to validate the test procedure and confirm that the scale that had formed was indeed a relatively insoluble compound such as CaCO$_3$. Small pieces of scale removed with a razor blade, and submerged in 200 mL of distilled water for 24 hours, did not dissolve, and it was concluded that any scale formed on the heating element was indeed an insoluble compound, such as CaCO$_3$, and not a soluble salt such as NaCl. This conclusion was strongly supported by the fact that there were only two major chemicals contained in the prepared test sample and those were CaCl$_2$, and NaHCO$_3$. Hence, the present test procedure, was effective at isolating the options of solids that could form, if any would indeed precipitate, as there were limited types of ions of which to form any type of large amounts of solid scale.

While the plasma-induced fouling mechanism has been validated, this study could be built upon in a few ways, including by conducting fouling tests with various plasma-treated produced water samples. This could help demonstrate the robustness of such a
system in treating a diverse set of waters. For example, this study does not address any possible effects by other constituents that may be present in produced water, such as the possible effect of precipitation fouling due to the presence of sulfate in water, nor the effect of plasma arc-in-water systems on sulfate. It should be noted that sulfate was not monitored during this study, as such concentrations in produced waters from natural gas exploration, have been reported to be relatively low, with records of approximately 4,000 natural gas storage produced waters analyzed, and determination that the maximum sulfate concentration was 47 mg/L [104].

With CaCO$_3$ fouling problems associated with the presence of both calcium ions and bicarbonate ions in water [16, 95], this study introduced a new fouling mitigation method, which utilized a plasma discharge as a non-chemical device for affecting bicarbonate ions in produced water. Subsequently, using fouling tests with manually hardened municipal and distilled water, bicarbonate control was verified as a mechanism for mitigation of CaCO$_3$ fouling

3.4.1 Mechanism of plasma induced bicarbonate removal: pH vs. local heating

The proposed mechanism for the modulation of bicarbonate ions by plasma in water has been, the effect of intense, highly, localized heating (or “stochastic heating”) [98, 105, 106]. This mechanism, which works by dissociating bicarbonate ions to hydroxyl ions (OH$^-$) and CO$_2$ (gas) as described in the prior reports [98, 107], may have played a role in this study. However, consistently observed decreases in pH suggest the generation of H$^+$ ions, not only played a role but may have played the dominant role in removal of bicarbonate ions for this arc-in-water system.
For the local heating effect, once bicarbonate is dissociated into OH⁻, and CO₂, the hydroxyl ions react with other bicarbonate ions, to produce carbonate ions (CO₃^{2−}), which then react with Ca^{2+} to form CaCO₃ particles [27,29].

For the generation of H⁺, bicarbonate ions are converted to H₂O and CO₂ (gas). This may be the basis of the new plasma induced fouling prevention method, which works without the addition of solid chemicals to process water.

Although tests were conducted with an expectation of observing evidence of a local heating effect by precipitation of CaCO₃, calcium ion concentration did not decrease, and it was noticeable that the decreases in bicarbonate ions occurred with decreases in pH, suggesting that the generation of H⁺ ions caused the decrease in bicarbonate. A comparison of these two mechanisms and the chemical reactions associated with the major steps of these mechanisms is indicated in Table 8.

It has been well reported in literature that when humid air is a carrier gas for plasma, or when air is a carrier gas for a plasma GAD in or in contact with water, plasma GAD induced dissociation of oxygen (O₂) and nitrogen (N₂), and further reaction of oxygen and nitrogen atoms with (O₂) and (N₂) leads to the production of nitric oxide (NO) [73, 108]. Further, the oxidation of this NO in air, generates nitrogen dioxide (NO₂), and this NO₂ in water, results in production of nitric acid (HNO₃), through any one of many reactions as described by Burlica et al. [59]. It should be noted that HNO₃ is a strong acid, completely ionized to H⁺ and NO₃⁻ ions in dilute water solution [109]. Thus it is believed that the generation of H⁺ ions as a result of HNO₃, production may have played a strong role in this new fouling prevention method. It should also be noted
that ionization of water via electron impact and charge transfer with positive ions, denoted, $M^+$ [52, 59, 98], can also lead to the formation of acid.

<table>
<thead>
<tr>
<th>Step</th>
<th>Mechanism 1: Local Heating</th>
<th>Mechanism 2: Generation of $H^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$HCO_3^- \rightarrow OH^- (aq) + CO_2 (g)$↑</td>
<td>$H_2O + e \rightarrow H_2O^+ + 2e$</td>
</tr>
<tr>
<td>2</td>
<td>$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$</td>
<td>$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$</td>
</tr>
<tr>
<td>3</td>
<td>$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3(s)$</td>
<td>$H^+ + HCO_3^- \rightarrow H_2O + CO_2(g)$↑</td>
</tr>
</tbody>
</table>

In the present study, the generation of $H^+$ ions was evident by rapid decreases in pH, which indicates abundance in generation of $H^+$ ions rather than $OH^-$. These decreases in pH were observed accompanying the decreases in bicarbonate concentration, and this suggests that generation of $H^+$ ions was the dominating mechanism in bicarbonate removal.

Although $CO_2$ in gas phase was not monitored, it should be noted that the ratio of $HCO_3^-$ destruction to $CO_2$ generation, differs for the competing mechanisms. Comparing
the mechanisms of intense local heating [98] against the generation of H\(^+\) (as shown in Table 4)., one can see that in the case of the method of local heating, for every two moles of HCO\(_3^-\) consumed, one mole of CO\(_2\) is produced, while for the case of generation of H\(^+\), for every mole of HCO\(_3^-\) consumed, one mol of CO\(_2\) is produced. Such a study of CO\(_2\) production could further elucidate the mechanism of bicarbonate removal if the effect on bicarbonate is isolated from other mechanisms that may produce CO\(_2\); also, if one mechanism is dominant over the other (as both mechanisms may play a role in bicarbonate removal), or if oxygen and nitrogen-containing gases are not used. Brief tests with nitrogen and argon showed negligible effect on bicarbonate removal; results of such tests are included in Appendix A.

It is concluded that while the local heating effect could also play a role in the decrease in bicarbonate, the generation of H\(^+\) ions was the dominant mechanism.

**3.5 Chapter conclusions**

Before concluding, it should be restated that the majority of the contents in this chapter was published by the author of this thesis and colleagues in the referenced journal [66], in a journal paper entitled, “New fouling prevention method using a plasma gliding arc for produced water treatment”. The sections of this chapter were used to present hypotheses, experimental work and discussions, to elucidate the feasibility of using a plasma GAD to treat produced water and prevent it from causing a CaCO\(_3\) fouling problem.

In this chapter, a new plasma-based method was introduced, utilizing a two-part mechanistic approach to investigate the plasma induced removal of bicarbonate, and to quantify the scaling ability of bicarbonate-depleted water. Results showed that the plasma
GAD in water system was capable of effectively decreasing bicarbonate concentration to levels as low as zero, and subsequently the effect of bicarbonate modulation was verified as a mechanism for CaCO$_3$ fouling prevention, by conducting separate fouling tests with water samples having controlled amounts of bicarbonate and calcium ions. Scaling/fouling tests with such waters, showed that a decrease of bicarbonate from 500 mg/L to 100 mg/L showed an order of magnitude decrease in scale thickness and mass on a 1-kW heating element.

It should be noted that while the general science and engineering of plasma induced bicarbonate removal has been discussed, and the potential for pretreatment of water prior to distillation for complete cleaning to levels of discharge, the bicarbonate concentrations studied in the fouling tests were in the range of those described by Mitchell [19] and previously indicated in Table 1 of Section 2. In discussing target parameters of influent water quality for water that will be used for gel frac operations, and/or slickwater frac operations, Mitchell [19] suggested bicarbonate concentrations of < 500 mg/L and < 400 mg/L, respectively for operation of these processes.

The study included in this chapter represents not only the first reported study of plasma discharges in produced water, but it also represents both a new plasma application and a new fouling prevention method. While energy cost of this system is not such that other methods will be immediately replaced, there is excitement about the potential for such applications, which have multiple simultaneous effects (which will be indicated in subsequent chapters), these studies bridge science with engineering to provide the springboard necessary to launch cutting edge solutions into industry. Benefits may be realized in energy cost, as well as in environmental and economic factors.
The next chapters seek to describe methods of enhancing the effect of these plasma systems while simultaneously commenting on the multiple effects on produced water. Future research suggested by this results presented in the current chapter include two topics: (1) a comprehensive experimental fouling study of scale thickness versus time for given heat flux and initial water conditions; and (2) investigations of methods and engineering of systems that can increase the efficiency, propensity, and treatment capacity of plasma discharges in seawaters, waste waters, produced waters and other aqueous solutions.
4.0 Enhancement of arc-in-water system by stretching arc discharge in water*

4.1 Introduction

Oil and gas production processes generate large volumes of liquid waste. Both the flowback waters, generated during drilling, and produced waters, generated during production, contain various organic and inorganic components. Since approximately 250×10^6 barrels per day (i.e., ~40×10^6 m^3 per day) of produced water are generated globally, there is a growing need for new methods to treat large volumes of produced water robustly and efficiently. A variety of methods are currently utilized to treat produced waters for the purpose of discharge as well as recycling and reuse in subsequent hydraulic fracturing operations. High voltage (HV) plasma discharges may offer unique solutions, as plasma discharges have been studied in application to water for various parameters including disinfection [61], removal of dispersed oil/grease and soluble hydrocarbons, and water softening [105, 110].

While the plasma GAD was explained in detail in Chapter 2.4.1, a detailed description is given of the exact GAD generating device, referred to as a “plasmatron”, [69], used in the studies included in this thesis. Previous studies including those presented in Chapter 3, generated HV plasma discharges utilizing this three-dimensional GAD system [43, 52, 111-113].

The main concept of the 3-D GAD is to use compressed gas to move (i.e. glide) the arc discharge along two circular ring-like or disc-like electrodes, preventing the occurrence of any local hot spots although there is an excessively elevated arc

* It should be noted that much of the work by the author, presented in this Chapter 4 was published in the referenced paper, reference # [67] Cho, Y., K. Wright, H. Kim, D. Cho, A. Rabinovich, and A. Fridman, Stretched arc discharge in produced water. Review of Scientific Instruments, 2015. 86(1): p. 013501. The contents of this section are based on a study that was developed to enhance the arc in water system presented in the previous chapter.
temperature [114, 115]. For the plasma generating device used in the experimental work here, the compressed gas was tangentially injected at six locations into the space between the two disc-like electrodes, and made to form a reverse vortex flow, inside the body of the plasmatron. This plasmatron was used as a component in the present plasma-water reactor. While a detailed description of this device has been offered elsewhere [61], it is briefly described here, as it is important to understanding the enhancements offered by the stretched arc system for water treatment.

The plasmatron utilizes a relatively small gap between two circular electrodes, e.g., 2 mm because a larger gap would result in an increase in required breakdown voltage, and for a gap larger than 0.3 mm, there would not be breakdown, as a more powerful power supply than the 10-kV open circuit power supply used in the present study. If the gap was shorter than 2 mm, the flow inside the gap would have experienced an increase in frictional resistance due to the viscosity of air at an elevated temperature, and a higher flow rate would have been necessary.

For the apparatus used in this study, a plasmatron was installed at the bottom of the reactor vessel, with the top circular electrode entering the space where produced water would be located inside the mostly plastic, cylindrical reactor. The compressed gas was always initiated before the reactor was filled with water, so as to prevent water from entering the area between the cylindrical electrodes where plasma would initiate, and the ends of the plasma arc would glide. Allowing water into the plasmatron would have extinguished the plasma.

The compressed gas propelled the arc a short distance above the top electrode through the orifice which feeds through the center of the top circular disc electrode, and
into the reactor. Compressed air also exits the plasmatron here into and through the volume of water in the reactor.

With the ends of the arc traversing but remaining connected to the disc-like electrodes, the portion of the arc that exits the orifice of the plasmatron is relatively small, and does not directly contact most of the water inside the reactor. Hence the need to improve this contact with water is applicable to bench-scale experimental work, as well as to the efficacy of further scaling up such a system, as the volumes of produced water to be treated are huge.

The feasibility of stretching an arc discharge in produced water was investigated, to increase the capability of a plasma system to treat larger volumes of produced water. The electric conductivity of produced water, which can vary up to orders of magnitude of $10^5$ mS/cm, provided both a challenge and opportunity for the application of plasmas. A ground electrode and two high voltage electrodes were used to stretch an arc discharge in produced water. One electrode was positioned closer to the ground electrode. Stretching the arc had the benefit of visibly increasing contact between the arc and water, and resulted in more efficient plasma treatment.

This study attempted to stretch the plasma from its roots along the circular electrodes inside the plasmatron and into the volume of water. It was believed that enhancements in treatment, such as removal of bicarbonate, would be realized due to increased contact with plasma and water and better mixing between water and active plasma species generated from the arc.

With the produced water containing so many dissolved ions, including sodium, chloride, calcium, and magnesium [8], the conductivities of produced waters are high,
with a maximum value of approximately 200 mS/cm. This made the use of the water as an electrode feasible, with the potential to enhance the contact area between the plasma and water. The key determinant and enabling condition that makes this stretching of the arc possible is the high electric conductivity of produced water. While the plasma reactor offered great attributes, including protection of electrodes, the use of water as an electrode was a challenge for a few reasons, including that the electrically conductive metal body of the plasmatron in contact with water would prevent breakdown between the metal and the water, and instead work to simply conduct electricity. Also, with the power supply used, the distance of the water from the ground electrode would be such that breakdown would require a voltage that exceeded that of which was able to be supplied by the excitation source.

