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Treatment Of Bakken Produced Water Using Supercritical Water Desalination

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TREATMENT OF BAKKEN PRODUCED WATER USING SUPERCRITICAL
WATER DESALINATION

by

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May 05, 2020

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For my dad Joel, my mom Emily,

my sister Esther,

my brothers Emmanuel and Daniel.

The most compassionate and genuine family!

ABSTRACT

Recent advances in horizontal drilling and hydraulic fracturing have significantly increased freshwater usage. Oil and gas wells in the United States tend to generate over 23 billion barrels of produced water per year of which about 32 million b/day are high total dissolved solids (TDS > 200,000 mg/L) while the world is gradually running short of fresh water. Environmental concerns associated with water usage and concentrated wastewater disposal have led to the growing consideration to treat and recycle brine for reusable purposes like crop irrigation, livestock watering and hydraulic fracturing.

In this study, an emerging and promising technology called supercritical water desalination (SCWD) has been developed. The aims of this study were to treat Bakken oil field brine, examine the applicability of the product water for reuse and evaluate the performance of supercritical water desalination. The results showed that at 240 bar water recovery efficiency from Bakken produced water increased with critical temperatures T_c above 400ºC. Subsequently, the investigated additives proved to be excellent in the destruction of organics (~ 98% reduction efficiency) and targeted salt precipitation (~ 99% salt removal). The resulting ion analysis of the effluent stream demonstrates the SCWD approach as a highly efficient means for water recovery (~ 99% efficiency) with potential for zero liquid discharge (ZLD). SCWD is the most efficient, reliable and environmentally friendly technology, compared to conventional desalination treatments like reverse osmosis (RO), multistage flash (MSF), multieffect distillation (MED) and vapor compression distillation (VCD). The evaluation of the product water for livestock watering, irrigation and hydraulic fracturing demonstrates the SCWD technology as the most robust standalone method to treat hypersaline brine and produce high-quality product water.

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CHAPTER 1: INTRODUCTION

1.1   General Background

U.S oil and gas production has increased significantly over the past 10 years due to advances in unconventional drilling and production techniques that allowed economic access to shale and tight formations. According to the EIA, in 2019 the U.S annual crude oil production of about 4.5 billion barrels (23% and 11% higher than the total production in 2017 and 2018 respectively) surpassed the previous record of 4 billion barrels set in 2018 [1]. With U.S becoming the global leading producer of oil and natural gas, total productions are projected to average 4.8 billion barrels and 4.9 billion barrels in 2020 and 2021 respectively [2].

Shale and tight plays accounted for 70% of total U.S dry gas production and 60% of crude oil production in 2018. Natural gas production recorded an average of 111.5 billion cubic feet per day (Bcf/d) in 2019, a 10% increase from the 2018 average [3]. The Permian basin, Eagle ford and Bakken in **Figure 1.1**, are three key plays that currently contribute about 82 % of total U.S shale and tight oil production [4].

The Bakken play considered the biggest oil and gas discovery in the last decade is a major natural gas producer in the U.S. However, this achievement is accompanied by generation of large quantities of hyper saline wastewater (flow back, produced or oilfield brine) during oil and gas extraction. The oil and gas industry use large volumes of water to enhance production during drilling and hydraulic fracturing of both conventional and

unconventional wells. Hydraulic fracturing fluids injected into the oil and gas wells mixes with formation water and flow back to the surface as saline wastewater.

Oil and gas wells in the United States on average tend to generate over 23 billion barrels of produced water (>40% of this is discharged into the environment) per year of which about 32 million b/day are high TDS (>200,000mg/l) flowback and produced water (F/P) [5] [6] . This represents a growing concern for the potential effect on water usage and their environmental impact. It would be desirable to reduce the TDS sufficiently to access high value water markets in the petroleum industry, for crop irrigation, livestock and other industrial uses. Hence, effective treatment technologies are required for recycling hypersaline brine.

Recycling of F/P water for use in the petroleum industry include drilling and workover operations such as fracking which requires a water quality < 70,000 mg/L total dissolved solids (TD) [7]. Currently oil field wastewater is managed through mechanisms such as deep-well injection, treatment and discharge to surface as well as direct reuse. Unlike produced water from shale formations like Permian, Niobrara and Eagle Ford. Bakken oilfield brine have high levels of TDS and must first be treated before recycle [8] [9]. They are typically very saline with total dissolved solids (TDS) in the range of 200,000mg/L to 350,000mg/L [10].

Conventional wastewater treatment technologies such as Reverse Osmosis (RO), Multieffect distillation (MED), Multi-stage distillation (MSF) and Microfiltration (MF)

which typically treats salt water with TDS < 45,000mg/L may be inadequate for accepting the Bakken oilfield produced water due to membrane fouling, inability to remove NORM and generation of highly concentrated secondary brine (> 45,000mg/L) [10] . Therefore, highly efficient treatment systems for oil field brine in shale producing areas would mitigate the environmental impact and improve water usage required for the development of unconventional oil and gas in the U.S. Thereby creating a market opportunity for water technologies capable of handling hypersaline brine.

A proposed treatment technique is the Supercritical Water Desalination (SCWD) process with high potential for zero liquid discharge (ZLD). SCWD uses the principle of decreasing salts solubility at the critical point of water (221 Bar & 374°C). This occurs as a result of water's significantly weakened hydrogen bond, diminished density, ion product and static electric constant. Thus, changing the behavior of water in a supercritical state from a polar solvent to non-polar solvent. The solubility of each salt constituent essentially drops, resulting in removal of large amounts of dissolved solids within the supercritical region.

In this study, Bakken produced water samples from different well locations in western North Dakota have been obtained and a treatment method has been developed to reduce the dominant inorganic ions such as Na^+, Cl^-, Ca^{2+}, Mg^{2+}, K^+ and Ba^{2+} (> 91%) [10]. The main goal of this project is to demonstrate SCWD as an effective technology for removal of organic and inorganic components present in produced water.
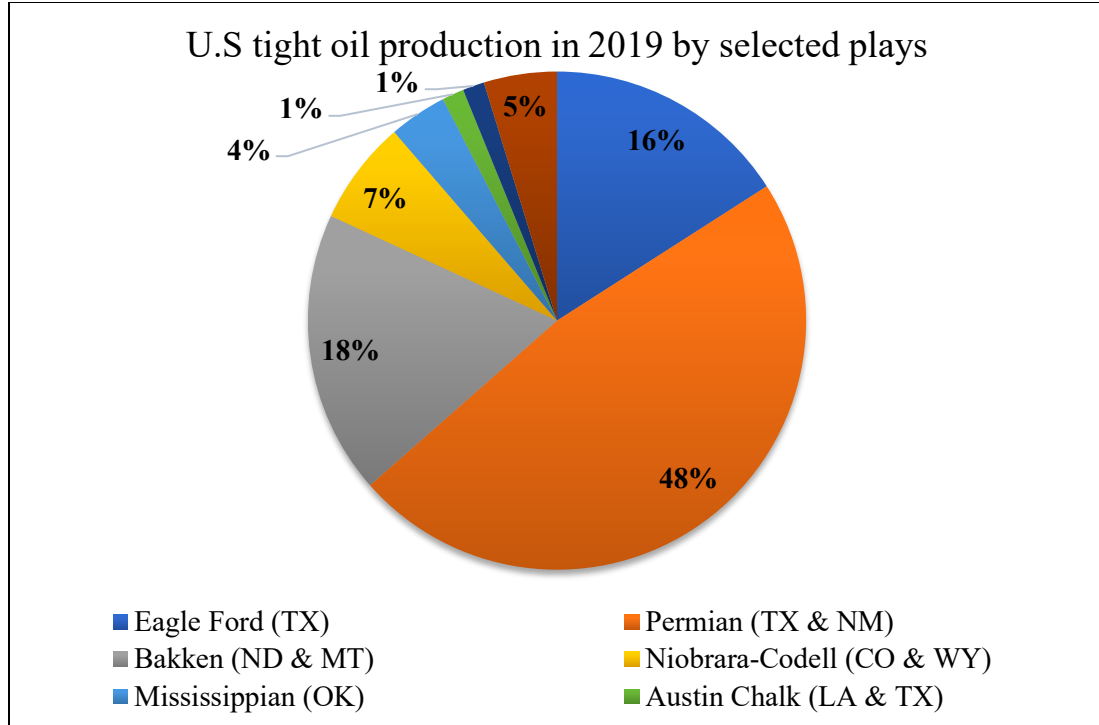
Figure **1.1**: Contribution of key plays to total U.S shale and tight oil production [4].

1.2   Research Objective

This study aims to evaluate the performance of a new and innovative approach (Supercritical Water Desalination) to recycle high TDS oil field brine (produced water) thereby reducing environmental impact and improving management of water usage associated with oil and gas production in the U.S. This work applies the principle of supercritical fluids to remove inorganic compounds from aqueous streams at conditions above the critical point of water (374°C, 221 bar). Supercritical water oxidation (SCWO) which makes use of increased solubility of oxidants is also used during SCWD to decompose and destroy the organic compounds present.

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This research is conducted by subjecting produced water samples obtained from various wells in the Bakken formation to conditions determined during a preliminary experiment of $NaCl$-H_2O solutions. Ion composition from the raw produced water samples has been analyzed and obtained. The treated effluent samples will be compared with compositional guidelines for livestock watering, irrigation and hydraulic fracturing water. This will be employed to evaluate the performance of the SCWD system for recycling.

1.3   Thesis Outline

This chapter details the introduction, objective and outline of this study. A literature review on hydraulic fracturing, produced water compositions and conventional desalination technologies is presented in Chapter 2. This chapter also presents merits and significant drawbacks of these technologies in treating produced water.

Chapter 3 briefly summarizes the supercritical water process and concepts employed in this treatment system. Temperature and pressure behavior relating to solubility and salt removal are explained. Merits and limitations associated with this process are also highlighted.

Chapter 4 introduces the methodology, sample preparation procedure and experimentation. Methodology describes the procedure in $NaCl$-H_2O experiment and adjustments made during PW experiments.

Chapter 5 briefly presents evaluation on the preliminary results obtained from NaCl-H_2O experiment. It discusses the organic oxidation process and inorganic ion separation efficiency in PW experiment.

Chapter 6 discusses application of the treated streams for livestock watering, irrigation and hydraulic fracturing. It also evaluates the performance of the supercritical water desalination technique.

Chapter 6 states the conclusions derived from this work and recommends potential areas for future development.

CHAPTER 2: LITERATURE REVIEW

The energy industry uses a tremendous amount of water for various applications, including oil & gas operations, power plants and coal mining. The petroleum industry is particularly one of the largest consumers. Increasing global energy demands combined with recent advances in horizontal drilling and hydraulic fracturing have increased oil and gas production from unconventional sources such as shale formations, tight sand and coal bed methane (CBM). Due to loss in reservoir pressure during extraction, water is injected into the producing well to maintain hydraulic pressure and increase oil recovery. Oil and natural gas produced from shale formations are trapped in low permeability fine-grained sedimentary rocks that require some level of fracturing to extract. Tight sand formations contain trapped oil and gas in low permeable limestone or sandstone rocks while coalbed methane is extracted by depressurizing coal seams found within coal reservoirs. **Figure 2.1,** shows key shale gas and tight oil regions in the U.S.

U.S. crude oil production from unconventional wells in tight oil formations increased by 81% from 2004 to 2018. While in shale formations, natural gas production from unconventional wells increased by 83% within the same period [11]. Oil and natural gas from tight sands and shale formations currently account for about 60% of the U.S total crude oil production [3]. Presently, the Permian, Bakken and Eagle Ford are the three largest producing plays in the country.
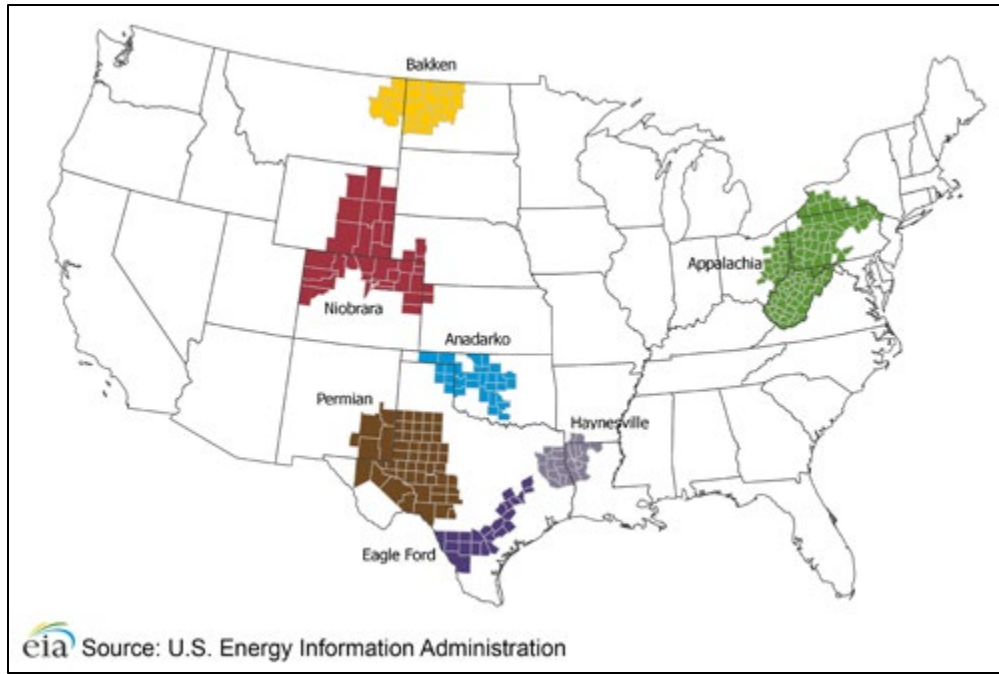
Figure 2.1: key tight oil and shale gas plays in the U.S. [12]

2.1   Bakken Shale

The U.S has the largest deposits of shale reserves in the world. Seven major shale plays are largely responsible for the U.S oil and gas growth and include the Marcellus Shale and Utica shale in the Appalachia region, Bakken shale in North Dakota, Haynesville in eastern Texas to northwestern Louisiana, Niobrara shale in Colorado and western Wyoming, Eagle Ford Shale in south Texas, and the Permian Basin in western Texas [13]. The Bakken shale in North Dakota currently contributes 13% of the total crude oil production in the United States [12].

A majority of the oil production in the Bakken shale comes from the formation in North Dakota which has an estimated 7.4 billion barrels of recoverable reserves [13]. The Bakken formation has seen a tremendous increase in crude oil output from 180,000 b/day in 2008 to average of 1,400,000 b/day in 2019 while natural gas production presently averages 2.9 Bcf/d [12]. After Texas, North Dakota has been the second largest crude oil producing state since 2012 [14].

2.1.1 Bakken formation water

The Bakken Shale comprises of three distinct members, the Upper, Middle and Lower Bakken. The oil producing Middle Bakken member is composed of silt-sized dolomite, carbonate and silicate minerals. The Upper and Lower members are high in organic matter with an average of 8% and 10% of TOC respectively [15]. The depositional environment of the Middle Bakken was coastal marine and later transgressed into the Upper Bakken deep marine environment [15].

Produced water from the Bakken shale is generally characterized with high total dissolved solids (TDS). This poses significant challenges of scaling and corrosion during production as well as environmental impact of its management and disposal [10]. Several researchers have investigated the correlation of produced water constituents with their parent oil bearing formation [8] [10] [16]. Dissolved salts in the brine (mainly NaCl; 90%) originate from halite deposits formed within the oil and gas-enriched shale formations.

The Bakken formation water is typically very saline due to dissolved salts such as halite and anhydrite [10]. Since constituents of produced water vary with location and geology of the formation, water chemistry is essential for understanding produced water quality from oilfields in the Bakken and to determine the appropriate treatment technique to be employed. For example, calcium, magnesium, potassium and barium which are readily found soluble in produced water, are abundant in formation rocks likes limestone and dolomite. However, strontium and barium are not abundant in the Bakken [8]. After interaction of hydraulic fluid with formation rocks, chemicals present in the formation rock will be found in measurable quantity in produced water [8] [16].

2.2   Hydraulic Fracturing

Horizontal drilling and hydraulic fracturing have been significantly utilized for the economic recovery of shale oil and gas in the Bakken. Fracking (hydraulic fracturing) involves pumping 90% - 95% water mixed with 0.5% – 2% chemical additives (acids, surfactants, clay stabilizer, scale inhibitors etc.) and proppant (silica or sand used to hold the fissures open) under high pressure to enhance formation permeability and porosity. This is done to ease the flow of trapped oil and gas from the low permeable formation to the wellbore [17]. At initial stages of the fracking process, injected fluid mixed with formation water tends to return to the surface. This fluid is referred to as flow back water [18]. Flow back represents the initial portion of injected fluid that return to the surface from a few hours to several weeks after hydraulic fracturing. It consists about 8% - 80%

of the hydraulic fracturing fluids, dissolved compounds and minerals from the rock formation and hydrocarbons [19] [20].

2.2.1 Hydraulic Fracturing Fluids

Based on various literatures, common chemical additives found in fracking fluid are listed in **Table 2.1**. Information on the type of chemicals compounds used is only limited to the additives not inhibited by proprietary protection.

The large quantity of water mixed with highly variable and complex compounds used as fracturing additives underlines the need to comprehend the interaction of the injected fluids with formation water. As well as the environmental implication of the subsequent flowback water and produced water composition. Since shale gas development requires significant amount of water for drilling and hydraulic fracturing, the next section tries to quantify the amount of water used as reported in the literature.

Table 2.1: Common chemical additives present in hydraulic fracturing fluids [20] [21] [22].

Chemical Additives	Uses	Common chemical compounds
Proppants	Hold fissures open for flow of trapped hydrocarbon from fractured formation to the production well.	Silica sand, quartz; ceramic proppant
Gelling agents	Used to increase fluid viscosity to suspend and carry the proppants into the fractures.	Guar gum, cellulose; alcohols
Acids	Adjust pH of the fracturing fluid and dissolves carbonate minerals to create channels in the wellbore.	Fumaric acid; acetic acid; sulfuric; hydrochloric acid
Clay Stabilizers	Inhibits clay swelling with the shale formation that can block pores and reduce flow.	Potassium chloride; tetramethyl ammonium chloride
Iron controllers	Prevents oxidation and precipitation ferric iron that could block rock formation.	Citric acid; thioglycolic acid; sodium erythorbate
Crosslinkers	Increases viscosity of the fracturing fluid to carry proppants as temperature increases.	Potassium hydroxide; ammonium chloride; borate salts; ethylene glycol
Biocides	Inhibits biological activity such as bacteria growth in the wellbore that can prevent fluid flow and corrode well casing and tubing.	Benzalkonium chlorides; glutaraldehyde; 2,2-dibromo-3-nitrilopropionamide
pH adjusters	Controls the pH of the fluid to increase the efficiency of other additives such as controllers.	Acetic acid; potassium or sodium carbonate; sodium hydroxide
Friction reducers	Reduces friction to permit injection of fracturing fluid at optimum conditions; also used as gelling agents' alternatives.	Petroleum distillates; 2-propenamide
Surfactants	Used to reduce surface tension, improve viscosity and recovery of fracturing fluids.	Isopropyl Alcohol; naphthalene; ethylene glycol; Lauryl Sulfate
Breakers	Degrades crosslinking and reduces viscosity of gelled fluid for easy recovery.	sodium chloride; peroxydisulfate
Scale inhibitors	Prevents the deposition of carbonate, iron and sulfate scales from plugging wellbore and pipes in the formation.	Polycarboxylate; methylene phosphonic acid
Corrosion controllers	Prevents the formation of rust by decreasing the effects of corrosive acids and salts on well casings, pipes and tubes.	Ammonium bisulfite; amines; acetone; isopropanol; acetaldehyde

2.2.2   Frack Water Volume

Water used during fracking is larger than any other well development process. The quantity of water utilized depends on the type of well drilled and the fracturing stage (diluted acid stage and proppant stage) [23]. **Figure 2.2** shows the average volume of water used per well in four major shale plays in the U.S. Horizontal wells typically require more water than vertical or direction wells due to long extensive horizontal sections. Generally, an average of 600,000 gallons and 3 - 4 million gallons are used for drilling and hydraulic fracturing in horizontal wells, respectively. An average of 500,000 gallons of water is used in vertical and directional wells for fracking [23] [24].

Furthermore, water usage varies by geologic formations due to variation in lateral length of the formation. For example, based on Chesapeake Energy operating data an average of 3.3 million gallons and 4.5 million gallons of water were used in the Barnett shale, and Marcellus shale, respectively. While Eagle Ford and Haynesville shale had an average of 4.9 million and 5.4 million gallons per well as shown in **Figure 2.2** [24]. The water volume for fracturing a well in North Dakota's Bakken play currently requires 1 million to 5 million gallons a day, depending on the number of stages (Multi-stage or Single stage) [25] [26]. Water consumption levels will continuously grow with technological advancement and increasing energy demand. The North Dakota Mineral Resources (NDDMR) estimates that demand for water in the next few decades will be within the range of 20 million to 30 million gallons per day [26].
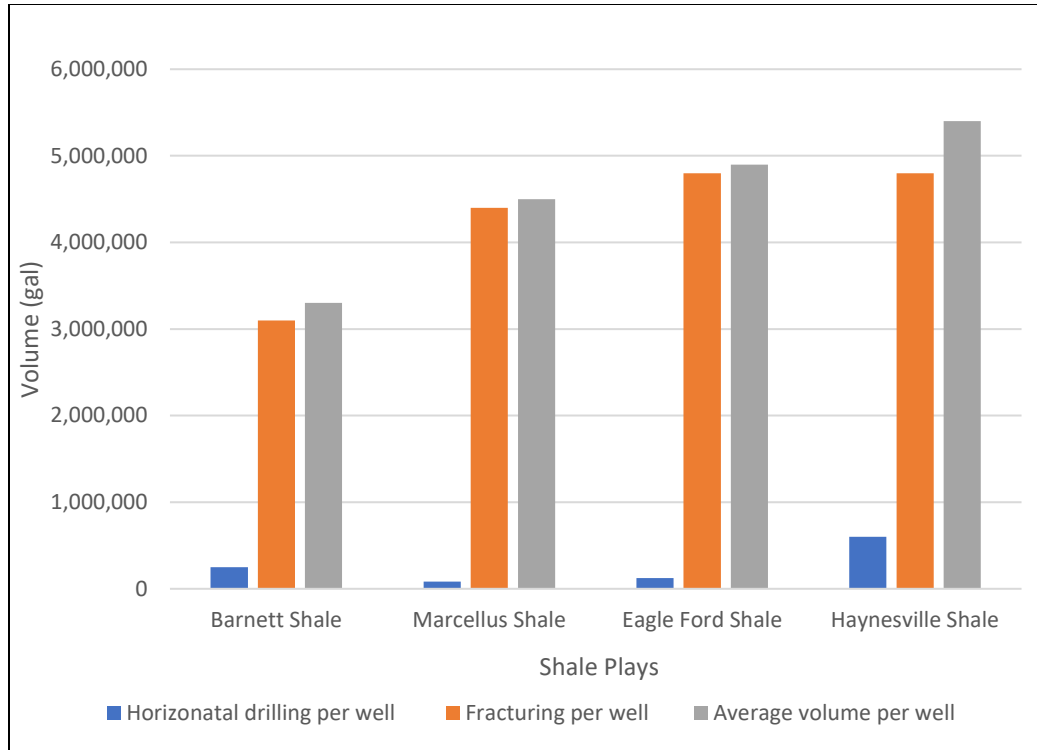
Figure 2.2: Estimated volume of water per well in four major shale plays [24].