Hence, locating a second HV electrode in the water alone would not allow the stretching of the arc. The plasma reactor was re-engineered to be equipped not only with an additional HV electrode, labeled HV electrode-2, but with an electrical insulator between the plasmatron body and the water inside the reactor. To overcome the need for a more powerful power supply to support breakdown, the plasma discharge was initiated between the cylindrical electrodes and then the lead supplying high voltage to HV electrode-1 was disconnected, making it so that HV electrode-2, located inside the produced water, was the active HV electrode. Hence, the feasibility of stretching an arc discharge was tested with the use of this additional HV electrode located in water, as well as the other aforementioned technical enhancements. Tests with produced water from a shale-oil site were used to test the effect of this system on bicarbonate in water and see if enhancements were realized.
Demonstration of the capabilities of the stretched arc would be quantified by comparison of bicarbonate abatement or the lack thereof for the two systems: the standard GAD and the stretched arc. Results of these tests could validate the preferential use of one system over the other, and better system could then be used to affect other target parameters in produced waters. While the major goal of this system was to enhance the ability of the plasma-in-water reactor to generate bicarbonate depleted waters, due to the fouling mitigation benefits, other desirable and simultaneous effects could also be exhibited.

4.2 Experimental set-up and procedure for stretched arc in produced water

The experimental setup used in the work included in this chapter, is shown in Figure 17. This setup included a plasma reactor, and an influent and effluent water tank for providing produced water for the plasma reactor, and collecting plasma treated produced water, respectively. While these tanks are not shown in the figure, the water inlet and outlet of the plasma reactor are indicated.

The non-metal and metal portions of the plasm GAD generator, i.e. the plasmatron, is indicated in Figure 17. The ground electrode is the bottom electrode, and the top metal portion of the plasmatron represents HV electrode-1. HV electrode-2 is indicated, oriented radially and extending partially into the side wall of the cylindrical non-conducting transparent acrylic reactor vessel. The acrylic vessel used to contain the produced water had an inner diameter of 10 cm. The high voltage DC power supply is also indicated in Figure 17.
For the tests presented in this Chapter, produced water from a shale-oil site (Eagle Ford, Texas) was utilized. This water was pumped from a water tank, to the plasma reactor, at a flow rate of 0.1 L/min. The reactor had an overflow water outlet, located in the sidewall of the cylindrical reactor vessel at a height 16 cm from the base, and keeping the amount of produced water in the reactor at a constant water level although water was slowly entering and exiting. The overflow outlet was located at a position such that while water was treated in a once-through system, the 1.2-L capacity made it so that all
molecules of produced water would experience a residence time inside the reactor, of 12 minutes, before exiting at the overflow valve.

It should be noted that the power supply was current-limiting type, with a maximum voltage of approximately 2 kV, with the load, at a frequency of 125 kHz.

Preliminary tests at varied air flow rates, from 0.5 to 2.0 scfm, helped to determine optimum gas flow rate. It was observed that while the removal of bicarbonate ions was more effective with decreasing air flow rate, brief tests with a 0.5-scfn flow rate, allowed water from the reactor vessel to enter into the plasmatron as the air volume was not large enough. Thus 1 scfm was consistently utilized as the flow rate for all tests. From previous tests with argon, nitrogen, and oxygen as the carrier gas, it was determined that these gases did not exhibit the same effect on bicarbonate ions in water, as when air was used as a carrier gas, so air was consistently used for all tests.

Needing to electrically insulate the produced water from the metal electrodes, so that HV polarity could indeed be placed on the produced water, a machinable glass ceramic, material trade name, Macor (Corning, Inc.) was machined to cover the top of the plasmatron’s exit orifice to prevent contact with water (with the help of the compressed air which kept the water from entering inside the “plasmatron”).

The apparatus utilized one ground electrode and two HV electrodes: one with a gap distance of 2 mm from the ground electrode, and the other (i.e., the second HV electrode) positioned much further away, a distance of 5 cm from the ground electrode. It should be noted that this HV electrode upon being submerged by the produced water inside a water-filled reactor, would be more like an electrical lead for the produced water,
and the produced water itself would become a HV electrode. Figure 17 indicated the orientation of these electrodes and the ceramic insulator.

It should be noted that at time, t < 0, before the power supply was turned on, both HV electrodes were connected to the power supply. When the power supply was turned on, an arc was immediately formed between the ground and HV electrode 1, between their 2-mm gap, with ends of plasma gliding along the circular electrodes, and the plasma propelled by compressed air a short distance into the water reactor.

When a stable GAD was maintained inside the plasmatron (i.e., for about 10 s), the power line connecting the power supply to HV electrode-1 was disconnected, an action that resulted in extension of the arc toward HV electrode-2. This process resulted in a visibly expanded volume of arc discharge, and the stretched arc maintained between HV electrode-2 and the ground electrode indefinitely.

A digital phosphor oscilloscope (TDS3014C, Tektronix) was used to record voltage and current profiles after the arc was stretched in produced water. A magnetic core current probe was utilized (CM-10-L, Ion Physics Corporation, Fremont, NH), to obtain the measurement of the current profile, while a high voltage probe (P6015A, High Voltage Probe 1000X 75 MHz, Tektronix), was used to measure the voltage profile.

4.3 Results of stretched arc in produced water

While it was possible to stretch an arc discharge into produced water, it did not work with tap water. Hence the lowest electrical conductivity threshold of water, was to be determined by adding NaCl to water to vary the conductivity of water samples. It was found that the minimum electrical conductivity of water which the stretched arc system at
which the stretched arc system would work was 9 mS/cm, with the power supply used in this study.

Photographs of the arc before and after being stretched in produced water with a conductivity of 50 mS/cm is shown in Figure 18. Before stretching, the compressed air at 1 scfm was responsible for pushing the arc a short distance outside of the plasmatron toward the water volume. After stretching the arc, although air flow rate remained at 1 scfm, a larger arc discharge was observed, illuminating the produced water volume.
Figure 18: Arc before and after stretching in produced water [67].
Before stretching the power delivered to the produced water as monitored from the power supply, was 360 W (i.e., 1.2 kV and 0.3 A). The After stretching, the power was 600 W (i.e., 2 kV and 0.3 A). In addition to monitoring the current and voltage, results of the oscilloscope measurement indicate the current and voltage profile over the course of 40 microseconds.

![Figure 19: Oscillogram of characteristics of power supply used in present study [67].](image)

It should be noted that peak to peak current is shown over the course of 40 microseconds, there can be variations in this value over time. Furthermore, while the ammeter reading on the power supply was 0.3 A plasma tests before and after stretching of the arc, the RMS current calculated from this specific plot and a similar plot for the GAD treatment
was closer to 0.22 A. While this was slightly lower than 0.3 A, the value for both tests were constant.

Results of assessment of bicarbonate concentration are indicated. Table 9 shows results of produced water treatment by GAD, i.e., the case without stretching of the arc, in comparison to bicarbonate concentration upon treatment with the stretched arc.

| Table 9: Results of water chemistry analysis upon treatment: GAD vs. stretched arc |
|--------------------------------------|-----------------|-------------------|------------------|
|                                      | Baseline        | GAD (360 W)      | Stretched arc (600 W) |
| pH                                   | 7.28            | 7.9              | 7.96             |
| HCO₃⁻ (mg/L)                         | 809             | 596              | 428              |

The plasma stretched arc was able to decrease bicarbonate ion concentration from 809 to 428 ppm. For both cases, slight increases in pH were observed.

4.4 Discussion of stretched arc in produced water

The threshold for conductivity for which the arc could be stretched was 9 mS/cm. Given this limit for this system it was determined that the present method of stretching an arc could be applicable to produced waters, as such waters have conductivities ranging from 50 to 200 mS/cm, [8] as well as sea water, as it has conductivity of approximately 50 mS/cm.

Treatment of produced water with the stretched arc exhibited larger decreases in bicarbonate ions than for the standard GAD system. Still, with the stretched arc operating at a higher voltage, the energy cost needed to be calculated to compare which system had
the lowest energy cost. The 0.6 kW stretched arc system was able to decrease bicarbonate from 809 to 428 mg/L, exhibiting an energy cost shown here:

\[
\text{Energy cost}_{\text{stretched arc}} = \frac{(0.6 \text{ kW})}{\left(\frac{809 \text{ mg}}{L} - 428 \text{ mg} \frac{L}{L}\right) \times \left(\frac{1 \text{ g}}{1000 \text{ mg}}\right) \times \left(0.1 \frac{L}{\text{min}}\right) \left(60 \text{ min} \frac{1}{1 \text{ hour}}\right)}
\]

\[
= 0.262 \text{ } \frac{\text{kWh}}{g}
\]

In regard to the energy cost per unit of bicarbonate concentration, this value corresponds to 0.94 kJ/L per ppm of HCO$_3^-$ removed. As for the GAD system, the energy cost was:

\[
\text{Energy cost}_{\text{GAD}} = \frac{(0.36 \text{ kW})}{\left(\frac{809 \text{ mg}}{L} - 596 \text{ mg} \frac{L}{L}\right) \times \left(\frac{1 \text{ g}}{1000 \text{ mg}}\right) \times \left(0.1 \frac{L}{\text{min}}\right) \left(60 \text{ min} \frac{1}{1 \text{ hour}}\right)}
\]

\[
= 0.281 \text{ } \frac{\text{kWh}}{g}
\]

In regard to the energy cost per unit of bicarbonate concentration, this value corresponds to 1.01 kJ/L per ppm of HCO$_3^-$ removed. The stretched arc system was 7% more energy efficient at removing bicarbonate ions from water.

This enhancement in efficiency of bicarbonate removal shows that the stretched arc has advantages over the standard arc-in-water system. Treatment of oil-field produced water by GAD, resulted in a 26% decrease in bicarbonate ion concentration, compared to a 47% decrease for the stretched arc system. Stretching the arc discharge into produced water, brought the plasma active species, including UV into direct contact with produced water. With the high-temperature arc, surrounded by produced water, the stretched arc
configuration encouraged better heat and mass transfer between the arc and produced water. The stretched arc shows better energy efficiency than the GAD, as quantified by effect on bicarbonate. The stretched arc delivered a greater power, and showed better capability to treat a larger volume of produced water.

4.4.1 pH and mechanism of bicarbonate removal

Upon observing the results of the PH for each of the plasma treatment tests, it could be seen that pH increased for both cases, which may offered insight into the mechanism(s) of bicarbonate removal. This phenomenon could have been caused by the difference in the content of the waters, i.e. results presented in Chapter 3 were for gas-field produced waters, while the results presented in this chapter are for oil-field produced water. The oilfield produced water was visibly too dark to see through, and had noticeable amounts of oil dissolved within it. Hence, the presence of organics or other contents of these waters could prevent the mechanism of bicarbonate removal, although bicarbonate was indeed removed in both tests with both types of waters.

One must also consider that these test with oil-field produced waters were all conducted as once-through tests in which produced water molecules each had a residence time in the reactor of 12 minutes, although 1,200 mL of produced water was always contained in the reactor. This is in comparison to 10-minute tests with 650 mL of produced water inside the reactor.in a batch test with some recirculation.

It is also interesting to note, that for the plasma treatment tests with gas-field produced waters, the pH was shown to slightly increase within the first 10 minutes of many of the tests reported (see Appendix B), and then after 10 minutes, steep decreases in pH were observed. This suggests that at least for some period of time, OH⁻ appeared in
higher concentration than $H^+$ ions. Looking back at the reactions in Table 8 of Chapter 3, it is apparent that both OH$^-$ and $H^+$ ions could be generated. While $H^+$ ions are generated through any one of the mechanisms listed, OH$^-$ could be generated through a heating or local heating effect. It is proposed that while generation of $H^+$ ions is still the dominating mechanism for bicarbonate removal, pH slightly increases as bicarbonate acts as a buffer for the $H^+$ ions, while OH$^-$ concentration slightly increases. Then once much of the bicarbonate ions are depleted, while the generation of $H^+$ continues through any of the listed mechanisms, the pH starts to steeply decrease. The reaction which results in generation of OH$^-$ (as indicated previously in Table 8) is shown below:

$$HCO_3^- \rightarrow OH^- (aq) + CO_2 (g) \uparrow$$

Hence, if a mechanism of heating is occurring simultaneously with generation of $H^+$ ions, the aforementioned effect, could take place, effectively increasing the pH for a short period of time.

4.5 Chapter conclusions

This study included development of a stretched arc system, indicating that for highly conductive water, a larger plasma arc could be formed, stretching the arc from inside the plasmatron, into produced water, toward a second HV electrode. The minimum threshold of electrical conductivity for this system was experimentally found to be 9 mS/cm, showing that such a system could be applicable to produced waters and seawater, waters having conductivities above this threshold. The stretching of the arc was achieved, without increasing the flow rate of the carrier gas, but by ensuring the GAD generator was electrically insulated from water, and utilizing two high voltages electrodes. The connection to the HV electrode, closest to the ground, was disconnected.
after a short time \((t < 10\, \text{s})\), so that plasma could form between HV electrode-2 and the ground. Qualitative enhancements were observed as quantified by the efficiency of \(\text{HCO}_3^-\) removal for the case of treatment with the stretched arc system versus treatment with the GAD at the same current of 0.22 A, measured with an oscilloscope. While the oil-field produced water that was tested was more resistant to the mechanism of bicarbonate removal than the gas-field produced water, bicarbonate concentration was still decreased for more than a liter of produced water within 12 minutes of treatment time. The benefit of stretching the arc was that the contact between the arc and water was significantly increased, which in turn resulted in more efficient plasma treatment, both in performance and energy cost.
5.0 Mechanical vapor compression distillation of plasma-treated produced water

5.1 Introduction

This chapter takes into consideration, full treatment of produced water, by testing a unit that can meet desalination target goals for produced water. Toward this goal, a mechanical vapor compression (MVC) distillation system [35, 116, 117] was designed and built to distill plasma-treated produced water, on the premise that the pretreatment of the produced water would sufficiently protect the distillation unit from a CaCO$_3$ fouling problem.