According to the North Dakota State Water Commission (NDIC), hydraulic fracturing in North Dakota's Bakken shale currently accounts for approximately 4% of total freshwater consumption [27]. However, the Bakken like every other semi-arid area with growing environmental concerns surrounding freshwater usage may utilize alternative sources of water for industrial processes. This will reduce the impact of freshwater withdrawals (such as depletion) from surface and groundwater reserves.

2.2.3   Water Sources

Water used for fracturing are withdrawn from freshwater distribution sources such as water depots and transported to wellsites. These depots either obtain water from surface or ground water reserves. The most common source of surface water in the Bakken is from the Missouri river and Lake Sakakawea. Oil industries in North Dakota acquire large volumes of freshwater from the Missouri river system for hydraulic fracturing [28] [29].

The U.S Army Corps of Engineers set withdrawal limits from Lake Sakakawea and the Missouri river to 10.3 billion gallons per year. While about 3.7 billion gallons of groundwater is permitted for withdrawal every year while [25]. In 2016, Horner et al. [29] concluded that the obtainable ground water in ND was inadequate to meet the increasing freshwater demand. To compensate for the groundwater supply, the U.S Army Corps of Engineers permitted an annual surplus of 32.5 billion gallons available for withdrawal from Lake Sakakawea [29]. Although the North Dakota State Water Commission (NDSWC) believes there is adequate supply from surface resources. Access and transportation to the Missouri River system remain a critical concern to oil developers [29].

Another possible source of water for the Bakken oil recovery is the treatment and use of brackish groundwater, flowback and produced water. Although the economics of treatment technologies on a commercial scale remains a daunting challenge. Benefits of

recycling produced water indicate a viable environmental and economic advantage to consider. For example, the recovery of valuable materials such as lithium-ion for energy production in batteries, lithium carbonate for treating eating disorders and mental illnesses. The extraction of valuable mineral is not only environmentally friendly but also provides resource opportunities to offset the energy penalty associated with desalination technologies.

2.3   Produced water

Produced water (oilfield brine) is saline water that returns to the surface along with hydrocarbon during oil and gas production. It is a mixture of injected hydraulic fracture fluid, hydrocarbons and naturally occurring water (formation water) [30]. Produced water represents the largest volume of byproduct stream associated with oil and gas production. In a 2017 report, Groundwater Research & Education Foundation (GREF) estimated over 23 billion barrels of oilfield brine are generated every year in the U.S [31]. According to NDIC, North Dakota generated 505 million barrels of produced water in 2017, with 73% from unconventional active oil wells (12,434 active wells) and 27% from conventional oil wells (2,577 active wells) [31].

Increasing demand for freshwater has created new technological opportunities for wastewater recycling. Produced water (also known as brine or saltwater) typically ranges from saline (< 35,000 mg/L) to hypersaline saline (> 50,000 mg/L) TDS levels [32]. It contains a variety of inorganic and organic compounds that can be extracted and reused.

Highly efficient treatment methods would be required to recycle produced water for purposes such as irrigation, livestock watering, and other industrial processes. Therefore, the compositional characteristics of produced water coupled with current management options will be reviewed following this section.

2.3.1 Characteristics of Produced water

Oil field brine exhibit chemical properties of the formation rock (reservoir) from which they were produced. The quality and quantity of PW can be complex and vary considerably depending on the location, the geochemistry of the formation and the type of hydrocarbon [7]. **Table 2.2** shows concentrations of chemical components found in produced water from shale plays in the U.S. [33, 34, 25, 35, 36].

Flowback and produced water quality changes with location and time. Based on volume, Duraisamy et. al. suggested gas wells often discharged produced water 10 times more toxic that their counterpart oil wells, but volumes are significantly lower in the former [37]. Based on time, composition and volume within the same well or differing wells, changes as the well ages [7].

In the literature, produced water constituents can be classified into.

- Oil and Grease
- Benzene, ethyl benzene, xylene and toluene (BTEX) – BTEX are volatile aromatic compounds present in amounts less than 100 mg/L. They are readily found in

produced water and escape to the atmosphere during treatment. Fakhru'l-Razi et al. [33] reported concentrations commonly ranges from 0.39-35 mg/l.

- Dissolved gases – PW usually contains large amounts of CO_2, H_2S and O_2 which are formed due to bacterial activities in water [38].

- Dissolved and dispersed oil compounds – BTEX, aliphatic hydrocarbons, carboxylic acid, Polyaromatic Hydrocarbons (PAHs) and heavy alkyl phenols like C_6-C_9 [39].

- Dissolved minerals – Inorganic compounds (dissolved salts), heavy metals and natural occurring radioactive materials [38]. The chemistry of produced water is significantly affected by the presence of cations and anions. Sodium, potassium, calcium, magnesium, barium, strontium and iron (Fe^{2+}/ Fe^{3+}) are cations readily found in produced water, while anions present include chlorine, sulfate, carbonate and bicarbonates Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^- [38]. The salinity of the produced water is determined mainly by the amount of sodium and chloride ($< 300,000$mg/l) present. Both represent about 81% in produced water from conventional wells and 90% from unconventional wells [30]. Strontium, calcium, magnesium, potassium, barium are also present in smaller amounts and are responsible for the scale forming potential and conductivity of the water [6].

- Heavy metals and Naturally Occurring Radioactive Materials (NORM) – Concentration of heavy metals such as cadmium, chromium, copper, lead, nickel,

silver, and zinc are several times higher than those found in seawater [38]. 226Ra and 228Ra and barium are the most abundant NORM compounds in PW [31].

- Production solids and chemicals – Solids include corrosion and anti-scale products, waxes, clay, carbonates, silts, proppant, $BaSO_4$, Fe_2O_3 and SiO_2 [33] Chemicals include, clay stabilizer, corrosion inhibitors, scale, biocides, paraffin inhibitors, defoamers, breakers, and coagulants. etc.

- Organic acids and phenols – Formic acid, hexanoic acid, pentanoic acid, acetic acid butanoic acid and propanoic acid. Gas field produced water are reported to have higher concentrations of phenols than oil field produced water [31].

- Conductivity, salinity and total dissolved solids (TDS) – The conductivity and TDS levels of produced water vary depending on the location of the well, geology of the formation and the type of hydrocarbon extracted. For example, a study conducted by Stephan et al. [40] on produced water from the Bakken reported a conductivity range of 205,000 to 220,800 µS/cm as shown in **Table 2.2** In another research conducted in Barnett shale play, the conductivity was found to be in a range of 34,000–179,000 µS/cm [41]. Based on TDS levels, Hayes et al. [42] reported a range of 680 – 345,000 mg/L.

Table 2.2: Compositional concentration in produced water from three major shale plays.

Parameter	Bakken [25]	Barnett [35].	Marcellus [36].
Conductivity (μS/cm)	205,000-220,800	34,800-179,000	479-763,000
pH	5.47-6.53	6.5-7.2	4.9-8.4
TOC (mg/L)	-	6.2-36.2	1.2-5,680
TDS	150,000-219,000	16,400-97,800	680-345,000
Chloride (mg/L)	90,000-133,000	9,600-60,800	64-196,000
Bicarbonate (mg/L)	122-610	-	-
Sulfate (mg/L)	300-1,000	120-1,260	0-763
Ca^{2+}	7540-13,500	1110-6,730	38-41,000
Na^+	47,100-74,600	4370-28,200	63.8-117,000
K^+	0-5,770	80-750	38-3,950
Mg^{2+}	630-1,750	149-755	17-2,550
Fe^{2+}	<120	12.1-93.8	2.68-574
Al^{3+}	-	0.37-2.21	0.22-47.2
B	39.9-192	7.0-31.9	0.808-145
Ba^{2+}	0-24.6	0.93-17.9	0.24-13,800
Cu^{2+}	<0.21	0.06-0.52	0.253-4,150
Li^+	-	2.56-37.4	3.410-323
Mn^+	4-10.2	0.25-2.20	0.369-18.600
Pb^{2+}	-	<0.02	0.003-0.970
Sr^{2+}	518-1,010	48-1,550	0.580-8,460
Zn	2-11.3	0.10-0.36	0.087-247
Ni	-	0.03-0.05	0.007-0.769

Table 2.2 shows 16,400 – 97,800 mg/L was found in produced water from Barnett shale play [35]. According to Kondash et. al. high TDS formation produced waters, such as the Bakken or Marcellus, must first be diluted or treated before reuse, [69].

2.3.2 Wastewater Disposal and Management

Produced water may be managed by Public Owned Treatment Works (POTW) and Centralized Waste Treatment (CWT) facilities before discharged to surface waters. The U.S Environmental Protection Agency's (EPA) Clean Water Act (CWA) establishes regulating standards for discharging produced water in surface bodies. It governs the quality of pollutants permissible for release in surface waters. For instance, while CWT facilities are mainly used for direct discharge in the Marcellus and Utica shales areas of Pennsylvania, Ohio and West Virginia. Produced water with limited treatment such as settling/skimming are discharged for agriculture and wildlife propagation in Wyoming and California [41]. Brine from North Dakota are presently being managed by injection in disposal wells [32].

The following are options commonly practiced for produced water management [33] [38] [41].

- Downhole separation of water from oil and gas streams using polymer gels: This is not always possible, and application varies from formation to formation.

- Produced water injection into Class II saltwater disposal wells: Typically involves transportation cost to private or commercial disposal facilities and are regulated under the Safe Water Drinking Act (SWDA).

- Discharge to surface water bodies: Legislative and regulatory requirements must be met for discharge to surface water bodies. Surface discharge is allowed under Subpart

E, F and H and requires permit from EPA's National Pollutant Discharge Elimination System (NPDES).

- Direct reuse in oil and gas extraction processes.

- Smart treatment for beneficial use: Targeted treatment for industrial processes. For example, California particularly utilizes produced water for irrigating a variety of crops.

2.3.2.1 Water-Handling

A study conducted by Stephan et al. [25] on water assessment in the Bakken suggested that the high cost of transportation during acquisition is a result of distance from the water source to the well site, wait time and charges for trucking (average cost of $130/hr.). Transportation cost for the disposal of wastewater from wellsite to injection wells represent the largest estimated expenditure for the entire water-handling exercise. This presents a potential market for oilfield treatment technologies.

2.4   Conventional Treatment Methods

Oilfield brine may be treated using membrane or thermal techniques or a combination of these processes to achieve the desired water quality. In the literature, there are various technical assessments for the application of these treatment processes [42] [43]. The general objectives for operators treating produced water are:

- De-oiling by removing oil and grease.

- Disinfection by destroying microbial activities.

- Removal of dissolved soluble organics, dissolved gas, suspended solid, dissolved salts, excess water hardness and naturally occurring radioactive materials (NORM).

- Addition of calcium or magnesium ions into the produced water to adjust sodium adsorption ratio (SAR) for irrigation application.

Since the aim of this study is demonstrate a robust technique for desalinating produced water. This section focuses on describing conventional thermal treatment processes with a few commonly used membrane methods. Although, some membrane methods are most efficient as pretreatment for high TDS brine and not as a standalone. Common membrane treatment processes primarily used for brackish and/or seawater desalination are discussed

2.4.1   Membrane Treatment Processes

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are pressure driven membrane that allow product feed to permeate through membranes. Fouling of the membrane from organics is a significant disadvantage and would require chemicals for cleaning. This leads to downtime, reduced separation efficiency and equipment lifespan. Pore sizes in the mentioned membrane methods trend from smaller to larger range RO>NF>UF>MF. While the reverse is the case in terms of energy consumption as the trends from lower to higher energy consumption. The effluent quality is in the order MF > UF > NF > RO. Upon review it can be assumed that NF is

the best option for divalent and large molecular compounds since it has a higher rate of salt transport and requires lower energy than the RO membrane.

2.4.1.1   Microfiltration/Ultrafiltration

Microfiltration typically operates at low pressure (1-30psi) and is used to reduce turbidity, remove giardia, cryptosporidium and suspended solids ranging from 0.1 µm –3 µm [43]. When there is no concentrated flow, MF technology can operate in either crossflow or dead-end filtration (see **Figure 2.3**). MF technologies are not suited for salt removal but can be used as a pretreatment process in combination with desalination technologies [44].
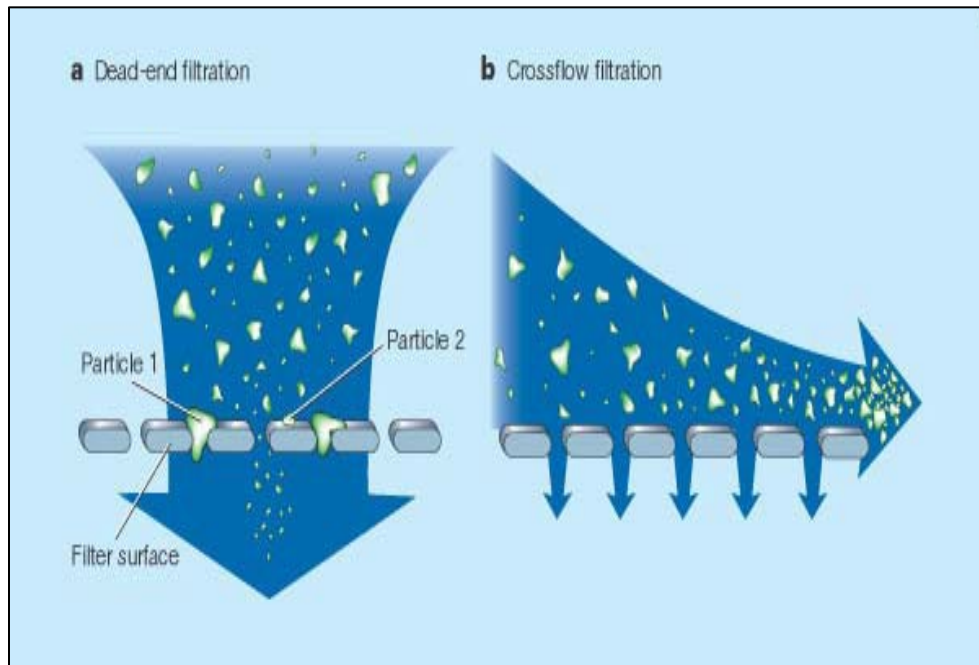
Figure 2.3: Microfiltration mode of operation; a) Dead-end; b) Crossflow (Source: [45]).

Unlike microfiltration technologies, ultrafiltration membranes are used to remove color, odor and colloidal organic matter ranging from 0.01 µm to 0.1 µm. UF operates at low pressure of 1 – 30psi and is reportedly more efficient than microfiltration for removing oil, viruses, hydrocarbons, dissolved constituent and suspended solids from produced water [43]. In a study conducted to treat produced water treatment Asatekin et al. 2009, incorporated amphiphilic copolymer additive such as polyacrylonitrile-graft-poly (ethylene oxide) with UF membranes and obtained a 96% removal rate of the dispersed and free oils [46].

A significant limitation to both MF and UF is fouling of the membranes which can reduce the rejection efficiency. Thus, pretreatment of the feed stream is typically required. Ebrahimi et. al. suggested flocculation prior to treating wastewater to reduce fouling and increase efficiency [47]. Depending of the application, periodic backwashing is usually employed to clean the MF and UF membranes.

2.4.1.2 Polymeric MF/UF membranes

Polymeric and ceramic membranes are commercially available for wastewater treatment. Polymeric MF/UF membranes are made from polyacrylonitrile and polyvinylidene and are inexpensive [42].

2.4.1.3 Ceramic MF/UF membranes.

Ceramic membranes are typically made from oxides, nitrides or carbides of metals such as aluminum, titanium and zirconium [46]. As a result, they are thermally, mechanically

and chemically more stable than polymeric MF/UF membranes. Various research studies reported the capability of ceramic membranes to remove organic matter, suspended particles, oil and grease in wastewater [48]. On a commercial scale, ceramic membranes have been used to treat suspended solids in oilfield produced water such as in wellington water works [48]. Ceramic membranes require less energy requirements than polymeric membranes. However, the capital cost for ceramic membranes are higher than polymeric membranes. Furthermore, they require pretreatment and backwashing is typically used to clean the membranes to avoid fouling [43].

2.4.1.4   Reverse osmosis

Reverse osmosis (RO) and nanofiltration (NF) are examples of pressure driven membrane technologies typically used in brackish and seawater desalination. Both types of membrane act on charged ions or molecules. Uncharged molecules will pass through the membrane, depending on the size. Some molecules may be too large to pass through the membrane and are retained in the concentrate (**see Figure 2.4**). Both processes are harmed due to fouling and scaling from particulates, biological material, and high concentrations of slightly soluble salts. So, pretreatment is necessary to provide an acceptable feed water stream [49]. Their life expectancy is between 3 and 7 years [43].

RO is currently the most mature desalination technology for water treatment. With a global market share of about 60% for seawater desalination. It accounts for approximately 50% of desalinated water produced worldwide. RO is mainly used for

brackish and seawater treatment with a water recovery rate of nearly 95% and 50% respectively. RO membranes operate by rejecting monovalent and multivalent ions, molecules, and metals. They have a rejection rate of 99.5 percent for dissolved ions. A significant disadvantage to RO technology is scaling and fouling of the membrane resulting in lower efficiency. Also, it generates large amounts of hypersaline concentrates that pose disposal problems. Such as, for every gallon of desalinated seawater produced, about 1.5 gallons of highly concentrated reject waste is generated. In produced water application, RO may be efficient in a combined approach depending on the feed quality. In addition, TDS above > 45,000 mg/L would require significant pretreatment to prevent fouling and scaling [50].
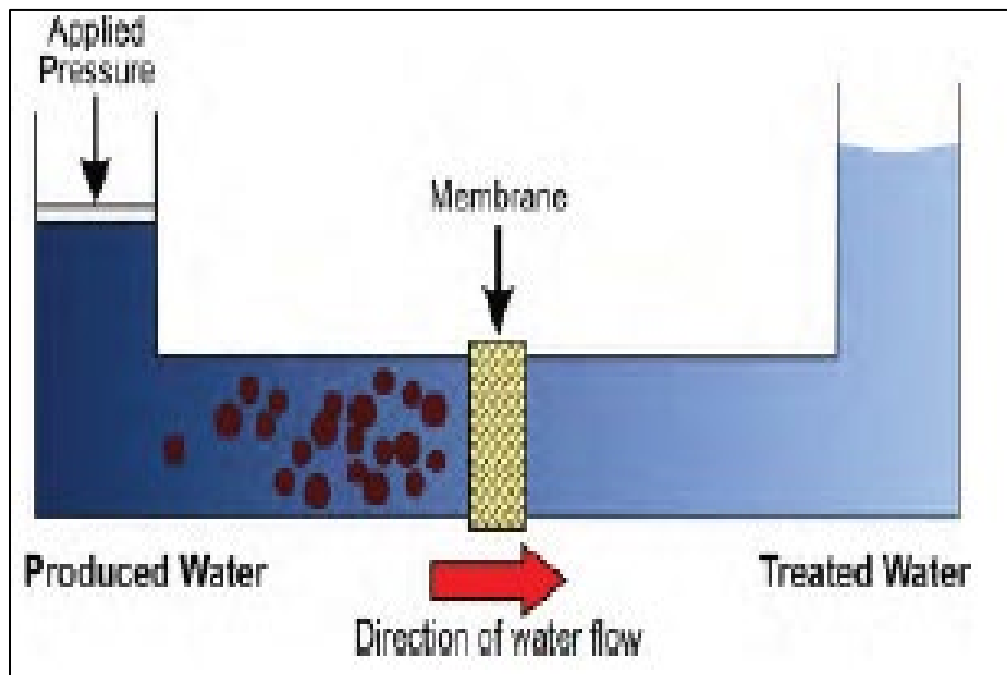
Figure 2.4: Reverse Osmosis process schematics (Source: [51]).

2.4.1.5   Seawater Reverse Osmosis

Seawater RO (SWRO) is applicable to feed streams up to 45,000 mg/L TDS [43]. Depending on the organic compound's chemical structure and feed stream quality, SWRO rejection rate ranges from 20% - 90% [50]. A significant limitation of SWRO technology is membrane fouling and scaling and as a result frequently requires pretreatment. $CaSO_4$, CaF_2, and $BaSO_4$ are foul and scale causing salts that harm SWRO membranes. Disposal is required since SWRO systems often generate large volumes of highly concentrated secondary wastewater. RO systems have been reported to be employed for produced water treatment, but the membranes were damaged due to inadequate pretreatment [19].

2.4.1.6   Brackish Water Reverse Osmosis

BWRO membranes are applicable for removing dissolved divalent ion constituents from feed stream with TDS range of 500 and 25,000 mg/L. They typically achieve dissolved ions separation rate of >94% NaCl and a water recovery rate up to 85%. Xu and Drewes [50] conducted a study to investigate the potential of using BWRO for extracting iodide from produced water. The result showed severe damage to BWRO membranes. Like SWRO membranes, fouling and scaling in BWRO are major concerns associated with organics and inorganics removal. However, higher water recovery exhibited by the BWRO process means a reduction in generation of concentrated secondary brine and lower disposal costs.