While the performance of the plasma treatment system was sufficient for water softening, the MVC system would be utilized and tested for its capability to remove sodium and chloride ions, TDS and TSS in frac/produced water. Hence, since plasma-treated water significantly reduced the concentration of bicarbonate ions in produced water [66], a calcium carbonate mineral fouling problem in the distillation unit [118] could be prevented or minimized.

An MVC distillation unit was designed and operated to generate a clean distillate upon processing plasma-treated water. In this chapter, results are presented on the capability of this system to treat tap water, a plasma-treated produced water sample, and a plasma-treated sample that was further treated with the use of sodium carbonate (Na$_2$CO$_3$) to remove calcium ions from water. It should be noted that fouling tests were not conducted with this unit, instead, the main goal of this study was to demonstrate the capabilities of the MVC to process the plasma-treated produced water, containing high concentrations of calcium ions.
5.2 Experimental set-up and procedure for MVC distillation of PTPW

5.2.1 Mechanical Vapor Compression (MVC) Distillation System

Three major components were utilized for the MVC distillation system, including a mechanical vapor compressor, an evaporator, and a condenser, which are shown in Figure 20 – 22 respectively.

Figure 20: Photograph of mechanical vapor compressor used in the present study.
The condenser used in this system was an API shell & tube heat exchanger with 1-shell-pass and 4-tube-passes (API Heat Transfer Inc., Buffalo, NY, Model 4-Y-60-MAHTR-4-L-SS).

The resulting MVC distillation system was tested for distillation performance. The cost of the MVC distillation process was experimentally determined. The system was
designed so that almost all of the electric energy used to run the compressor would be recovered in the form of using superheated vapor to preheat the incoming water. Therefore, once the process started, using an electric start-up heater inside the evaporator, and steady thermal conditions were obtained, there would not be additional electrical energy consumption other than the compressor work. This was an advantage of MVC systems over ordinary distillation units. Still, this system required a pretreatment water softening step, which was offered by the plasma system.

The components of the MVC distillation unit were assembled using stainless steel pipe fittings, as both the hot water and water vapor at elevated temperatures provide a high-risk corrosion environment, in addition to the fact that some frac/produced water can be highly acidic. Figure 23 shows a photograph of the fully assembled MVC distillation system before the installation of thermal insulation layers.
5.2.2 Instrumentation of MVC Distillation System

A number of thermocouples and pressure gages were installed in the distillation system to monitor these temperatures and pressures as necessary for heat transfer behavior of the MVC distillation process. Figure 24 shows a schematic diagram of the MVC distillation system. It should be noted that a band heater was installed on the steam line after the outlet of the compressor. This band heater was not used for any of the reported tests.
It should be noted that if tests were conducted for long enough periods of time, the concentrated brine at the bottom of the evaporator would have to be disposed of, and would require a component such as a crystallizer. This crystallizer was not needed for the batch tests presented here, but upon operation of flow tests over time, once water in the evaporator was concentrated to a level where TDS was ~ 380,000 ppm, this water would need to be purged into a crystallizer. Such a function would work by building an electric conductivity (EC) meter into the line exiting the bottom of the evaporator, and attached to a solenoid control valve, to control the flow rate of the purged brine, possibly at an EC of about 260 mS/cm.
In regard to attributes of the system that were monitored during testing, the thermocouples used in this system were connected to an analog-to-digital data acquisition (DAQ) system for data transmission to a computer. Pressure measurements were collected manually upon observation of the pressure gage readings. The pressure gages were used to monitor the water vapor inside the evaporator as it was at vacuum pressures, as well as pressure after this water vapor had been compressed by the MVC. Hence, the enthalpy change in the water vapor could be assessed.

A photograph of the mostly insulated MVC system with the major components and supporting instrumentation is shown in Figure 25.

Figure 25: Photograph of MVC distillation system with thermal insulation installed, mechanical vapor compressor, evaporator, condenser, band heater, and pump connected using stainless steel pipefittings.
The test system was thermally insulated in order to minimize heat loss to the surroundings.

The 1–kW band heater which again, was not used, was added in the steam side after the MVC and before the regenerative HX coils inside the evaporator. This heater was to be used only in case extra heat was needed, and since this band heater was exposed to water vapor only, and not the concentrated brine, the band heater could provide such extra heat without experiencing a fouling problem.

Table 10: Nomenclature of temperatures monitored, associated description, as well as Data Acquisition System (DAQ) channel assignment.

<table>
<thead>
<tr>
<th>#</th>
<th>Temperature Measured</th>
<th>Description</th>
<th>DAQ Channel #</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>Tube-side IN Condenser</td>
<td>Water</td>
<td>0</td>
</tr>
<tr>
<td>T2</td>
<td>Tube-side OUT Condenser</td>
<td>Water</td>
<td>1</td>
</tr>
<tr>
<td>T3</td>
<td>Shell-side IN Condenser</td>
<td>Steam</td>
<td>2</td>
</tr>
<tr>
<td>T4</td>
<td>Shell-side OUT Condenser</td>
<td>Condensate</td>
<td>3</td>
</tr>
<tr>
<td>T5</td>
<td>Inlet to Evaporator</td>
<td>Water</td>
<td>4</td>
</tr>
<tr>
<td>T6</td>
<td>Steam OUT Evaporator (into MVC)</td>
<td>Steam</td>
<td>5</td>
</tr>
<tr>
<td>T7</td>
<td>Steam after Coil inside Evaporator</td>
<td>Steam</td>
<td>6</td>
</tr>
<tr>
<td>T8</td>
<td>Outlet from Evaporator into Pump</td>
<td>Water</td>
<td>7</td>
</tr>
<tr>
<td>T9</td>
<td>MVC Cooling Water</td>
<td>Water</td>
<td>8</td>
</tr>
<tr>
<td>T10</td>
<td>Ambient Air</td>
<td>Air</td>
<td>9</td>
</tr>
<tr>
<td>T11</td>
<td>Reservoir Tank (= T1)</td>
<td>Water</td>
<td>10</td>
</tr>
<tr>
<td>T12</td>
<td>Steam out MVC (Into Band Heater)</td>
<td>Steam</td>
<td>11</td>
</tr>
<tr>
<td>T13</td>
<td>Steam into Evaporator coil (out of Band Heater)</td>
<td>Steam</td>
<td>12</td>
</tr>
</tbody>
</table>

Thermocouples were positioned throughout the system; some were even slightly redundant i.e. T3 and T7. The locations of the thermocouples as described in Table 10
were indicated in the schematic in Figure 24. It should be noted that the accuracy of the thermocouples (not including any error in the DAQ) was: the greater of 1.1 °C or 0.4%, so for the temperatures observed during this study, the error which could be assigned to each thermocouple was ± 1.1 °C.

5.2.3. Estimation of Heat Transfer Rates from Condenser Operation

The shell & tube condenser used in this study had a 1-shell-pass and 4-tube-pass geometry. The capacity and specifications included the following: (1) Steam, shell side: 94.62 kg/hour (26.28 g/s); (2) Water, tube side: 3.63 m³/h (= 3630 kg/h =1.0083 kg/s); (3) the max heat transfer rate was 58.6 kW. It should be noted that this condenser was operated at a much lower capacity than it could handle.

The heat transfer rates across the condenser were calculated based on the experimentally measured temperatures, flow rate, and yield. The heat transfer rate, q as calculated from the steam side of the condenser was:

\[ q = \dot{Q}_{\text{Steam Side}} \]

or

\[ q = \dot{Q}_{\text{to cool hot steam to 100 °C}} + \dot{Q}_{\text{to condense steam}} + \dot{Q}_{\text{to cool condensed steam}} \]

This can further be shown as:

\[ q = \dot{Q}_{\text{Steam Side}} = \]

\[ (\dot{m}_{\text{Steam}}) \cdot [(h_{g,\text{steam,T3}}) - (h_{g,\text{steam,100 °C}})] + [(\dot{m}_{\text{steam}})(h_{fg,\text{steam}})] + [(\dot{m}_{\text{Steam Side}})(c_p,\text{water})(100 °C - T4)]. \]
Assuming steam is entering the condenser at 100 °C, this equation can further be simplified, considering only the last two terms in this expression. Hence the equation, Eq. (1) below could be used to monitor the heat transfer rate:

\[
q = \dot{Q}_{\text{Steam side}} = [(\dot{m}_{\text{steam}})(h_{fg,\text{steam}})] + [(\dot{m}_{\text{Steam Side}})(c_{p,\text{water}})(100^\circ C - T 4)] \\
(1)
\]

The heat transfer rate inside the condenser could also be calculated based on the temperatures in the water side of the condenser:

\[
q = \dot{Q}_{\text{Water side}} = \dot{m}_{\text{Water side}}c_{p}(T 1 - T 2) \\
(2)
\]

The experimentally determined heat transfer rates were to be determined using these equations shown.

**5.2.4 Estimation of Heat Transfer Rates from Evaporator Operation**

Without an MVC the heat transfer rate that would be required from a heating element to vaporize a desired yield of 30 GPD of water would be:

\[
\dot{E} = \dot{m}_{c_p} \Delta T + \dot{m}h_{fg} \\
\dot{E} = \left(0.001319 \frac{kg}{s}\right) \left(4.186 \frac{kJ}{kgK} (100 - 20) + 2257 \frac{kJ}{kg}\right) \\
= 0.44 kW + 2.98 kW \\
\dot{E} = 3.42 kW
\]
The evaporator however contains a heater with a measured power of 1.6 kW (203 V AC; 8 A). To supply the necessary heat to vaporize the desired yield, heat was to be recovered from the steam itself, by pumping it through a coil of tubes inside the evaporator to encourage heat transfer from the steam to the water inside the evaporator. As heat exchange between 100 °C steam and 100 °C water will not take place, an MVC was used to encourage vacuum pressures and lower saturation temperatures inside the evaporator, while having compressed steam at slightly higher temperature inside the evaporator tube. The steam leaving the evaporator is compressed by a MVC, allowing a temperature rise, and subsequent temperature difference between the steam side and water side of the evaporator of ~ 2 °C.

5.2.5 Heat Transfer Analysis in Mechanical Vapor Compressor

The steam compressor used in this system was a 0.8 kW mechanical vapor compressor. Assuming a steam flow rate equal to the desired yield of \( \dot{m} = 0.013194 \text{ kg/s} \), if the MVC were to compress steam at 100 °C (\( P_{\text{sat}} = 101 \text{ kPa} \); \( h_g = 2676.1 \text{ kJ/kg} \)) to steam at 102 (\( P_{\text{sat}} = 109.14 \text{ kPa} \); \( h_g = 2679.18 \text{ kJ/kg} \)), the energy required would be:

\[
\Delta \dot{E}_{\text{steam out MVC}} = \dot{m}_{\text{yield}} (h_{g,\text{steam out MVC}} - h_{g,\text{steam in MVC}})
\]

\[
\Delta \dot{E}_{\text{steam out MVC}} = \left(0.0013194 \frac{\text{kg}}{\text{s}}\right) \cdot \left(2679.18 \frac{\text{kJ}}{\text{kg}} - 2676.1 \frac{\text{kJ}}{\text{kg}}\right)
\]

\[\Delta \dot{E}_{7-6} = 0.0040 \text{ kW} = 4 \text{ W} \text{ (Compressor size w/ zero loss)}\]

This compressor had more than enough power to compress the steam at the desired yield.

\[800 \text{ W} = \left(0.0013194 \frac{\text{kg}}{\text{s}}\right) \cdot \left(x \frac{\text{kJ}}{\text{kg}} - 2676.1 \frac{\text{kJ}}{\text{kg}}\right)\]
\[ X = 3282 \text{ \textit{kJ/kg}} \text{ (corresponds to a temperature} > 450 \text{ °C)} \]

5.2.6 Heat Transfer Analysis in MVC Distillation

After steam exited the MVC (and passed an optional band heater, which was left off for all experiments), the steam entered a coil, which was located inside of the evaporator. This configuration allowed heat gained by the steam to be transferred back to the water located inside the evaporator. The steam coil inside the evaporator was made of 6 m of stainless steel 304 with a coil diameter of 0.2 m and a tube diameter of 0.0127, giving a total outer surface area, \( = \pi dl = 0.239 \text{ m}^2 \). Assuming no phase change inside the coil and a flow rate equal to the desired yield, 0.001319 kg/s, the heat transfer rate inside the coil could be computed from

\[ q = (\dot{m}_{\text{Steam}}) \cdot [(h_{g,\text{steam,T3}}) - (h_{g,\text{steam,T3=100°C}})] \].

Table 11 shows the theoretical heat transfer rate across the evaporator steam coil based on the steam inlet temperature into the coil and assuming steam leaves the coil at 100 °C without any phase change. This table also shows the potential heat transfer rates if steam was indeed condensed and all of its latent heat was recaptured.
Table 11: Theoretical heat transfer rates from steam coil inside evaporator if steam does not condense vs. if steam does condense, assuming water in evaporator is at 100 ºC.