2.4.1.7 Nanofiltration

Like RO, Nanofiltration is a crossflow membrane filtration process. Nanofiltration membranes have a higher rate of salt transport than RO and preferentially retain higher charged ions such as calcium and sulfate. They are commonly used to desalinate brackish groundwater. NF is used as a robust metal removal and water softening technology. It has a separation efficiency of >99% for divalent ions, radionuclide and metals. The recovery efficiency from brackish water can be high as 90% [43]. NF membrane are limited to treating water less 45,000 mg/L. With membranes being sensitive to scale and foul causing organics, pretreatment of the feed stream is usually required. Another disadvantage is that chemical cleaning to remove scales may increase operation cost. NF membranes have been investigated on both pilot- and bench-scale for treatment of produced water and have been revealed to require less energy than RO with better separation performance for divalent ions and large molecular compounds [52]. However, they are not suitable as a standalone treatment for produced water. They can be an efficient pretreatment method in a combined system with other technologies [50].

2.4.1.8 Forward osmosis

Forward osmosis (FO) is an osmotically driven membrane process. FO membranes uses dense hydrophilic, *cellulose acetate* active layer cast onto either a woven polyester mesh or a micro-porous support structure. As shown in **Figure 2.5** water

tends to diffuse from a solution of low osmotic pressure to high osmotic pressure (i.e. High salt concentration stream to diluted solution). FO processes can operate with feed TDS ranging from 500 mg/L to more than 35,000 mg/L [53]. To the best of the author's knowledge, there are no documented applications of FO to treat produced water.
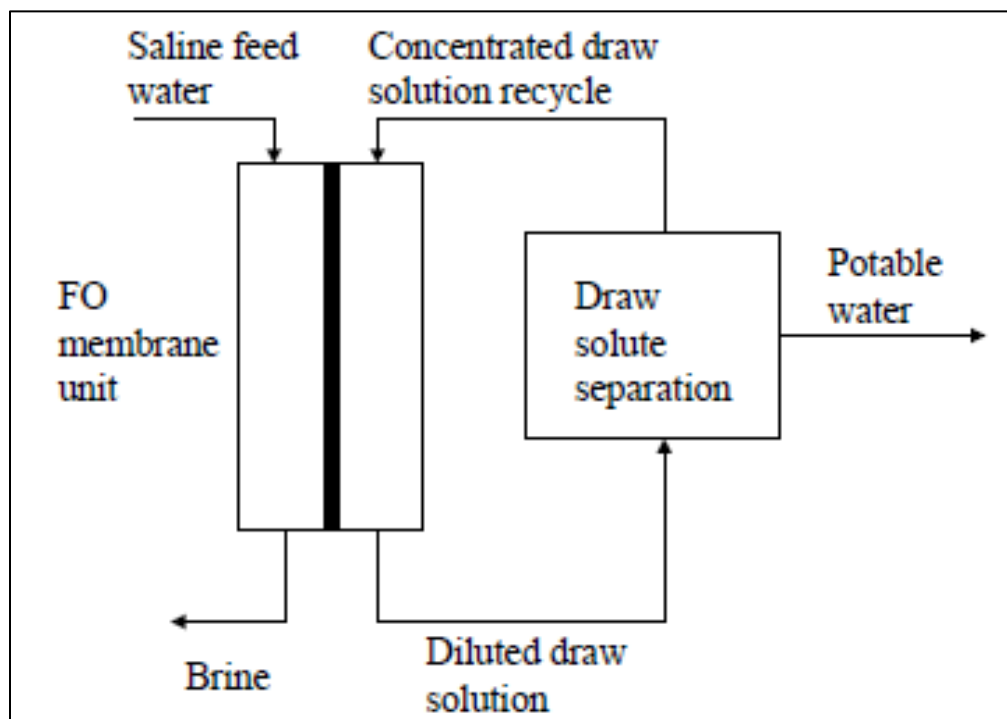
Figure 2.5: Schematic of a Forward Osmosis technology (Source: [43]).

2.4.2 Thermal Treatment Processes

Thermal treatment technologies are especially implemented in arid to semi-arid regions where energy cost is relatively low such as in the Middle East. They are majorly used for seawater desalination in low-cost oil producing countries like Saudi Arabia and the UAE. Multistage flash (MSF) distillation, vapor compression distillation (VCD) and

multieffect distillation (MED) are the most common thermal technologies employed for brackish, seawater and produced water desalination. In addition, they can be combined to achieve improved water recovery efficiency. For example, MSF has been studied in combination with MD and RO for the treatment of coal seam water in Australia [54]. The study showed an increase in product water quality compared to lower quality when utilized as a standalone treatment. Also, their wide range of TDS applicability and tolerance for highly saline concentrations, makes thermal technologies significantly advantageous. However, unlike their counterpart membrane desalination technology (RO), thermal techniques require a large amount of energy to achieve higher separation efficiency. MED conceptually consists on recycling the enthalpy of evaporation in successive effects (solar energy can be employed as the heat source), while MSF involves the evaporation and condensation of water (normally coupled to power generation facilities for low grade heat).

2.4.2.1   Membrane Distillation

Membrane distillation (MD) is a thermally driven separation process where constituents are separated when the heated feed stream passes through the membrane. The resulting vapor from the heated stream then condenses into product water. Mass transfer through membranes occur due to pressure gradient. It has a lower operating cost compared to conventional distillation processes. Materials used in MD process include polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidene difluoride

(PVDF). There are four methods of operating MD process: direct contact MD (DCMD), vacuum (VMD), air gap (AGMD), and sweeping gas (SGMD) [30] [43].

Direct contact membrane distillation (DCMD) occurs when water diffuses through the membrane pores from the heated section until it condenses in the colder section as the treated water (see **Figure 2.6**). Unlike RO, DCMD process can treats hot produced water stream without cooling < 35,000 mg/L [51].
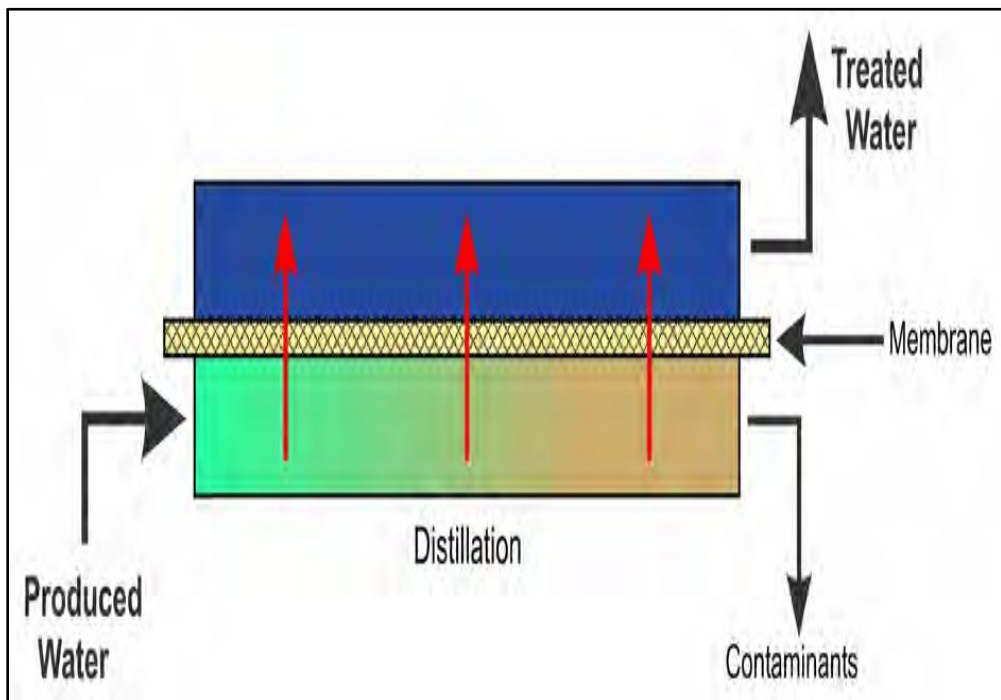
Figure 2.6: Schematics of membrane distillation [51].

In AGMD, the membrane used contains a section with air gap and a cold plate section. As water vapor diffuses through the membrane it enters the latent air gap and condenses on the cold plate. MD processes are employed for brackish and/or seawater

desalination but there is no documented application for produced water treatment available in the literature. Although MD membranes have a high resistance to oxidation [43]. It would most likely require aggressive chemical cleaning to reduce scaling or fouling. This would increase operational downtime and cost.

2.4.2.2   Multistage flash

MSF distillation is a mature technology mostly applied for brackish and seawater desalination. The process occurs by flash evaporation when the feed stream moves from one distillation chamber to the other. In the MSF system, temperature increases along the distillation chambers while pressure reduces. The heated feed stream progressively flows from a high-pressure chamber to a low-pressure chamber. Thereby flashing to steam in the lower pressure chamber [30]. MSF has a water recovery range of 20% - 30%. It often requiring SAR adjustment due to effluent stream containing 2–10 mg/L of TDS [55]. A significant limitation is the formation of scale on heat transfer surfaces, leading to post-treatment and operational downtime. The energy required for MSF operation is between 3.35 and 4.70 kWh/bbl [43]. MSF has an operational lifespan of >20 years and has a wide range of feed stream applicability when used in a combined approach with other technologies [52].

2.4.2.3   Multieffect distillation

Multieffect distillation process converts a portion of saline feed stream to vapor by first applying energy to heat the feed water to its boiling point. The feed stream is heated with pressurized steam from the first effect (see **Figure 2.7**). The resulting vapor is then condensed to product water. The "multi effect" is designed to minimize energy consumption. MED is primarily suitable for desalting seawater with a water recovery rate of about 35% [42]. MED can be applied to various feed water qualities. A major challenge is the formation of scale which significantly limits the separation performance of MED. Thus, pretreatments such as scale inhibition will be necessary. In addition, post-treatment techniques like acid dosing may be required. The energy required to produce a barrel of desalinated water in MED process ranges from 1.3 to 1.9 kWh [39].
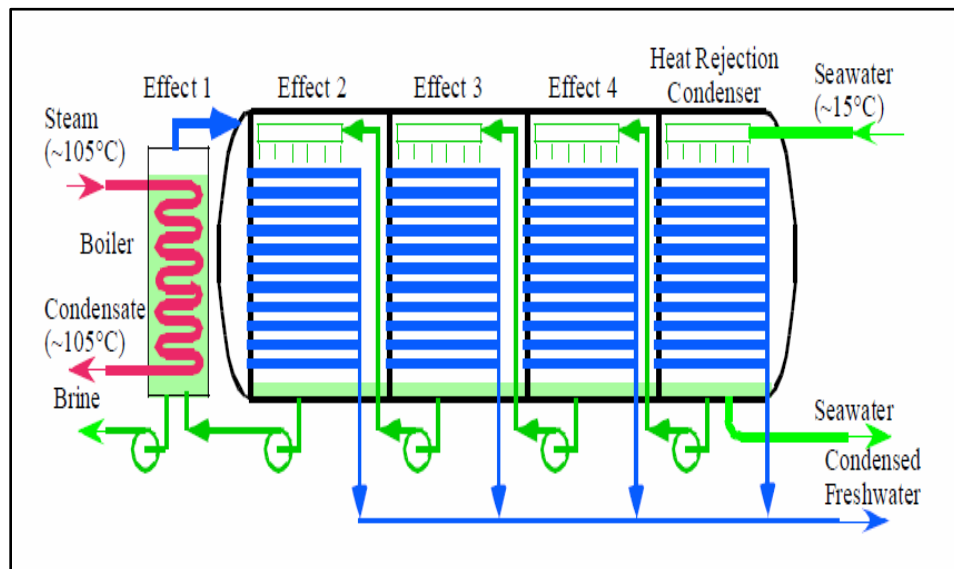
Figure 2.7: Schematic of a MED system using steam as a heat source (Source: [43]).