<table>
<thead>
<tr>
<th>Steam inlet temperature, T13 (ºC)</th>
<th>If steam does not condense</th>
<th>If steam does condense</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Enthalpy, hg (kJ/kg)</td>
<td>Change in enthalpy, Δh_g = h_{g,T13} - h_{g,100} (kJ/kg)</td>
</tr>
<tr>
<td></td>
<td>2676.1</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>2676.1</td>
<td>0</td>
</tr>
<tr>
<td>100.5</td>
<td>2676.87</td>
<td>0.77</td>
</tr>
<tr>
<td>101</td>
<td>2677.64</td>
<td>1.54</td>
</tr>
<tr>
<td>101.5</td>
<td>2678.41</td>
<td>2.31</td>
</tr>
<tr>
<td>102</td>
<td>2679.18</td>
<td>3.08</td>
</tr>
<tr>
<td>102.5</td>
<td>2679.95</td>
<td>3.85</td>
</tr>
<tr>
<td>103</td>
<td>2680.72</td>
<td>4.62</td>
</tr>
<tr>
<td>103.5</td>
<td>2681.49</td>
<td>5.39</td>
</tr>
<tr>
<td>104</td>
<td>2682.26</td>
<td>6.16</td>
</tr>
<tr>
<td>104.5</td>
<td>2683.03</td>
<td>6.93</td>
</tr>
<tr>
<td>105</td>
<td>2683.8</td>
<td>7.7</td>
</tr>
</tbody>
</table>

It should be noted that the surface area of the coil is such that transfer of latent heat should be possible; assuming a temperature difference of 2 ºC across a steel coil with thickness of 0.003 m, the heat transfer rate through the steel coil could be estimated at

\[q_{\text{conduction}} = \frac{kA\Delta T}{L} = \frac{16 W}{mK} \left(0.239 \ m^2\right)\left(100 \ ºC - 98 \ ºC\right) = \frac{2.549 \ kW}{0.003 \ m}\]
The system was to be analyzed to see whether latent heat was recaptured and if so, how much. Since the 1.6-kW heater only had capability of vaporizing:

\[
\dot{m} = \frac{\dot{E}}{h_{fg}}
\]

\[
\dot{m} = \frac{1.6 \text{ kW}}{2257 \text{ kJ/kg}} = 0.00061731 \frac{kg}{s} = 2.55 \text{ LPH}
\]

this yield should be compared to the tests presented, to make some analysis of whether or not some phase change occurred inside the steam coil. If latent heat was recaptured and hence phase change occurred, it would be expected that yields greater than 2.55 LPH would have been achieved, a comparison which will be made in the results section. To maximize the yield of this system further, phase change must be encouraged inside of the evaporator coil, a process which for example could result in a pressurized water-steam mixture at 102 °C, or ideally, pressurized liquid water at 102 °C exiting the steam coil. If steam was completely condensed to pure water at this temperature, 2251.68 kJ/kg of energy could be transferred to the water inside the evaporator. It should be noted that all steam would eventually be condensed inside the condenser where the temperature difference, as well as the liquid to steam ratio is much greater. Hence, energy would be captured by the water that would eventually enter the evaporator during the flow test, making it so that the evaporator could expend less energy to heat the water to a saturation temperature.
5.2.7. Produced Water used in MVC Distillation Tests

The goals of the tests were to operate a MVC distillation unit with plasma-treated produced water and to assess water quality of condensate from these tests including total dissolved solids (TDS), total suspended solids (TSS), electrical conductivity, pH, salinity, turbidity, alkalinity (ppm as CaCO$_3$), hardness (ppm as CaCO$_3$), bicarbonate ions, sulfate reducing bacteria (SRB), and acid-producing bacteria (APB).

The test fluids distilled for this study included, 1) Tap water; 2) Plasma-treated produced water (PTPW) and 3) Plasma-treated produced water with Na$_2$CO$_3$ added. For distillation test 1, the tap water used was Camden municipal tap water. For distillation test 2, a plasma-treated produced water (PTPW) sample was used. The PTPW sample was prepared by circulating 16 gal of Produced waters at 10 GPM for 120 min through a submerged arc.

The PTPW + Na$_2$CO$_3$ sample was prepared by adding Na$_2$CO$_3$ to plasma-treated produced water at an appropriate ratio to remove all the calcium ions from the water. While 38 L was softened, only 8.5 gal would eventually be used for the actual distillation test. The amount of Na$_2$CO$_3$ added was based on the calcium concentration in the PTPW. Assuming that the calcium in produced water is associated with chlorine, the soda softening reaction can be seen below:

\[
CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl
\]

Hence CO$_3$ is added at a 1:1 mole ratio to Ca$^{2+}$ to consume all of the calcium. The calcium concentration was estimated at 8 g/L, in 38 L of PTPW. The values used to
calculate the appropriate amount of Na$_2$CO$_3$ required to soften PTPW at such a concentration are shown below in table.

<table>
<thead>
<tr>
<th>Ca$^{2+}$ concentration</th>
<th>Volume of PTPW</th>
<th>Total mass of Ca$^{2+}$</th>
<th>Molar mass of Ca$^{2+}$</th>
<th>Total mol of Ca$^{2+}$ to be added</th>
<th>Total mol of Na$_2$CO$_3$ to be added</th>
<th>Molar mass of Na$_2$CO$_3$ to be added</th>
<th>Total mass of Na$_2$CO$_3$ to be added</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 g/L</td>
<td>38 L</td>
<td>304 g</td>
<td>40 g/mol</td>
<td>7.6 mol</td>
<td>7.6 mol</td>
<td>106 g/mol</td>
<td>805.6 g</td>
</tr>
</tbody>
</table>

Once a total mass of 805.6 grams of Na$_2$CO$_3$ was added to 38 L of PTPW inside of a tank, and mixed with a stainless steel rod, this sample was then allowed to settle for 24 hours. After this period it was observed that a rock solid material had formed at the bottom of the tank, most likely CaCO$_3$, and had clogged the exit of the tank. The PTPW + Na$_2$CO$_3$ sample had to be pumped from the top of the tank and filtered through 5 micron bag filters into another tank. The initial tank had to be unclogged manually with a metal rod, and further cleared using a dilute solution of nitric acid. A picture of a portion of the manually removed solids is shown in Figure 26.
While the exact nature of the solid was not analyzed, softening with sodium carbonate is a well-known process, and change in hardness of the water samples can indicate that this solid is CaCO$_3$.

The table below shows a summary of the water properties of produced water and treated produced water used in distillation tests.

Figure 26: Picture of CaCO$_3$ that was removed from tank after softening PTPW with Na$_2$CO$_3$. This piece is about 3” long, and only represents a small portion removed.
Table 13: Properties of plasma-treated produced water and plasma-treated produced water with Na$_2$CO$_3$ added (to be used in distillation tests)

<table>
<thead>
<tr>
<th></th>
<th>PTPW</th>
<th>PTPW + Na$_2$CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Dissolved Solids, TDS (ppm):</td>
<td>61,740 ± 219</td>
<td>76,540 ± 55</td>
</tr>
<tr>
<td>Total Suspended Solids, TSS (ppm):</td>
<td>190 ± 17.2</td>
<td>236.4 ± 5.2</td>
</tr>
<tr>
<td>Electrical Conductivity (mS/cm):</td>
<td>107.28 ± 0.0837</td>
<td>117.86 ± 0.2510</td>
</tr>
<tr>
<td>pH:</td>
<td>7.85 ± 0.30</td>
<td>10.32 ± 0.02</td>
</tr>
<tr>
<td>Salinity (ppm):</td>
<td>7,436 ± 54</td>
<td>91,332 ± 47</td>
</tr>
<tr>
<td>Turbidity (NTU):</td>
<td>39.82 ± 6.14</td>
<td>1.92 ± 0.01</td>
</tr>
<tr>
<td>Alkalinity (ppm as CaCO$_3$):</td>
<td>270 ± 11</td>
<td>8,520 ± 811</td>
</tr>
<tr>
<td>Hardness (ppm as CaCO$_3$):</td>
<td>9,200 ± 758.3</td>
<td>782 ± 152.1</td>
</tr>
<tr>
<td>Bicarbonate (ppm):</td>
<td>327 ± 12</td>
<td>3,513 ± 332</td>
</tr>
<tr>
<td>SRB (CFU/mL):</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>APB (CFU/mL):</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Three different water samples were used for the MVC tests, which were tap water, plasma-treated produced water, and plasma-treated produced water, where calcium ions were removed by adding Na$_2$CO$_3$.
<table>
<thead>
<tr>
<th>Sample in Tank B:</th>
<th>Tap Water</th>
<th>Plasma-Treated Produced Water</th>
<th>Plasma-treated produced water (calcium ions removed by adding Na₂CO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume in Tank B:</td>
<td>60.8 L (16 gal)</td>
<td>60.8 L</td>
<td>60.8 L</td>
</tr>
<tr>
<td>Condenser flow rate:</td>
<td>9.5 LPM (2.5 GPM)</td>
<td>9.5 LPM</td>
<td>9.5 LPM</td>
</tr>
<tr>
<td>Water volume in evaporator:</td>
<td>31.9 ± 0.9 L (8.4 ± 0.2 gal)</td>
<td>31.9 ± 0.9 L (8.4 ± 0.2 gal)</td>
<td>31.9 ± 0.9 L (8.4 ± 0.2 gal)</td>
</tr>
<tr>
<td>Total volume needed:</td>
<td>25 gal</td>
<td>25 gal</td>
<td>25 gal</td>
</tr>
</tbody>
</table>

In regard to the general testing time, the liquid temperature inside the evaporator based on the given parameters (Vₑᵥₐᵖ = 8.4 gal) should have reached within 10 degrees of 100 °C by t = 2 h. The exact temperature at t = 2 h might not be exact but to keep tests standard, the MVC cooling water (currently TAP once through) and the MVC were to be turned on at t = 2 h. Theoretically, the time to reach a temperature of for example, 98 °C could be estimated using the following equation:

\[
t = \frac{mc\Delta T}{E} = \frac{(1 \frac{kg}{L})(31.9 \, L)(4.186 \frac{kJ}{kg \cdot K})(98 - 20)}{1.6 \, kW} = 6509.7 \, s = 1.8 \, h
\]

At t = 2 h, the MVC was turned on.
5.3 Results of MVC distillation of plasma-treated produced water

5.3.1 Distillation of Tap Water

Upon power to the 1.6-kW heater being turned on, the test was initiated, and the 8.5 gal of water took approximately 2 hours to get within 10 degrees of 100 °C. Figure 27 (a) and (b) show both the water temperature and pressure inside the evaporator, and the pressure at the MVC outlet, during this 2 hour start-up period and for the subsequent 2 hours of testing time during distillation of tap water.

Steam temperatures recorded during distillation tests are shown in Figure 28. The temperature of the steam entering the evaporator coil was approximately at 101 °C. Although the quality of steam or steam-water mixture that entered the shell side of the condenser was not exactly measured, it was believed to be mostly steam.
Water temperatures in and out of the condenser at the tubeside together with the condensate water temperature from the shellside outlet are shown in Figure 29. The water temperature at the tubeside remained at room temperature of approximately 21-25 °C until the compressor was turned on at $t = 2$ h. As the compressor was turned on and steam entered the shellside, the tubeside water temperature gradually increased with time.
Figure 29: Temperatures across condenser during distillation of tap water

Figure 30 shows the amount of the condensate collected and measured every 20 min using a plastic container and a precision mass balance. Except for the first measured amount of condensate, almost constant condensate of approximately 1 L was obtained every 20 min, resulting in a yield of approximately 3 L/h.
Figure 30: Volume of samples collected every 20 minutes from condensate tank during distillation of tap water

Figure 31 shows the heat transfer rates, which were calculated for the condenser in two different methods: (1) using the steam side temperatures and condensate yield; (2) using water side condenser temperatures and the experimentally determined (flow-in-a-bucket test) flow rates. It should be noted that for $t < 2$ h, steam did not pass through the condenser so any calculated heat transfer rates could be attributed to minor temperature differences between thermocouples.
These heat transfer rates were calculated utilizing equation (1) and (2) as previously indicated. During steady operation, the condenser demonstrated heat transfer rates in the range of 1.7 -2.1 kW.

**5.3.2 Distillation of Plasma-treated Produced Water**

The water temperature and pressure inside the evaporator, and the pressure at the MVC outlet are shown in Figure 31.
Figure 31: Results of distillation test with plasma-treated produced water including: (a) water temperature inside the evaporator and (b) pressure inside the evaporator and at the MVC outlet.

Steam temperatures recorded during distillation of plasma treated produced water are shown in Figure 32. The temperature of the steam entering the evaporator coil was approximately at 101°C. Although the quality of steam or steam-water mixture that entered the shellside of the condenser was not exactly measured, it was believed to be mostly steam.
The steam temperature measurement, T12 seems to give inaccurate steam temperature measurements. This was not observed for the distillation tests with tap water. For this test with plasma-treated produced water, the thermocouple measurement at T12 appeared to increase at ~3.3 h to 120 ºC. This was believed to not be a measurement of the steam itself, as the redundant temperature measurement, T13 indicated temperatures of ~101 ºC. This increase in temperature registered by thermocouple is attributed to its location, directly next to the MVC outlet, as it is believed that this temperature indicates an increase in the temperature of the mechanical parts of the MVC and the MVC body, with heat transferred a short distance through the well-insulated stainless steel piping. Temperature changes in the actual compressor body are not studied here but the fluctuation in T12 may show that such a parameter should continue to be monitored. T12
after \( t = 3 \) h cannot be taken to measure steam temperature; \( T_{13} \) is accurate (noting that
the band heater was never turned on).

Water temperatures in and out of the condenser at the tubeside together with the
condensate water temperature from the shellside outlet are shown in Figure 33. The water
temperature at the tubeside remained at the room temperature of approximately \( 21 - 25 \) \(^\circ\) C until the compressor was turned on at \( t = 2 \) h. As the compressor was turned on and
steam entered the shellside, the tubeside water temperature gradually increased with time.

![Figure 33: Temperatures across the condenser during distillation of plasma-treated-produced water](image)

Figure 34 shows the amount of the condensate collected and measured every 20 min from
the test with plasma-treated produced water. Almost constant condensate of
approximately 1.1 L was obtained every 20 min, resulting in a yield of approximately 3.3
L/h.
Figure 34: Volume of samples collected every 20 minutes from condensate tank during distillation of plasma-treated produced water

Figure 35 indicates the heat transfer rates calculated using equations (1) and (2) in Chapter 5.2.3. During steady operation, the condenser demonstrated heat transfer rates in the range of 1.8 - 2.5 kW.
5.3.3 Distillation of plasma-treated produced water with soda ash added

The water temperature and pressure inside the evaporator and at the MVC outlet is shown in Figure 36.
Figure 36: Volume of samples collected every 20 minutes from condensate tank during distillation of plasma-treated produced water with Na$_2$CO$_3$ added.

The steam temperatures during distillation of plasma-treated water with Na$_2$CO$_3$ added are shown in Figure 37. The temperature of the steam entering the evaporator coil was approximately 101°C. Although the quality of steam or steam-water mixture that entered the shellside of the condenser was not exactly measured, it was believed to be mostly steam.

Similar to the previous study with plasma-treated produced water, again, the thermocouple measurement T12 appeared to increase at ~3.3 h, although the redundant temperature measurement at T13 indicated ~101 °C. This increase in temperature is attributed to its proximity to the MVC body and furthermore to an increase in temperature of the mechanical parts of the actual MVC. T13 should be considered as the accurate measurement of actual steam (noting that the band heater between T12 and T13 was never turned on). The occurrence of this phenomenon with tests utilizing concentrated brine, may have indicated a challenge for the compressor in handling such
fluid, as some migration of particles in addition to steam through the system are possible due to entrainment of particles.

Figure 37: Steam temperatures during distillation of plasma-treated produced water with Na$_2$CO$_3$ added

Figure 38 includes the temperatures across the condenser, as well as the monitoring of ambient air temperature during distillation of plasma-treated produced water with Na$_2$CO$_3$ added. The water temperature at the tubeside remained at the room temperature of approximately 21-25 °C until the compressor was turned on at t = 2 h. As the compressor was turned on and steam entered the shellside, the tubeside water temperature gradually increased with time.
Figure 38: Temperatures across condenser during distillation of plasma-treated produced water with Na$_2$CO$_3$ added.

Figure 39 indicates the amount of condensate collected and measured every 20 min for the test with plasma-treated produced water with Na$_2$CO$_3$ added. Almost constant condensate of approximately 1 L was obtained every 20 min, resulting in a yield of approximately 3 L/h.
Figure 39: Volume of samples collected every 20 minutes from condensate tank during distillation of plasma-treated produced water with Na$_2$CO$_3$ added

The heat transfer rates across the condenser are shown in Figure 40, obtained during distillation of plasma-treated water with Na$_2$CO$_3$ added. These heat transfer rates were calculated utilizing equation (1) and (2) in Chapter 5.2.3. During steady operation, the condenser demonstrated heat transfer rates in the range of 1.8 - 2.75 kW
Figure 40: Heat transfer rates across condenser during distillation of plasma-treated produced water with Na$_2$CO$_3$ added.

5.3.4 Water analysis of condensate after MVC distillation

The water properties of the condensate samples taken at t = 240 min for each of the three tests presented here, are shown below in Table 9. Test 1 with tap water was conducted as the baseline run, confirming the validity of the MVC distillation operation and water property analysis. Test 2 which was conducted with plasma-treated produced water (PTPW) showed that the TDS was significantly decreased from 61,740 to 529 ppm, while the TSS was also significantly decreased from 190 to 5.6 ppm. Turbidity also dropped from 39.8 to 1.0 NTU. The color of plasma-treated produced water (PTPW) was yellow as shown in Figure 41, but after distillation, it changed to a clear transparent color, as reflected in the turbidity measurement.
Test 3, which was conducted with plasma-treated produced water (PTPW) with the addition of Na$_2$CO$_3$ showed that the TDS was significantly decreased from 76,540 to 697 ppm, while TSS was also significantly decreased from 236 to 6.8 ppm. Turbidity also dropped from 1.92 to 0.0 NTU. The color of plasma-treated produced water (PTPW) with the addition of Na$_2$CO$_3$ was clear/transparent even before distillation.
Table 9: Water properties of samples and distillate from distillation tests

<table>
<thead>
<tr>
<th>Water properties of samples and distillate</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total Dissolved Solids, TDS (ppm):</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tap</td>
<td>193</td>
<td>± 0</td>
<td>61,740</td>
</tr>
<tr>
<td>Tap - Distillate</td>
<td>± 0.1</td>
<td>± 0.1</td>
<td>529.2 ± 6</td>
</tr>
<tr>
<td>PTPW Distillate</td>
<td></td>
<td></td>
<td>76540 ± 55</td>
</tr>
<tr>
<td>PTPW + Na$_2$CO$_3$ Distillate</td>
<td></td>
<td></td>
<td>697 ± 2</td>
</tr>
<tr>
<td><strong>Total Suspended Solids, TSS (ppm):</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>± 2.6</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>± 1.2</td>
<td>± 1.8</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>236.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.8</td>
</tr>
<tr>
<td><strong>Electrical Conductivity (mS/cm):</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3936</td>
<td>± 0.0073</td>
<td>107.28</td>
</tr>
<tr>
<td></td>
<td>± 0.0005</td>
<td>± 0.0000</td>
<td>1.0536</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>117.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.4194</td>
</tr>
<tr>
<td><strong>pH:</strong></td>
<td>8.14</td>
<td>± 0.1</td>
<td>7.85</td>
</tr>
<tr>
<td></td>
<td>± 0.5</td>
<td>± 0.5</td>
<td>9.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.13</td>
</tr>
<tr>
<td><strong>Salinity (ppm):</strong></td>
<td>239</td>
<td>± 0</td>
<td>74366</td>
</tr>
<tr>
<td></td>
<td>± 62</td>
<td>± 0</td>
<td>592</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>91332</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>758</td>
</tr>
<tr>
<td><strong>Turbidity (NTU):</strong></td>
<td>0</td>
<td>± 0</td>
<td>39.82</td>
</tr>
<tr>
<td></td>
<td>± 0</td>
<td>± 0</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td><strong>Alkalinity (ppm as CaCO$_3$:</strong></td>
<td>90</td>
<td>± 0</td>
<td>270</td>
</tr>
<tr>
<td></td>
<td>± 15</td>
<td>± 0</td>
<td>495</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8520 ± 811</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.87 ± 3.3</td>
</tr>
<tr>
<td><strong>Hardness (ppm as CaCO$_3$:</strong></td>
<td>112.2</td>
<td>± 15.2</td>
<td>9200</td>
</tr>
<tr>
<td></td>
<td>± 17</td>
<td>± 0</td>
<td>95.2 ± 19.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>782</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.4</td>
</tr>
<tr>
<td><strong>Bicarbonate (ppm):</strong></td>
<td>108</td>
<td>± 0</td>
<td>327</td>
</tr>
<tr>
<td></td>
<td>± 18</td>
<td>± 0</td>
<td>888</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3513 ± 332</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td><strong>SRB (CFU/mL):</strong></td>
<td>n/a</td>
<td>n/a</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td><strong>APB (CFU/mL):</strong></td>
<td>n/a</td>
<td>n/a</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Picture of sample

Picture of filter upon TSS test
5.4 Discussion of MVC distillation of plasma-treated produced water

To analyze the phase change phenomena and associated heat transfer rate across the evaporator coil, a comparison could be made of what was possibly happening inside the coil. With water inside the evaporator at ~98 °C, a lower temperature than steam entering the evaporator coil at ~100 °C, heat transfer could occur. The rate of heat transfer in this coil was related to the mass flow rate and contents of the fluid exiting the coil in that there were three possibilities; the fluid leaving this coil (and heading toward the condenser) could be: a) steam at 100 °C (no heat transferred); b) a steam-water mixture at 100 °C; or c) water at 100 °C. Assuming steam mass flow rate inside the evaporator coil equals \( \dot{m}_{yield} \), the range of heat transfer rates for these three scenarios, based on the enthalpy of vaporization could be expected to be in the range of \( 0 \rightarrow (\dot{m}_{steam})(h_f) \), with \( h_f = 2257 \, kJ/kg \). Table 15 outlines this range of heat transfer rates based on whether steam or water (or a mixture of the two) exited the steam coil before entering the condenser.

<table>
<thead>
<tr>
<th>Entering steam coil</th>
<th>Exiting steam coil</th>
<th>Change in enthalpy (kJ/kg)</th>
<th>Heat transfer rate, ( q ) (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Steam at 100 °C</td>
<td>Steam at 100 °C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>b Steam at 100 °C</td>
<td>Steam-water mixture at 100 °C</td>
<td>0 → 2257</td>
<td>0 → (( \dot{m}_{steam} ))(( h_f ))</td>
</tr>
<tr>
<td>c Steam at 100 °C</td>
<td>Water at 100 °C</td>
<td>2257</td>
<td>(( \dot{m}_{steam} ))(( h_f ))</td>
</tr>
</tbody>
</table>
The results of the distillation tests were analyzed to determine where in the range outlined in Table 15, the distillation unit was performing.

If heater #1 (1.6 kW) were completely responsible for the generation of steam over the two hours which steam was produced during the tests presented in this study, this 1.6 kW heater would have been able to produce steam (which would eventually be condensed given the heat transfer rates inside the condenser) at a rate of \( \dot{m} = \frac{q}{h_{fg}} = \frac{1.6 \text{ kW}}{2257 \text{ J/kg}} \approx 2.55 \text{ LPH} \). Such a value could be used to help determine if phase change occurred inside the evaporator steam coil, as yields higher than this 2.55 LPH would suggest that steam was generated due to energy transfer from another source, not the heater itself.

While the tests fell short of the goal of 4.75 LPH (30 GPD), all tests showed that yield was higher than what it would be if the heater were used alone. To obtain the yields that were realized during these distillation tests, a heater of 1.72 kW, 1.78 kW, and 2.09 kW would have been required respectively. Table 16 indicates estimations of the heat flux across the steam coil for each of the distillation tests based on the difference in heater power that would be required to generate the actual yield realized during testing. Further comment is made on the percent of latent heat recaptured.
Table 16: Analysis of heat transfer rate across steam coil and recapture of latent heat

<table>
<thead>
<tr>
<th>Test Fluid</th>
<th>Yield, $\dot{m}$ (LPH)</th>
<th>Actual heater power supplied, $q_{heater 1}$ (kg/s)</th>
<th>Theoretical heater power needed, $q = \dot{m} h_f g$ (kW)</th>
<th>Difference in heater power, $q - q_{heater#}$ (kW)</th>
<th>Percent of latent heat recaptured, $\frac{q}{q_{heater}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap</td>
<td>2.72</td>
<td>0.00076</td>
<td>1.6</td>
<td>+ 0.12</td>
<td>7 %</td>
</tr>
<tr>
<td>PTPW</td>
<td>2.85</td>
<td>0.00079</td>
<td>1.6</td>
<td>+ 0.18</td>
<td>10.1%</td>
</tr>
<tr>
<td>PTPW + Na₂ CO₃</td>
<td>3.34</td>
<td>0.00093</td>
<td>1.6</td>
<td>+ 0.39</td>
<td>18.7 %</td>
</tr>
</tbody>
</table>

All tests indicated some recapture of latent heat.

Table 17 shows the total yield and cost obtained for each test, noting that steam was only generated during the last two hours of the tests.
Table 17: Total yield and energy cost of each distillation test

<table>
<thead>
<tr>
<th>Test Fluid</th>
<th>Total Yield in 2 hours (kg)</th>
<th>Yield (LPH)</th>
<th>Energy Cost, $C_{\text{Energy}} = \frac{(E_{\text{Heaters}} + E_{\text{MVC}}) \cdot ($)}{\text{Yield}}$ (kWh/kg)</th>
<th>Cost, $C_{$}$ ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Tap</td>
<td>5.44</td>
<td>2.72</td>
<td>0.88</td>
<td>$0.088/kg</td>
</tr>
<tr>
<td>2 PTPW</td>
<td>5.69</td>
<td>2.85</td>
<td>0.84</td>
<td>$0.084/kg</td>
</tr>
<tr>
<td>3 PTPW + Na$_2$CO$_3$</td>
<td>6.68</td>
<td>3.34</td>
<td>0.72</td>
<td>$0.072/kg</td>
</tr>
</tbody>
</table>

In the last columns of the table, energy cost and cost per unit mass of water produced was calculated. It should be noted that to calculate cost, an electricity cost of $0.10/kWh was assumed.

5.5 Chapter conclusions

Distillation tests were conducted with three water samples, including a tap water sample, a plasma-treated produced water sample, a sample with calcium removed from plasma treated-produced water using a traditional method of chemical addition of soda ash. It should be noted that the test with the soda ash softened PTPW indicated an initial increase in TDS of the water to be distilled. In analyzing the ability of the MVC system to recapture latent heat, it was observed that phase changes occurred for all tests with yields greater than 2.55 LPH achieved, and a recapture of 7 – 18.7 % of latent heat. In regard to water quality, the MVC distillation unit was capable of decreasing total dissolved ions of all tested fluids by over 99%, including that of plasma-treated produced waters.
6.0 Effect of stretched arc on organics and bacteria in produced water

6.1 Introduction

This study investigated the effect of a submerged arc-in-water configuration to simultaneously affect additional parameters including organics and bacteria, while bicarbonate was being removed. Chapter 4 presented an enhancement of the arc-in-water system, but in general oil-field produced water required more energy for treatment than gas-field produced water that was treated as indicated in Chapter 3. The presence of oil & grease in produced water may affect the energy cost, as well as the mechanisms working to remediate the produced waters. Hence, while the plasma system was able to exhibit versatility, by successfully treating multiple types of produced water, the simultaneous effect of the plasma-in-water system on multiple target parameters was to be explored and demonstrated on oil-field produced water. This was necessary to provide a better idea of the energy cost of this system, with many benefits realized while bicarbonate ions are being removed.