Figure 2.7 shows a schematic of a conventional MED system using steam as a heat source, with four effects. Rapid boiling and evaporation of the feed stream takes place on the outside of the evaporator tube. Vapor from the heated stream forms and condenses on the colder inside of the next tube which in turn heats the feed solution in the next effect.

2.4.2.4   Vapor compression distillation (VCD)

In VCD, heat of evaporation of the feed stream occurs by thermally or mechanically compressing steam within the unit. Thereby utilizing the increasing temperature of the vapor as a source of energy. A schematic of a vapor compression distillation mode of operation is illustrated in **Figure 2.8**. The VCD process is a mature desalination technology used for seawater desalination as well as treating produced water and can be combined with RO to treat waste stream as a near-zero liquid discharge (ZLD) unit. Scale formation and corrosion are potentially reduced with a high capacity compressor which allows the VCD to operate at temperatures < 70°C. The power consumption of larger units is approximately 30 kWh/kgal of product water (1.3 kWh/bbl) [56]. Vapor compression has a water recovery range of 40% for seawater and the energy consumption for evaporation and crystallization in a ZLD unit is 4.2 to 10.5 kWh/bbl [37] [43].
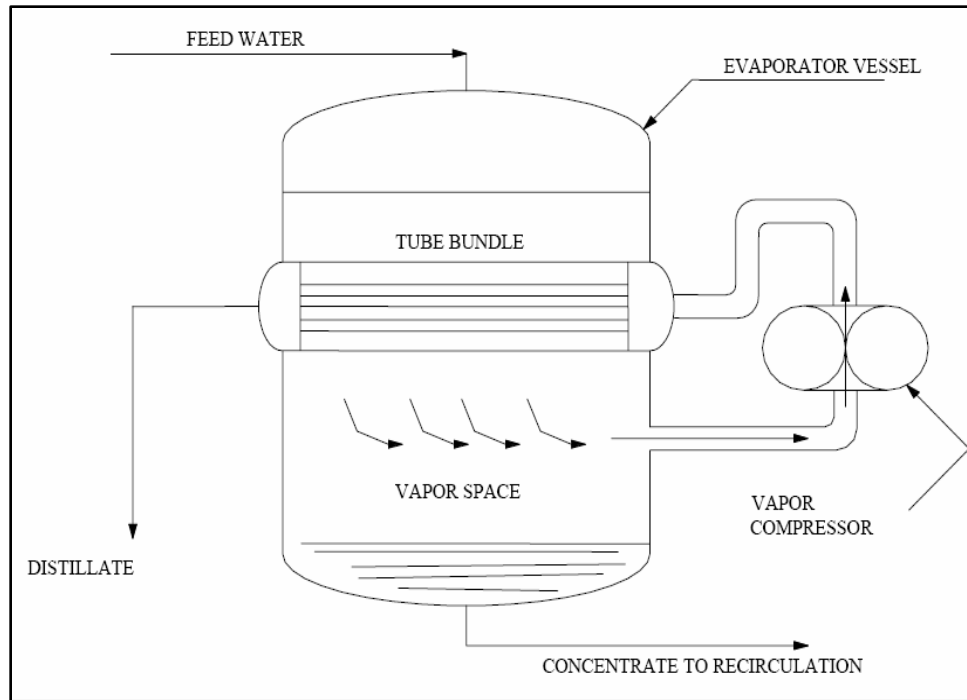
Figure 2.8: Simplified schematic of a VCD unit (Source: [48]).

2.4.2.5   Dewvaporation: AltelaRainSM process

Dewvaporation is an example of a full scale commercial produced water desalination

technology developed by Altela Inc. that employs dewvaporation process. The principle

of counter current heat is used to evaporate the feed stream in one chamber.

Consequently, vapor rises and condenses on the opposite chamber to produce distilled

water (see **Figure 2.9**). It has a treatment capacity of 100bbl/day of about 60,000 mg/L

TDS produced water. According to AlterRainSM [57] the concentration of chloride has

been reported to reduce from 25,300 to 59 mg/L, TDS and from 41,700 to 106 mg/L.

Similarly, benzene concentration reduced from 450 mg/L to non-detectable.
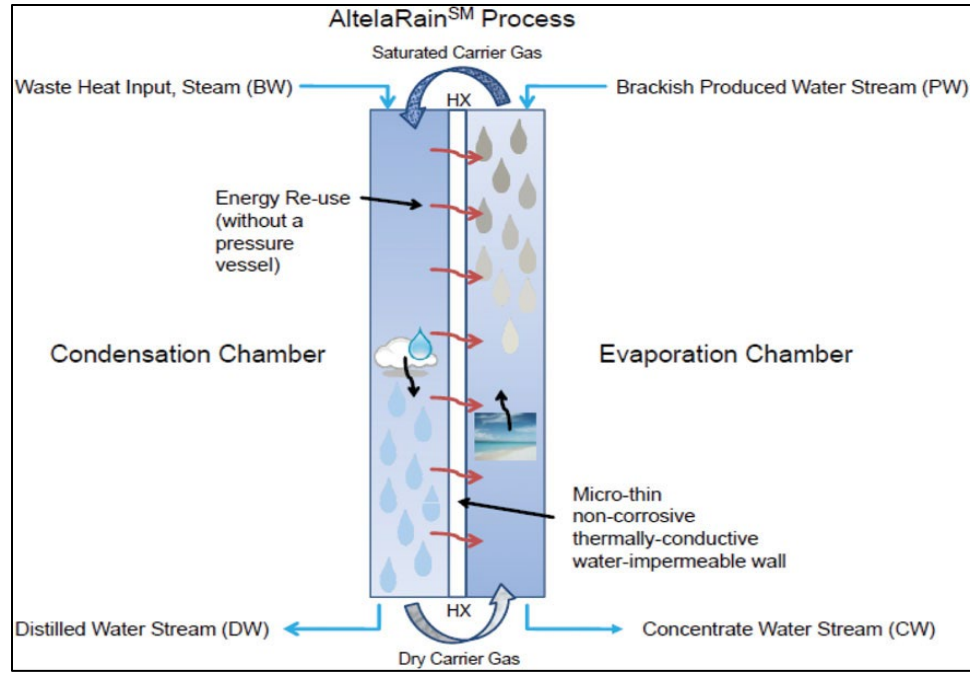
Figure 2.9: Schematic diagram of AltelaRainSM process (Source: [58]).

2.5   Summary of Desalination Technologies

It is evident upon review, that current desalination technologies are riddled with challenges such as scaling, fouling, high energy requirements and generation highly concentrated secondary waste. It has also demonstrated the application of technologies such as RO, NF, MED, MSF and VCD are largely limited to feed water quality less than 45,000 mg/L. Their water recovery efficiency reduces drastically with increasing feed water concentration beyond ~ 50,000 mg/L. This highlights the importance for extensive pretreatment crucial to mitigate highly concentrated water constituents which can severely damage membranes.

Table 2.3: Summary of conventional desalination technologies

Technology	Characteristics	Advantages	Limitations	Influent Concentration (mg/L)	Product water efficiency
Reverse osmosis (RO)	Metal ions, acids, sugars, aqueous salts, natural resins, divalent ions, monovalent salts, BOD, COD, ions etc. Energy requirement can be < 0.7 Kwh/bbl [49] [6]	• Flexible with high pH. • The process is reliable • High product water quality when feed stream is properly pre-treated.	• Requires pre-treatment • Sensitive to fouling and scale components. • Highly concentrated secondary waste. • Membranes requires chemical cleaning after treatment. • Not suitable for saline water higher > 45,00 mg/L	< 45,000 mg/L	~ 90% for brackish water ~50% for seawater [43]
Nanofiltration (NF)	Water softening and removal of divalent ions, large molecular compounds [52] Energy requirement of ~ 0.08 Kwh/bbl for high-pressure pumps [43]	• Higher rate of salt transport than RO. • >99% for divalent ions, large molecular compounds. [43] • Removal of hardness. • Less energy requirement than RO • Membranes have high pH tolerance.	• Highly sensitive to scaling. • Damage to membrane caused by fouling. • Pre-treatment is required to prevent scaling and fouling. • System requires chemical cleaning after treatment. • Not suitable for saline water higher > 45,00 mg/L	< 25,000 mg/L	70% - 90% for brackish [43]
Multistage Flash (MSF)	Energy required ~ 3.35 – 4.70 kWh/bbl[43]	• Less equipment sensitivity like membrane processes. • Tolerates high feed concentration. • Can be used for a wide range of TDS in a combined approach. • Can be very efficient if feed concentration is extensively pre-treated	• Not suitable as a standalone. • Poor effluent quality. • Low product water recovery. • Requires pre-treatment • Not flexible. • Scaling and corrosion concerns. • System requires chemical cleaning after treatment. • Higher energy demand than membrane processes	< 45,000 mg/L	~ 30% for seawater
Multieffect distillation (MED)	Can be applicable to wide range of TDS. Energy required is about 1.3–1.9 kWh/bbl [39]				~ 35% for seawater [42]
Vapor compression distillation (VCD)	For seawater desalination. Energy requirement is 4.2– 10.5 kWh/bbl [37] [56]				< 40% for seawater [43]

Such as those caused by hydrophobic organic compounds and sparingly soluble salts (e.g. barium and calcium salts).Thus, suggesting their inability to treat for organics and separate targeted inorganic salts in produced water.

Furthermore, it is clear from the summary shown in **Table 2.3**, that RO, NF, MED, MSF and VCD are not equipped to adequately treat hypersaline brine up to 300,000 mg/L. Particularly the production of highly concentrated streams while treating saline water well below TDS levels of 50,000 mg/L, reveals their insufficiency as a standalone treatment method. Therefore, large amounts of hypersaline discharge streams coupled with poor product water quality demonstrates the need for developing a unique method capable of removing dissolved oil and gases, metals ions, organic acids, inorganic salts, etc. in high TDS produced water.

This study proposes an emerging and promising method called supercritical water desalination with functionalities for adequate organics destruction and salt precipitation with potential for zero liquid discharge (ZLD). Chapter 3 discusses, the fundamental principles and concepts of this technology that would be exploited for treating high TDS brine to levels acceptable for reuse.

CHAPTER 3: SUPERCRITICAL WATER DESALINATION

3.1 Introduction

Supercritical water desalination (SCWD) is an emerging technology that exploits changes in the unique properties of water for the treatment of saltwater streams with zero liquid discharge (ZLD). This generates little to no secondary concentrated waste stream. Supercritical water (SCW) is water at the pressure and temperature above the critical point of water (T_c = 374.2°C & p_c = 221.2 bar). Water behavior changes significantly and loses it solvation properties when it moves from ambient to supercritical conditions. The ability to form hydrogen bonds in water drastically reduces in this supercritical state. Thus, it changes from a polar solvent to a non-polar solvent, as a result soluble inorganic compounds (salts) become insoluble and precipitate as a solid phase.