This chapter provides data for plasma treatment using a stretched arc system in oil-field produced water to assess the simultaneous effects occurring, in addition to bicarbonate ion removal. Included with assessment of bicarbonate ions and other associated water quality parameters, a general assessment of bacteria is conducted. Focus is placed on two forms of bacteria characteristic of oil field produced waters, namely, Sulfate Reducing Bacteria (SRB) and Acid Producing Bacteria (APB), which can cause corrosion problems for oil and gas companies.

The objectives of the present study were to demonstrate the simultaneous effect of a plasma stretched arc on various attributes of produced water. The effect of the system
on modulating various water parameters including bicarbonate ions (for the purpose of preventing CaCO₃ fouling), as well as effects on bacteria and oil and grease was demonstrated. While bicarbonate ions were modulated from 400 mg/L to 150 mg/L within 10 minutes of treatment, a 4-log reduction was observed in SRB and ATP within 5 min of treatment, and oil & grease content was decreased in 550 mL of produced water from 40 mg/L to below 10 mg/L within five minutes of treatment. These tests demonstrated the potential use of arc-in-water systems for treatment of produced water from both oil and gas exploration. The mechanism of bicarbonate removal is elucidated from previous studies as decreases in pH were not observed for tests containing oil & grease.

6.1.1 Sulfate-Reducing Bacteria (SRB) and Acid-Producing Bacteria (APB)

Corrosion is an electrochemical process, involving oxidation of a metal, and reduction of a chemical species, and such reactions can be influenced by microbiological activities, especially when the organism is in close contact with the metal [119]. The resulting metal deterioration is known as biocorrosion, or microbially-influenced corrosion (MIC) [119], which is a terminology used by NACE (the national Association of Corrosion Engineers), to address this type of corrosion. SRBs and APBs are a problem for oil and gas companies because they can cause MIC. In this chapter SRB and APB in produced water will be assessed. It should be noted that assessment methods for SRB, APB, and other water assessment procedures and kits utilized to generate data in this thesis are indicated in Appendix D.

Sulfate-reducing bacteria (SRB) obtain energy by oxidizing organic compounds, while reducing sulfur compounds such as sulfate, sulfite, thiosulfate, as well as sulfur to
sulfide[120]. To phrase it another way, in a form of anaerobic respiration, SRBs breathe sulfate rather than oxygen. Such anaerobic bacteria (although some SRBs actually can tolerate some oxygen [119]), can cause corrosive by-products, e.g., H$_2$S, which has an obnoxious characteristic rotten egg odor and is toxic even in low concentrations, and biological fouling [21]. In general oil, gas and shipping industries are seriously affected by the sulfides generated by SRB, with biogenic sulfide production leading to health and safety problems, environmental hazards and severe economic losses due to reservoir souring (increased sulfur content) and the corrosion of equipment [119].

Acetic, formic and lactic acids are common metabolic by-products of Acid Producing Bacteria (APB). Interestingly enough, in addition to the potential corrosion of metals, the acids produced by APB can also serve as nutrients for SRB and methanogens and it has been suggested that SRB proliferate at sites of corrosion due to the activities of APB [119]. The general methods for assessing the amount of SRB and APB in produced water samples, is indicated in Appendix D, along with other water assessment methods utilized in this thesis.

In addition to the bacteria that are troublesome for the oil and gas industry, namely SRB, and APB, a general assessment of bacteria was collected in the form of assessment of adenosine triphosphate (ATP), a substance which all living cells contain, and that serves as the universal energy donor for metabolic reactions [121]. Assessment of ATP was used to effectively and quickly quantify the amount of all of the bacteria in the produced water samples. Hence it was expected that an ATP assessment would account for SRB, APB, and non-SRB/APB bacteria. It should be noted that cATP units, i.e., picograms of ATP/mL units were converted into Microbial equivalents/mL (ME/mL)
based on the established conversion that 1 E. coli-sized bacteria contains 0.001 pg of ATP [122]. This was done to allow for results of ATP assessment to be communicated on the same basis as traditional culture tests. For further details on the assessment method for ATP, and other water assessment techniques used to generate this thesis, see Appendix D.

6.2 Experimental set-up and procedure for effect of stretched arc

The present tests included in this chapter, utilized a stretched arc discharge in water, a set-up previously reported in Chapter 4 of this thesis and in Cho et al. [67]. This system was used to treat 550 mL of produced water from oil exploration (Eagleford, Texas). Briefly, the stretched arc system relied on a plasmatron, and a high voltage lead which was installed through the sidewall of the acrylic reactor and into the produced water, to make highly conductive produced water into a cathode. The power supply parameters were 2 kV/0.3A; and air was injected at 1 SCFM into the GAD generator.
Table 18: Tests and assessments conducted on oil-field produced water samples as presented in this chapter

<table>
<thead>
<tr>
<th>Tests and assessments conducted on oil-field produced water</th>
<th>Plasma Power On</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base-line</td>
</tr>
<tr>
<td></td>
<td>(min)</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Part 1 of study: 550 mL pre-filtered before plasma tests</td>
<td></td>
</tr>
<tr>
<td>1 Video Stills</td>
<td>Y</td>
</tr>
<tr>
<td>2 ATP</td>
<td>Y</td>
</tr>
<tr>
<td>3 SRB</td>
<td>Y</td>
</tr>
<tr>
<td>4 APB</td>
<td>Y</td>
</tr>
<tr>
<td>5 Standard Assessments</td>
<td>Y</td>
</tr>
<tr>
<td>6 Bicarbonate</td>
<td>Y</td>
</tr>
<tr>
<td>7 pH</td>
<td>Y</td>
</tr>
<tr>
<td>8 Temperature</td>
<td>Y</td>
</tr>
<tr>
<td>9 Volume</td>
<td>Y</td>
</tr>
<tr>
<td>10 Total Dissolved Solids</td>
<td>Y</td>
</tr>
<tr>
<td>11 Conductivity</td>
<td>Y</td>
</tr>
<tr>
<td>12 Salinity</td>
<td>Y</td>
</tr>
<tr>
<td>13 Hardness</td>
<td>Y</td>
</tr>
<tr>
<td>14 Photograph of sample</td>
<td>Y</td>
</tr>
</tbody>
</table>

Batch plasma tests were conducted, each utilizing 550 mL of produced water. These samples were all filtered with a 5-micron filter before plasma treatment, to remove any excess TSS. It should be noted that even after filtration, the produced water maintained its opaque, dark black color. There were no easily observable changes in the appearance of the water samples upon filtration.

At the beginning of each test, a 550 mL baseline sample of produced water was pumped into the reactor. Batch tests were conducted of 30 s, 1 min, 2 min, 3 min, 4 min, 5 min, 7 min, and 10 min. During the 5 min test only, video was taken to show video stills of visible changes in the water.
Upon completion of each batch test, the power was turned off, the temperature of the sample was measured, and the volume of sample was pumped out of the reactor and measured. Once all tests were completed and the samples were allowed to cool, photographs of the samples were taken inside 250 mL sized lab glassware, again to monitor any visible changes in the produced water. Bacteria assessments were prepared and conducted including assessment of adenosine triphosphate (ATP); APB; and SRB. ATP assessments were performed on all samples, but SRB and APB assessments were only performed on the baseline, 1-minute, and 5-minute samples. Other assessments conducted included alkalinity, pH, bicarbonate ions (calculated), calcium hardness, total dissolved solids (TDS), total suspended solids (TSS), salinity, conductivity, and turbidity.

6.3 Results

6.3.1 Effect of stretched arc on organics in produced water

There were some qualitative observations that could be made about the enhanced arc-in-water system. The effect of this arc-in-water system with the arc stretched was tested on a produced water sample from Eagleford, Texas to visually monitor any noticeable changes in organics contents of the produced water.

Figure 41 shows video stills of the reactor during a 5-min plasma treatment with produced water being treated in real time to show characteristic changes of produced water. The stills are within ± 0.5 seconds of actual time.
Figure 41: Video stills of Reactor with produced water being treated in real time to show characteristic changes of produced water over 5 minutes. Shots are within ± 0.5 seconds of actual time.
While the plasma in Figure 42 is initially not very visible due to the darkness of the water sample, over time, and within about 2 minutes, the presence of the bright stretched arc discharge becomes apparent. This change indicates a change in the contents of the water.

After treatment, 250 mL of each sample was collected into 250 mL lab glassware. Figure 42 shows digital photographs of baseline samples and plasma treated samples, which were taken within 3 hours after test completion to show characteristic color after removing each sample from plasma reactor. The baseline produced water sample was initially an opaque black color but upon plasma treatment became noticeably less dark, arriving at an amber color.
Figure 42: Digital photographs of baseline samples and plasma treated samples taken within 3 hours after test completion to show characteristic color after removing sample from plasma reactor.

6.3.2 Effect of stretched arc on bacteria in produced water – SRB, APB, ATP

Along with monitoring of the organic content of the produced water, microbiological assessments were performed to determine the disinfecting capabilities of
the plasma arc-in-water system with respect to bacteria characteristic of produced water. The produced water samples were assessed for sulfate reducing bacteria (SRB) and acid producing bacteria (APB) content, as well as Adenosine triphosphate (ATP), which was a general indication of living organisms in the sample. The results of the bacteria assessments for the baseline sample and the plasma treated samples over the course of 5 min are shown in the Table 19.

<table>
<thead>
<tr>
<th>Bacteria Assesments</th>
<th>Control 0 min</th>
<th>Plasma Treatment Time 30 s 1 min 5 min</th>
<th>Energy cost for 1-log reduction (kJ/L) kWh/L ($)bbl</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATP (Microbial Equivalents/mL)</td>
<td>10^7.65</td>
<td>10^7.44 10^7.48 10^5.07</td>
<td>127 kJ/L 0.035 kWh/L $0.55 /bbl</td>
</tr>
<tr>
<td>SRB (CFU/mL)</td>
<td>10^4</td>
<td>10^4 10^4 &lt; 10^0 (SRB Inhibited)</td>
<td>81.8 kJ/L 0.022 kWh/L $0.35 /bbl</td>
</tr>
<tr>
<td>APB (CFU/mL)</td>
<td>10^4</td>
<td>10^4 10^4 10^0 (APB Inhibited)</td>
<td>81.8 kJ/L 0.022 kWh/L $0.35 /bbl</td>
</tr>
</tbody>
</table>

Table 19: Effect of stretched arc plasma treatment (air flow rate of 1 SCFM; power supply: 0.3 A; 2 kV) on bacteria in produced water (550 mL) and energy cost

Results of assessments by ATP tests are shown in Figure 43. For quantification of ATP, all samples were assessed within 9 hours of completion of plasma treatment tests (Baseline was assessed within 3 hours; baseline + filter was assessed within 3 hours;
Samples 30 s, 1 min, and 5 min were assessed within 3 hours, and samples 2 min, 3 min, 4 min, 5 min, 7 min, and 10 min were assessed within 9 hours of test completion.

Hence, the results include but do not account specifically for potential residual effects on bacteria due to plasma treatment, nor does it account for any growth of bacteria colonies in that time. Future studies can include narrower windows for bacteria assessment to study residual effects due to chemical reactions taking place after plasma power is turned off. It should be noted that while ATP is measured in picograms, an established conversion is utilized, assuming that 1 E. coli-sized bacteria contains 0.001 pg of ATP.
6.3.3 Effect of stretched arc on produced water properties

Results are shown for assessment of various water properties upon plasma treatment of produced water. The effect of a plasma submerged arc on bicarbonate in the presence of oil & grease and bacteria is demonstrated in Figure 44.

Figure 44: Results of assessments of bicarbonate in produced water with stretched arc plasma treatment of oil-field produced water

Figures 45 indicates the results of assessments of pH of produced water with stretched arc plasma treatment of oil-field produced water
Figure 45: Results of assessments of pH of produced water with stretched arc plasma treatment

Figure 46 indicates results of assessments of hardness of produced water with stretched arc plasma treatment.
Figure 46: Results of assessments of hardness of produced water with stretched arc plasma treatment

Results of assessments of temperature of produced water with stretched arc plasma treatment are shown in Figure 47.
Figure 47: Results of assessments of temperature of produced water with stretched arc plasma treatment.

Figure 48 shows results of assessments of water volume of produced water with stretched arc plasma treatment.
Figure 48: Results of assessments of volume in produced water with stretched arc plasma treatment.

Figures 49 and 50 indicate results of assessments of TDS and conductivity respectively for stretched arc plasma treatment of produced water.
Figure 49: Results of assessments of TDS in produced water with stretched arc plasma treatment.

Figure 50: Results of assessments of conductivity of produced water with stretched arc plasma treatment
Figure 51 shows results of assessments of salinity of produced water with stretched arc plasma treatment.

![Graph showing salinity of produced water before and after plasma treatment](image)

**Figure 51: Results of assessments of salinity of produced water with stretched arc plasma treatment**

Upon outsourcing of samples for assessment of oil & grease and other parameters, the following results were obtained, as shown in Table 20.
Table 20: Results of oil & grease and dissolved metal analysis for baseline, plasma-treated and control samples.

<table>
<thead>
<tr>
<th></th>
<th>Baseline produced water from oil exploration</th>
<th>Plasma-Treated Plasma Power On 5 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Oil &amp; Grease (ppm)</td>
<td>41.6</td>
<td>7.05</td>
</tr>
<tr>
<td>2 Barium (ppm)</td>
<td>0.91</td>
<td>0.89</td>
</tr>
<tr>
<td>3 Calcium (ppm)</td>
<td>1,990</td>
<td>1,930</td>
</tr>
<tr>
<td>4 Magnesium (ppm)</td>
<td>168</td>
<td>165</td>
</tr>
<tr>
<td>5 Strontium (ppm)</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>6 Total Hardness (ppm as CaCO₃)</td>
<td>5,670</td>
<td>5,510</td>
</tr>
</tbody>
</table>

6.4 Discussion of effect of stretched arc on oilfield produced water

This chapter demonstrated simultaneous capabilities of a submerged arc system. Bicarbonate ion concentration was decreased from 450 mg/L to 150 mg/L. This decrease in bicarbonate was again accompanied by a slight increase in pH within the first 10 minutes of treatment, as bicarbonate acted as a buffer, consuming the H⁺ ions. Calcium hardness, with a very high initial concentration did not decrease. However in the second part of the study when 5-min tests were re-performed to obtain oil and grease data, slight decreases in calcium ion concentration were observed, with 5-min plasma treatment. Hence, it is likely that there is a mixture of mechanisms responsible for the removal of bicarbonate, however, the lack of effect on calcium indicates that it is not usually a heating effect that is leading to the removal of bicarbonate.

Results of bacteria assessments indicated that while most bacteria in the produced water was not from SRB and APB, SRB and APB were inhibited by plasma treatment.
6.5 Chapter conclusions

This chapter showed that while bicarbonate was removed from oil-field produced water, 4-log reductions were observed for SRB and APB within 5 min plasma treatment with an arc-in-water system, and visually observable organics were degraded within 3 min. Assessment of oil & grease concentration indicated a decrease from 40 mg/L to below 10 mg/L with 5 min plasma treatment.
7.0 Conclusions*

The work presented in this thesis is the best, most up-to-date effort at utilizing plasma discharges to treat industrial wastewaters, in particular, from oil and gas production. The plasma arc-in water system presented in this study showed a range of capabilities in treatment of produced water.

Plasma discharges in water are capable of addressing multiple targets simultaneously. Before the present study, much research of plasma treatment of water was confined to relatively clean water with single treatment targets manually added to such waters. Such laboratory benchtop scale studies, were not able to demonstrate the effects of plasma discharges on actual industrial wastewaters. The present work contributes important understanding to plasma treatment of aqueous solutions, including industrial wastewaters. The extensive studies presented in this thesis utilized produced waters from oil and gas exploration, and demonstrated the impact on organics, bacteria, and the fouling ability of water, with a new fouling prevention method showing the capability to prevent formation of scale. Additionally, this work demonstrated that while CaCO₃ fouling prevention methods usually focus on removal of calcium ions, with calcium ion concentrations many times, 1 – 2 orders of magnitude, higher than bicarbonate, the removal of bicarbonate is a more prudent strategy for fouling prevention. With fouling tests conducted with waters containing limited bicarbonate ions showing no

scale, the safe and effective operation of a distillation unit with feed waters containing high calcium ion concentration, on the order of even $10^4$ mg/L, is made possible.

Results presented in the studies, indicating 10x less scale, was observed for fouling tests with 100 mg/L HCO$_3^-$ as opposed to 500 mg/L, in the presence of 5,000 mg/L of calcium ions. While plasma arc-in-water treatment was capable of decreasing bicarbonate ion concentration to as low as zero, simultaneous effects of sterilization, with 4-log reductions in bacteria characteristic of produced water, and effect on organics, with oil and grease content decreased to below 10 mg/L, were observed. This combination makes application of plasma discharges in water an effective option for consideration in treatment of produced waters. With capabilities to treat real industrial wastes indicated, further engineering enhancements such as those demonstrated by stretching the arc from inside the “plasmatron”, can result in better performance.

To summarize, the contributions of work presented in this thesis include the following:

1. Arc-in-water systems have been shown to have the capability to prevent scale and associated fouling in heat transfer systems by decreasing HCO$_3^-$ concentration of process waters, with generation of H$^+$ ions playing a greater role in this process than local heating, although pH of water was able to be maintained during treatment).

2. While removal of calcium ions is traditionally emphasized as the prominent method of water softening and fouling prevention, this study demonstrated that removal of bicarbonate ions from produced waters is a prudent and effective strategy, capable of preventing fouling even in the presence of feed waters with very high calcium ion concentrations on the order of $10^3$ - $10^4$ mg/L.
3. The arc-in-water system demonstrated simultaneous effects in real “dirty water” including sterilization, showing 4-log reductions in bacteria characteristic of produced water, as well as removal of organics, with oil and grease concentration decreased to below 10 mg/L within 5-min treatment, while previous plasma studies typically have only demonstrated effects with relatively “clean water” and single targets.

A plasma arc-in-water has been shown to have water softening capabilities with the demonstration of the removal of bicarbonate ions from produced waters. Such a system is capable of pre-treating produced water to prevent precipitation fouling caused by CaCO$_3$ in heat transfer systems including distillation units used for desalination. While such a combination of treatment is intended to produce potable water qualities, the effect of plasma pretreatment alone may be viable for re-use of produced water in oil and gas exploration. Organics can be oxidized, while bacteria is inactivated, and water is simultaneously softened through removal of bicarbonate ions. While energy cost must be considered, the removal of bicarbonate ions to levels which make the produced water suitable for both gel frac and slickwater frac operations is of interest. The versatility and multiple-effective nature of a plasma submerged arc makes it a potential tool in the remediation of produced water, and even opens up other possibilities to enhance other technologies, such as distillation, by preventing troublesome fouling problems.
8.0 List of References


18. Capper, L., *Designing an overall water treatment strategy that can minimize the cost of recycling produced water for reuse*, in 5th Shale Play Water Management 2014: Dallas, TX.


Appendix A: Energy costs for plasma tests presented in Chapter 3

Below, Table A1 indicates the energy costs for each of the plasma treatment tests presented in Chapter 3.

Table A1: Energy costs for each plasma test presented in Chapter 3

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Bicarbonate concentration at baseline (mg/L)</th>
<th>Bicarbonate concentration after 10-min plasma treatment (mg/L)</th>
<th>Voltage (kV)</th>
<th>Current (A)</th>
<th>Time to zero bicarbonate (min)</th>
<th>Change in bicarbonate (mg/L)</th>
<th>Energy of power supply over 10 min (kJ)</th>
<th>Energy cost to remove HCO₃⁻ for each 10 min test (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>699</td>
<td>467</td>
<td>2.1</td>
<td>0.1</td>
<td>n/a</td>
<td>232</td>
<td>0.232</td>
<td>0.151</td>
</tr>
<tr>
<td>2</td>
<td>685</td>
<td>475</td>
<td>2.1</td>
<td>0.1</td>
<td>n/a</td>
<td>210</td>
<td>0.21</td>
<td>0.137</td>
</tr>
<tr>
<td>3</td>
<td>778</td>
<td>560</td>
<td>2.1</td>
<td>0.1</td>
<td>n/a</td>
<td>218</td>
<td>0.218</td>
<td>0.142</td>
</tr>
<tr>
<td>4</td>
<td>745</td>
<td>370</td>
<td>2</td>
<td>0.1</td>
<td>n/a</td>
<td>375</td>
<td>0.375</td>
<td>0.244</td>
</tr>
<tr>
<td>5</td>
<td>685</td>
<td>458</td>
<td>2</td>
<td>0.1</td>
<td>n/a</td>
<td>227</td>
<td>0.227</td>
<td>0.148</td>
</tr>
<tr>
<td>6</td>
<td>685</td>
<td>203</td>
<td>1</td>
<td>0.2</td>
<td>n/a</td>
<td>482</td>
<td>0.482</td>
<td>0.313</td>
</tr>
<tr>
<td>7</td>
<td>760</td>
<td>364</td>
<td>2</td>
<td>0.1</td>
<td>50</td>
<td>396</td>
<td>0.396</td>
<td>0.257</td>
</tr>
<tr>
<td>8</td>
<td>747</td>
<td>347</td>
<td>2</td>
<td>0.1</td>
<td>30</td>
<td>400</td>
<td>0.4</td>
<td>0.260</td>
</tr>
<tr>
<td>9</td>
<td>684</td>
<td>317</td>
<td>2</td>
<td>0.1</td>
<td>30</td>
<td>367</td>
<td>0.367</td>
<td>0.239</td>
</tr>
<tr>
<td>10</td>
<td>752</td>
<td>472</td>
<td>2</td>
<td>0.1</td>
<td>30</td>
<td>280</td>
<td>0.28</td>
<td>0.182</td>
</tr>
<tr>
<td>11</td>
<td>685</td>
<td>292</td>
<td>2</td>
<td>0.1</td>
<td>30</td>
<td>393</td>
<td>0.393</td>
<td>0.255</td>
</tr>
<tr>
<td>12</td>
<td>685</td>
<td>83</td>
<td>2</td>
<td>0.1</td>
<td>20</td>
<td>602</td>
<td>0.602</td>
<td>0.391</td>
</tr>
</tbody>
</table>

Appendix B: Calculation of heat losses during fouling test

While losses to the environment during the fouling experiments were not of importance, consideration is given to this factor, as voltage and current data was not
collected, which could have helped verify the 1 kW heating capacity of the industry standard heating element. It should also be noted that results show that the industry standard “1 kW” heater may have been a bit lower, and also that the system was not insulated; this is shown by that fact that calculating the power used to vaporize 26 L of water, this corresponds to a heater power of $P = 0.62 \text{ kW}$ (associated calculations shown in Appendix).

While the heater was submerged in water, (excepting possibly at one unheated end), it is expected that most heater power was at least initially transferred to water, although with the experiment completely uninsulated over the 30 h that the heater was on, losses from the water and boiler vessel to the atmosphere were experienced. As this experimental study focuses on fouling along the heater, losses to the environment were not considered important, although exact data on the heating capacity of the heating element via current, and voltage measurements, could have enhanced this study by providing exact data on heat transfer rate.

$$\dot{E} = \frac{m(c\Delta T + h)}{t} \cdot \frac{E \cdot t}{mc + h}$$

\textit{Heater Power to vaporize water, } $\dot{E}$

$$\dot{E} = \frac{(26 \text{ kg}) \left[ (4.18 \frac{kJ}{\text{kg} \cdot ^\circ C}) (80 ^\circ C) + (2257 \text{ kJ/kg}) \right]}{(30 \text{ h} \cdot 3600 \frac{S}{h})}$$

\textit{Heater Power to vaporize water, } $\dot{E} = 0.62 \text{ kW}$

This implies that the exact heating capacity of the heating element could have been slightly lower than 1kW and furthermore, there were losses from the water and boiler
vessel to the atmosphere, although losses from the heater to the water are not believed to occur as the heater was completely submerged in water.

**Appendix C: Additional data on plasma treatment to support Chapter 3**

During testing for plasma GAD treatment of produced waters, some assessments were taken in somewhat of an ad hoc manner. Data for select tests on calcium ion concentration, and pH during testing are indicated, supporting the observation that in general, calcium ion concentration was not significantly affected, initial decreases in bicarbonate concentration were not accompanied by decreases in pH (as bicarbonate acted as a buffer for the H$^+$ ions generated), but eventually steep decreases in pH were always observed when bicarbonate was brought to levels approaching zero. Furthermore, this appendix contains data on energy cost calculations for select plasma treatment tests, and other brief analysis.

Table A2 provides data for plasma test # 1 as indicated in section 3. This table shows that initial decreases in bicarbonate were not accompanied by decreases in pH.
Table A2: Extra data for select plasma test presented in Chapter 3 – Test # 1

<table>
<thead>
<tr>
<th>Water Properties</th>
<th>0 min</th>
<th>10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bicarbonate (mg/L)</td>
<td>699</td>
<td>467</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>1280</td>
<td>1280</td>
</tr>
<tr>
<td>pH</td>
<td>7.47</td>
<td>8.18</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>25</td>
<td>39</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Power Supply</th>
<th>0 min</th>
<th>10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage (kV)</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Current (A)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculations</th>
<th>0 min</th>
<th>10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Energy (kJ)</td>
<td>0</td>
<td>(2100 V)(0.1A)(10 min)(60s/min) = 126 kJ</td>
</tr>
<tr>
<td>Mass of bicarbonate removed</td>
<td>0</td>
<td>(232 mg/L)(0.65L) = 151 mg</td>
</tr>
<tr>
<td>Energy cost (kJ/kg)</td>
<td>0</td>
<td>126 kJ/0.432 g = 834 kJ/g</td>
</tr>
</tbody>
</table>

Table A2, provides data for plasma test # 6 as indicated in Section 3. This table is provided to help expound on the general nature of the plasma treatment. Data was collected for an additional third data point, providing insight into treatment for durations greater than 10 min. The bicarbonate and pH data at 20 min of treatment is of interest. While the pH remained rather constant or even slightly increased within the first 10 minutes of treatment, by t = 20 min, the bicarbonate concentration approached zero, and the pH indicated that water was acidic. This was typical for most of the plasma treatment tests indicated in Chapter 3.
**Table A3: Extra data for select plasma test presented in Chapter 3 – Test # 6**

Data for select plasma test – Test # 6 in Section 3

<table>
<thead>
<tr>
<th></th>
<th>0 min</th>
<th>10 min</th>
<th>20 min</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bicarbonate (mg/L)</td>
<td>685</td>
<td>203</td>
<td>20</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>1160</td>
<td>1290</td>
<td>n/a</td>
</tr>
<tr>
<td>pH</td>
<td>7.76</td>
<td>7.82</td>
<td>5.04</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>24</td>
<td>37</td>
<td>42</td>
</tr>
<tr>
<td>Water volume* (mL)</td>
<td>650</td>
<td>n/a</td>
<td>570</td>
</tr>
<tr>
<td><strong>Power supply</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voltage (kV)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Current (A)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Energy calculations</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Energy</td>
<td>0</td>
<td>(1000 V)(0.2A)(10 min)(60s/min) = 120 kJ</td>
<td>(1000 V)(0.2A)(20 min)(60s/min) = 240 kJ</td>
</tr>
<tr>
<td>Mass of bicarbonate removed** (g)</td>
<td>0</td>
<td>(402 mg/L)(0.65L) = 261 mg = 0.261 g</td>
<td>(665 mg/L)(0.65L) = 432 mg = 0.432 g</td>
</tr>
<tr>
<td>Energy used to vaporize water (kJ)</td>
<td>0</td>
<td>n/a</td>
<td>E = mhfg = (0.08 kg)(2257 kJ/kg) = 180.6 kJ</td>
</tr>
<tr>
<td>Total energy cost for bicarbonate abatement (kJ/kg)</td>
<td>0</td>
<td>n/a</td>
<td>240 kJ/0.432 g = 555 kJ/g</td>
</tr>
<tr>
<td>Energy cost (kJ/kg) if energy to vaporize water excluded</td>
<td>0</td>
<td>n/a</td>
<td>(240 kJ - 180.6 kJ)/0.432 g = 137.5 kJ/g</td>
</tr>
</tbody>
</table>

*This value assumes that 50 mL samples were not collected at each data point, but indeed such a sample was collected.