Studies have shown lower density, reduced dielectric constant and diminished dissociation constant are all noticeable physico-chemical changes of water at supercritical conditions [59]. This makes nonpolar materials like hydrocarbons and oxygen gas highly soluble while polar materials like inorganic compounds and salts become insoluble. Thus, resulting in separation of solid precipitates and a clean liquid phase at the supercritical state. In this thesis, the principle of water losing its solvation ability for inorganic compounds will be applied for the removal of dissolved solids in produced water.

3.2   Supercritical water oxidation (SCWO)

SCWO occurs when organic materials such as dissolved hydrocarbons and oxygen gas undergo rapid oxidation in water above its critical point (T_c = 374.2°C & p_c = 221.2 bar). This process is efficient in organic destruction at relatively short reactor residence time (under 1 minute). Applications of SCWO have been commercially developed for biofuel formation and synthesis reactions. However, the most common commercial application of SCWO process is the destruction of organic waste (1-20 wt.% organics) [59]. Various studies to improve the SCWO process are ongoing in areas such as material compatibility and corrosion, salt nucleation and growth, reaction kinetics, etc. [59] [60].

Although, SCWO easily oxidizes organic compounds containing carbon, hydrogen, oxygen and nitrogen atom like those found in produced water. Oxidation of organic waste containing sulfates, chlorides, phosphates, bromide, etc. often lead to corrosion, salt precipitation and accumulation.

In this study, such challenge will be exploited in two ways during the SCWD process. First, for complete destruction of organics present in oilfield brine (such as phenols and other hydrocarbons) and to provide heat for the separation and precipitation of the inorganic species.

3.2.1 Supercritical water behavior

In order to utilize the supercritical water desalination process, it is important to first understand the influence of temperature and pressure on the phases present and how they reflect changes in the supercritical water. Several studies have been conducted to shed more light on water behavior at supercritical conditions. In his 1998 dissertation, Hoades reported that the density of supercritical water ($100kg/m^3$) at about $500^{\circ}C$ and 250 bar, is 10 times lower than that of ice and water at atmospheric pressure ($1000kg/m^3$) [61]. This results in a weakened and loose structure of hydrogen bonding in water, thus changing the behavior of water in a supercritical state from a polar solvent to a non-polar solvent. Also, the low solubility of salts at supercritical state is a result of the significantly diminished static dielectric constant of water.

The reduction in static dielectric constant of water is a function of density and temperature. Interestingly, this can be closely related since the hydrogen bonding in water at supercritical condition is influenced by density. The comparative static dielectric constant of water at supercritical state and STP are < 2 and 78.46 respectively [61] [62]. In addition, the ion product of water (10^{-23} (mol/kg^2)) at the supercritical condition is nine times lower than water at ambient condition.

Although, the low ion product and diminished static dielectric constant are largely responsible for the solvation behavior of supercritical water [61]. A direct relationship can be established between the weak hydrogen bond, reduced density, diminished static

dielectric constant and the low ion product of water at supercritical point compared to water at ambient condition. However, the ion product of SCW can be very high during preheating at subcritical temperatures (155ºC to 335ºC) due to relatively high concentration of positive hydrogen ions. This can create significant challenges when acidic solutions (e.g. HCl) are formed, leading to corrosion in the preheater and cooler [62].

There is limited research and data available to fully understand the characteristics of aqueous streams at supercritical conditions. Odu et al [63] conducted an experiment using 3.5 wt.% NaCl-H_2O solution to shed light on the effects of temperature and pressure in supercritical water phase equilibrium. It was observed that two stages of phase distribution, which are the vapor to liquid stage (V-L) and vapor to solid stage (V-S) were necessary for obtaining product water and solid salts, respectively. It also revealed that to avoid blockage and equipment failure the stages had to be operated at different supercritical conditions. In addition, transition (V-L-S) temperature between the two stages were reported at about 450ºC at 250 bar and 475ºC at 300 bar for the V-L and V-S respectively [63].

In this study, a proof of concept experiment for aqueous streams using NaCl-H_2O solutions were carried out prior to produced water testing. Temperature and pressure effects were investigated in the SCWD system to determine suitable conditions adequate for sufficient inorganic salts removal during the PW experiment.

3.3 Conceptual Design of Supercritical Water Desalination System

There are very few descriptions of supercritical water desalination units available in the literature. While some are in development stage or classified as proprietary information. However, if the fundamental principles of a guiding desalination units are employed, a theoretical SCWD unit would involve the following.

- High pressure pump.

- Heaters

- Supercritical reactor

- Heat exchangers

- Supercritical water and solids separator

As shown in **Figure 3.1**, after pretreatment of the aqueous stream, a high-pressure pump is used to feed the inlet stream through the preheated unit to the reactor at supercritical pressure. Heaters are needed to provide an energy source to raise the temperature of the reactor above the critical temperature of water (374^oC). In the case of brine, the preheated saline stream separates into a clean liquid phase (SCW) while inorganic salts precipitate out of solution at supercritical conditions. The two products can be separated using as suitable liquid-solid separation method that prevents the solid salts from re-dissolving in the SCW, i.e. the liquid-solid separator should maintain temperature and pressure of the supercritical system.
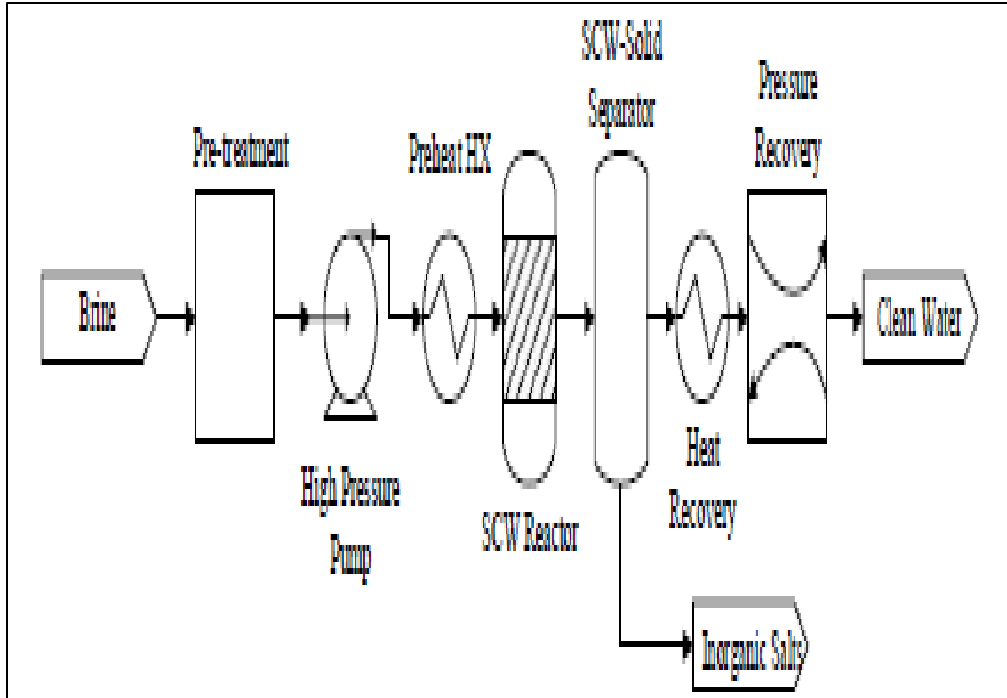
Figure 3.1: Conceptual supercritical water desalination system (Source [64]).

Furthermore, since the SCWD process is energy intensive, a heat exchanger is used. Since a heat-recovery system is necessary to make the process economical and commercially feasible. The heat exchanger will be utilized to reduce energy input and prevent significant heat loss by heat-transfer. Heat from the product supercritical water (still at T_c >374°C) is used to preheat the inlet stream to sub-critical temperatures prior to arriving at the reactor. Finally, the clean product water is collected and examined for separation efficiency.

3.3.1 Challenges to Supercritical Water Desalination Process

Although, SCW treatment of hypersaline brine is a promising approach, there are significant challenges that require considerations to make the technology commercially viable. These include: (i) high energy requirements; (ii) scaling and corrosion of process equipment; (iii) high capital costs with need to use expensive alloys; (iv) difficulty in removal of separated solids at supercritical conditions; and (v) recovery of individual salts.

3.3.1.1 **High Energy Requirements**: The process of reaching and sustaining supercritical phase requires high thermal energy input. For example, the enthalpy of water at 362°C (subcritical) is 1730 kJ/kg compared to 2700 kJ/kg at 397°C (supercritical). Studies report that the thermal energy consumption for SCW treatment is 450 MJ_{th}/m^3 of product water [63] [65]. This is much higher compared to 30 MJ_{el}/m^3 for RO system (equivalent to 100 MJ_{th}/m^3) and 300 MJ_{th}/m^3 for multi-stage flash plants, albeit considerably lower than standard evaporative systems (~2200 MJ_{th}/m^3). The energy requirements for SCW treatment must be significantly lowered to make it competitive to current desalination technologies [65].

3.3.1.2 **Scaling and Corrosion**: The extremely low solubility of inorganic salts in the SCW environment leads to salt precipitation inside the reactor [59]. These salts can rapidly accumulate on reactor walls and form plugs, leading to frequent shutdowns. Furthermore, the ionic product of water increases significantly near supercritical

conditions and can cause corrosion in the preheater [59]. Oxidation of organic compounds present in the feed also produce acidic solutions that can trigger corrosion. Typically, a neutralizing base is injected into the stream to reduce the impact, which adds to the low solubility salt burden. An alternative/improved method to control scaling and corrosion is necessary for reliable operation of SCW technology.

3.3.1.3 **High Capital Costs**: In order to achieve and sustain supercritical conditions, the process must operate at a high temperature (~374°C) and high pressure (~250 bar). These operating conditions and the aggressive process conditions resulting from corrosive species require special selection of materials of construction. Use of specialty alloys such as Hastelloy C-276, Inconel 625, Incoloy and Titanium Grade-1 have been reported by several researchers [63] [66]. These specialty alloys are expensive compared to more traditional materials such as SS 316. It is desirable to reduce the high capital cost of the supercritical technology in order to make it competitive with other commercial technologies.

3.3.1.4 **Destruction of Organics:** As previously mentioned, fracking fluids consist of a range of additives such as acids, biocides, emulsifier, foaming agents, and friction reducers to optimize the fracking process. A portion of these additives return to the surface as part of flowback. Produced water will also contain organics originating from the produced hydrocarbons. SCW is an excellent medium for solvation of organics [62].

However, addition of an oxidant is needed to ensure complete destruction of the organics to make the clean water suitable for fracking or other sensitive applications.

3.3.1.5   **Continuous Removal of Solids at Supercritical Conditions**: SCW treatment separates the brine into "clean" water and solids. At supercritical conditions, the dissolved salts precipitate due to reduced solubility in the SCW. These precipitated solids must be continuously removed to reduce fouling or plugging in the reactor. Various approaches have been reported for continuous solids removal, including hydro-cyclones, filters and flash separation [60]. However, each has their limitations to being commercialized. A low-cost and simple method of solids separation is necessary.

3.3.1.6   **Recovery of Value-Added Metals/Salts:** One of the advantages of supercritical treatment technology is that it can precipitate solids in a separate stream. These solids may contain high value materials that could serve as an additional revenue source from water treatment. A technology to separate and recover the individual high value metals/salts from the brine solutions should be explored.