** Mass calculations assume there are 650 mL at start and end of test; this assumption produces an error less than 1% in energy cost.

During Test # 6, 12.3% of the initial produced water volume evaporated, although the bulk temperature of the produced water remained below 50 C. With the energy to evaporate the 0.08 kg of water, $E = mh_{fg} = (0.08 \text{ kg})(2257 \text{kJ/kg}) = 180.6 \text{ kJ}$, when this
value is compared to the total energy supplied by the excitation source, Energy = (I)(V)(t) = (1000)(0.2)(20 min x 60 s/min) = 240 kJ, it is clear that 75% of the energy supplied was used to vaporize water (only a small amount was used to heat the bulk water by 18 °C, and that is E = mcΔT = (4.18 kJ/kg/K)(0.65 kg)(18) = 0.049 kJ. This heating and vaporization of produced water upon plasma GAD treatment is characteristic of the small volume of produced water that was treated; it can be expected that for treatment of larger volumes of water, and/or faster flow rates, less of this water would evaporate, and more would re-condense if any evaporation did occur. In addition to increasing water flow rates during treatment, increasing surface contact area between plasma and the produced water could help enhance the ability to modulate bicarbonate ions in water, especially if a local heating effect is to be realized as a contributing mechanism for bicarbonate abatement.

In regard to the mechanism of bicarbonate removal, upon observing the data in Table A3, coupled with the fact that the calcium ion concentration increased by 11.6 % in the first 10 min of treatment, rather than decreased, due to the evaporation of water, it is believed that while the abatement of bicarbonate may be due to multiple mechanisms, the preponderant mechanism is generation of H⁺ ions through one of the mechanisms outlined in Table 8 in Chapter 3. Considering the initial 10 min of plasma treatment as indicated for Test # 6, it would be expected that the decrease in bicarbonate of 482 mg/L for 650 mL would be accompanied by a decrease of calcium ions in a mole ratio of 2:1, if the local heating mechanism (previously indicated in section 3 but indicated below) was the preponderant mechanism of bicarbonate removal, given these chemical equations:

\[ HCO_3^- \rightarrow OH^- (aq) + CO_2 (g) \uparrow \]
With 2 moles of bicarbonate consumed per mole of calcium, the mass ratio would be: (2 moles Bicarbonate) x (61 grams/mol) = 122 grams, compared to (1 mole of calcium) x (40 grams/mol) = 40 grams. Hence the ratio of bicarbonate to calcium consumption should be: 3.05:1, so given that (0.482 g/L)(0.65L) = 0.313 g of bicarbonate was removed from produced water, it is expected that 0.313/3.05 = 0.103 grams of calcium would be removed from produced water, or more specifically, given that 0.65 L of produced water was treated, this would have resulted in decrease in calcium ion concentration of 0.103g/0.65L = 0.158 g/L, or 158 mg/L. This 158 mg/L of calcium would represent a 13.6 % decrease in calcium ion concentration, and taking into consideration the increase in ion concentration due to evaporation, of water, this should have resulted in a stable calcium ion concentration.

Still, considering that less than 12.3% of the produced water was evaporated, it is possible that local heating (the only currently proposed mechanism which includes calcium ion removal) did effect the calcium ions. Given the vaporization rate, it can be expected that without any other effects such as precipitation, etc. ion concentration including that of calcium would increase 12%, giving a calcium ion concentration of 1.123 x 1,160 mg/L = 1,303 mg/L. Since the calcium ion concentration was 1,290 mg/L at t= 10 min, it is possible that some calcium was removed although it is not large enough of an effect that it is outside the bounds of a measurement error. For test case # 6, if the local heating effect did remove calcium ions, it only removed on the order of 10 mg/L.
Appendix Table A4 shows additional data for plasma tests # 8, one of the tests that was allowed to continue, until bicarbonate was completely removed from produced water. This data follows the same trend of exhibiting a steep decrease in pH as bicarbonate concentration approaches zero.

<table>
<thead>
<tr>
<th>Water Properties</th>
<th>0 min</th>
<th>10 min</th>
<th>30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bicarbonate</td>
<td>747</td>
<td>347</td>
<td>0</td>
</tr>
<tr>
<td>Calcium</td>
<td>1040</td>
<td>1040</td>
<td>1080</td>
</tr>
<tr>
<td>TDS</td>
<td>33,500</td>
<td>33,000</td>
<td>36500</td>
</tr>
<tr>
<td>pH</td>
<td>7.93</td>
<td>7.64</td>
<td>3.78</td>
</tr>
<tr>
<td>Temp</td>
<td>24</td>
<td>35</td>
<td>44</td>
</tr>
<tr>
<td>Water volume</td>
<td>650</td>
<td>n/a</td>
<td>550</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Power Supply</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Current</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculations</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Energy</td>
<td>n/a</td>
<td></td>
<td>(2000 V)(0.1A)(10 min)(60s/min) = 120 kJ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(2000 V)(0.1A)(30 min)(60s/min) = 360 kJ</td>
</tr>
<tr>
<td>Mass of bicarbonate removed</td>
<td>n/a</td>
<td>(400 mg/L)(0.65L) = 260 mg = 0.260 g</td>
<td></td>
</tr>
<tr>
<td>Energy cost (kJ/kg)</td>
<td>n/a</td>
<td>120 kJ/0.260 g = 555 kJ/g</td>
<td>(747 mg/L)(0.65L) = 486 mg = 0.486 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>360 kJ/0.486 g = 741 kJ/g</td>
</tr>
</tbody>
</table>

Results of brief tests, performed with nitrogen and argon using the plasma GAD set-up in water are shown in Table A5. These tests were conducted to provide further comment on the mechanism of plasma-induced bicarbonate removal, by isolating the potential proposed mechanisms such as that most dependent on the effect of using air as a
carrier gas. Hence, without air as a carrier gas for plasma treatment of produced water, nitric acid should not form for the case of argon as a carrier gas, and if it forms in the case of using nitrogen as a carrier gas (with oxygen required to form nitrates potentially coming from water, through direct electron impact with water \([59, 123]\)), it should not result in as great of an effect on the decrease in pH. The results of bicarbonate and pH assessment upon plasma treatment of produced water using argon plasma and nitrogen plasma are shown below in Table A5:

Table A5: Extra data for select plasma test presented in Chapter 3 – Tests with different carrier gases

<table>
<thead>
<tr>
<th>Carrier gas used for test</th>
<th>Baseline</th>
<th>Plasma treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 min</td>
<td>10 min</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 7.37</td>
<td>HCO$_3^-$ = 685;</td>
<td>HCO$_3^-$ = 685;</td>
</tr>
<tr>
<td>Argon</td>
<td>pH = 7.37</td>
<td>pH = 8.54</td>
</tr>
<tr>
<td>HCO$_3^-$ = 470;</td>
<td>HCO$_3^-$ = 448;</td>
<td>HCO$_3^-$ = 444;</td>
</tr>
<tr>
<td>pH = 7.37</td>
<td>pH = 8.59</td>
<td>pH = 8.75</td>
</tr>
<tr>
<td>Argon</td>
<td>HCO$_3^-$ = 501;</td>
<td>HCO$_3^-$ = 546;</td>
</tr>
<tr>
<td>pH = 7.37</td>
<td>pH = 8.46</td>
<td>pH = 8.65</td>
</tr>
<tr>
<td>Argon</td>
<td>HCO$_3^-$ = 514;</td>
<td>HCO$_3^-$ = 458;</td>
</tr>
<tr>
<td>pH = 7.37</td>
<td>pH = 8.58</td>
<td>pH = 8.52</td>
</tr>
</tbody>
</table>
It should be noted that the test with nitrogen as a carrier gas resulted in 90 mL of water being vaporized in 40 min, while tests with argon as a carrier gas resulted in the vaporization of 30, 40 and 50 mL respectively, of produced water during testing.

**Appendix D: Water assessment techniques utilized in this thesis:**

The quantification of Adenosine Triphosphate (ATP) in water was used as a method to determine microbial content in water. Living cells contain adenosine triphosphate (ATP) which serves as the universal energy donor for metabolic reactions, and ATP bioluminescence is a technique for estimating microbial activity [121]. In this technique, an enzyme-substrate complex, luciferase-luciferin, converts the chemical energy associated with ATP into light by a stoichiometric reaction, making the amount of light emitted proportional to the concentration of ATP present [121]. Using a luminometer to measure bioluminescence in relative luminescence units (RLUs), upon comparison with a calibration solution for RLUs, this measurement can be converted to cellular ATP units of pictograms of ATP/mL [122]. Further, for the tests presented in this thesis, cATP units are converted into Microbial equivalents (ME’s) based on the established conversion that 1 E. coli-sized bacteria contains 0.001 pg of ATP [122]. This allows the results of ATP assessment to be communicated on the same basis as traditional culture tests. The kits used to facilitate this measurement technique were quench-gone test kits (LuminUltra Technologies, LTD). This assessment of ATP was utilized as a relatively quick method, of assessing the microbial life in water samples, as it is a direct indicator of total living biomass, or planktonic population [122].
The amount of Sulfate Reducing Bacteria was assessed. Commercially available bottles of Modified Postgate’s B (OSP Microcheck Inc.) were used for the measurement of SRB in produced water. The bottles used in this thesis were red colored topped bottles specified for brines having a TDS over 100,000 mg/L. For this test procedure, bottles are incubated and maintained at a constant temperature of 35 ± 0.5 °C. A positive reaction, i.e., presence of SRB, is indicated by the contents of the full height of a bottle turning to a black color. If the contents of this bottle do not turn black over the course of 10 days, then no SRBs are present. The interpretation of color change for the assessment bottles follows the following guide:

<table>
<thead>
<tr>
<th>Interpretation of color change</th>
<th>Days to turn positive</th>
<th>SRB (cfu/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 - 2</td>
<td>10,000 +</td>
</tr>
<tr>
<td></td>
<td>2 - 4</td>
<td>1,000 - 10,000</td>
</tr>
<tr>
<td></td>
<td>4 - 6</td>
<td>100 - 1,000</td>
</tr>
<tr>
<td></td>
<td>6 - 8</td>
<td>10 – 100</td>
</tr>
<tr>
<td></td>
<td>8 - 10</td>
<td>1 – 10</td>
</tr>
<tr>
<td></td>
<td>10 +</td>
<td>Negative</td>
</tr>
</tbody>
</table>

Following the trend of these instructions, the following equation was utilized for this study to compare results of SRB assessment.

\[
SRB \ (CFU/mL) = 10^{\frac{10-(Day \ turned \ positive)}{2}}
\]
For results in which the bottle did not turn black by day 10, this value was recorded as “< 10⁰ (SRB inhibited)”.

The amount of Acid Producing Bacteria in water was assessed. APB in produced water was assessed using a serial dilution method. Bottles of Phenol Red Dextrose (Gold Cap for over 10 % of TDS, OSP Microcheck Inc.) were used as culture media. These bottles were incubated and maintained at 35 ± 0.5 °C over the duration of 14 days. A positive reaction, i.e., presence of APB, would be indicated by the contents of the bottle appearing yellow. Given the serial dilution, the MPN number was obtained on a logarithmic scale. While the contents of each clear bottle started out red on day one, on day 14, the changing of color to yellow, or the lack thereof a change would be monitored. The changing of color of each bottle to a yellow color represented an order of magnitude of bacteria, i.e. one yellow bottle would mean 10¹, while 6 yellow bottles on day 14 would represent 10⁶. Hence, the equation for this relationship could be represented by:

\[
APB(CFU/mL) = 10^{(# of samples turned yellow i.e. positive on day 14)}
\]

NACE Standard TM0194-2004 was used for the counting of SRB and APB in produced water.

Hardness, in regards to describing water, usually refers to the content of calcium and magnesium ions. Depending on the range of calcium in water, various kits were utilized to assess hardness, usually from Hanna Instruments. These kits included, for high range (400 – 3,000 ppm) - HI 3842; for middle range (40 – 500 ppm) HI 3841; and for
low range (0 - 500 ppm) – HI 38033. In most cases in assessing produced waters, samples had to be diluted to obtain measurements in the range of these test kits. The general scheme for these hardness tests is EDTA-titration method (EPA 130.2).

Total alkalinity of produced water was assessed using test kits, from Hanna Instruments, one of which was HI 38014 (0 – 8,500 ppm).

pH was measured using a pH meter (Thermo Scientific Orion Star A215 pH/Conductivity Benchtop Meter Kit). This pH meter was calibrated prior to each use for the day.
Vita
of
Kamau Wright
Kamau.Wright@drexel.edu

Education

<table>
<thead>
<tr>
<th>Degree</th>
<th>Field</th>
<th>Institution</th>
<th>Year</th>
</tr>
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<tbody>
<tr>
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<td>Mechanical Engineering &amp; Mechanics</td>
<td>Drexel University</td>
<td>2015</td>
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</tr>
<tr>
<td>Bachelor of Science</td>
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</tr>
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</table>

Publications

Archival Journal Papers


Unpublished Theses and Technical Reports


Engineering Education Papers