CHAPTER 4: EXPERIMENTAL DESIGN AND PROCEDURES

The experiments are divided into two parts: 1) NaCl-H_2O based experiments to determine the best conditions to achieve desalination under supercritical conditions since it is the main constituent of brine and 2) produced water experiments using two samples under supercritical conditions (240 bar). The equipment and experimental setup used in this study was designed for a funded U.S Department of Energy (DE-EE0008394) project. The equipment and their operating procedures will be discussed in this chapter.

4.1   Lab-scale experimental setup

A schematic of the laboratory-scale supercritical water system is shown in **Figure 4.1**. The material for construction for the system was 316L stainless steel. The flow path is made mostly of Swagelok® fittings and tubing (1/4" and 1/8"), with the main body of the reactor being supplied by High Pressure Equipment Co. Construction materials which are appropriately rated for the operating temperatures and pressures of the system. The setup consists of a high-pressure pump (Eldex BBB-4) that has the capability of pumping 0-33 mL/min through three separate pump channels, for a total of 100ml/min (6kg/hr), at 345bar. Electric ceramic heaters capable of reaching above 500°C are used to externally heat the preheater and reactor sections to achieve the desired temperature for operating conditions. Additional instrumentation was installed to measure more temperatures and pressures in critical areas of the flow path and reactor.
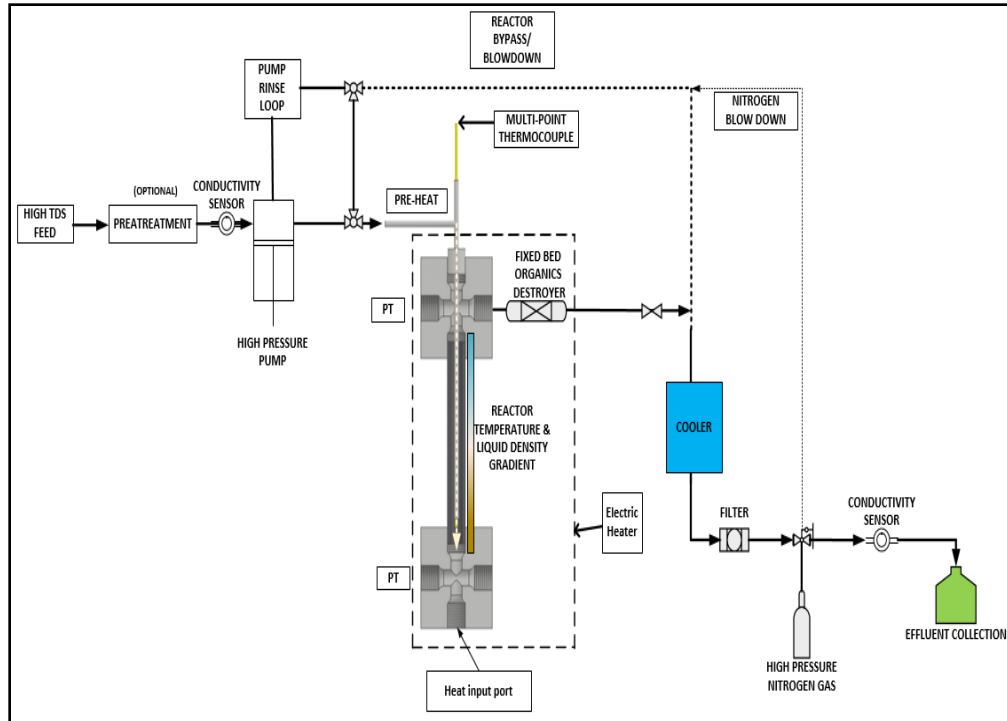
Figure 4.1: Schematics of the SCWD experimental apparatus.

Total dissolved salts (TDS) are measured at ambient pressure and temperature before the high-pressure pump and after the back-pressure regulator (BPR) using two inline conductivity sensors (400VP-13) wired to a Rosemount™ 1056 Dual-Input Intelligent Analyzer sourced from Emerson (see **Figure 4.2**). The product streams are cooled in a heat exchanger and filtered prior to the BPR. A 400-bar nitrogen gas bottle and high-pressure gas regulator is used to set the regulating pressure of the BPR. The reactor was designed to be modular with extra ports allowing for easy manipulation. A ¼" Watlow firerod is implemented as the source of heat addition to provide the localized supercritical zone within the reactor.

Thermocouples were used to verify the establishment of a temperature gradient and to further understand the heat transfer within the reactor. The system was designed to be capable of isolating the reactor from the upstream and downstream components to facilitate additional data/sample collections.

Figure 4.2: Photo of the SCWD Lab-scale setup.

4.2. Part 1: NaCl-H₂0 Experiment

A feed stream of a preset salt concentration was preheated to 360°C where it entered the reactor dip tube. The stream was further heated to the desired bottom reactor set point through the natural heat exchange with the fluid in the reactor, and with the

addition of heat through the hot rod. This localized heated zone was provided via the externally heated rod increasing the overall bulk temperature by approximately 20 to 80°C. Testing was performed at 10 wt.% and 20 wt.% as it represents the general range of concentrations present in a typical produced water sample. Flowrates were recorded and the exit conductivity monitored. The feed-bottle weights and volumes were tracked before and after each test. Results of the 10 wt.% and 20 wt.% are discussed in Chapter 5.

4.2.1 Operating Procedure and Measurements

The laboratory testing is operated semi-continuously, with the precipitated solids collected inside the reactor vessel, but with feed and effluent water streams continuously flowing. During testing, the system is brought to pressure and heated to the desired temperature. Once the desired inlet temperature (typically sub-critical at 360°C) is reached in the lower reactor, heat is applied via the internal heated rod. The temperature (heat input) from the heated rod is monitored in two places: via an internal thermocouple within the heated rod (i.e. surface temperature of the rod) and a thermocouple placed at the bottom of the reactor (fluid temperature in the hottest part of the reactor).

Additionally, a thermocouple placed at the reactor outlet measures the temperature of the bulk fluid exiting the reactor. Once steady state temperature and pressure conditions are reached, the feed is switched to a single component brine of known concentration and fed at a rate of ~10 ml/min. Brine begins to fill the upstream zone and reactor at approximately 7 minutes and 17 minutes respectively. While the

downstream section of the reactor fills up at approximately 8 minutes. The appropriate

volumes of these sections are shown in **Table 4.1**.

Table 4.1: Desalination system volume.

System Components	Measured Volumes (ml)
Upstream of Reactor Zone	32
Pre-heater	41
Reactor	167
Downstream of the Reactor	80

Once brine reaches the outlet conductivity sensor (~30 minutes), sampling of the

product water begins. Sampling typically takes place for 30 additional minutes, while

brine was continuously fed to the system. Several bulk samples are collected throughout

the test, with point samples collected, as necessary. For salt deposition analysis,

equipment was designed to blow down the system in the three isolated sections

mentioned in **Table 4.1**. The liquid samples from these individual sections are retained

separately and analyzed. Once the system has been emptied of liquids, the system is

depressurized, cooled and the solids are recovered from the reactor. Post experiment

liquid samples were analyzed with a conductivity meter which corrects conductivity to

25°C (Hanna Instruments Model: 5522-01).

4.2.2 Conductivity vs. Concentration Measurements:

Feed solutions were prepared on a weight percent basis. This is consistent with

supercritical water desalination thesis work done by Odu [63] and Hodes [61] for the high

concentration salts and is important as the correlation between TDS and conductivity

(mS/cm) is not linear at higher concentrations. For example, preparing a 20 wt.% sample with inputs of 200g NaCl and 800g water produced a total aqueous solution volume of 880ml. This matches closely with calculations done for measuring total volume of a solution after mixing solvents in aqueous solutions.

The experimental density for the salt solution is 1.136 g/ml. This is within 0.9% error of the density handbook value for 20 wt.% NaCl solutions - 1.147 g/ml [67]. According to these references, 20 wt.% NaCl should produce a conductivity of 220-242 mS/cm depending on temperature [68] [69]. The bench-top lab conductivity measurements for the 20 wt.% NaCl solutions were ~240mS/cm. Thus, inline conductivity sensors were then calibrated to match the experimentally verified conductivities.

Conductivity of a variety of NaCl concentrations were measured, graphed and compared to literature data. This was done to establish in-house correlation factors for conductivity vs. concentration. When corrected to 25 °C, these values match literature [68] [69] within 3% error. In addition, correlation factor between conductivity and concentration can vary depending on the composition of the dissolved salts. The results of this literature review and experimental verification are presented in **Figure 4.3** and **Table 4.2**.
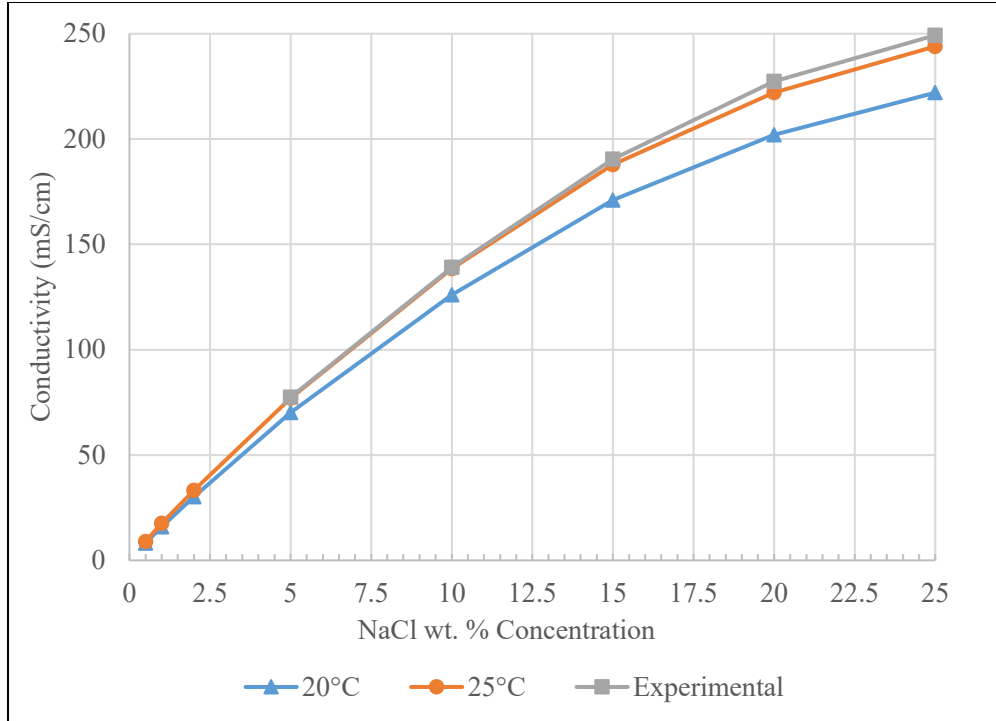
Figure 4.3: Concentration vs. Conductivity based on literature [67]- [69], coupled with experimental lab results.

Table 4.2: Concentration and conductivity with correction factor for NaCl.

Concentration (wt. %)	Conductivity At 20°C	Correction Factor 20°C	Conductivity At 25°C	Correction Factor 25°C
0.5	8.2	0.609	9.1	0.554
1	16	0.625	17.6	0.567
2	30.2	0.662	33.2	0.603
5	70.1	0.713	77.0	0.649
10	126	0.793	138.5	0.722
15	171	0.877	187.9	0.798
20	202	0.990	222.0	0.901
25	222	1.12	244	1.02

4.2.3 Mass Balance:

The pump flow is set to 10 ml/min while flowing deionized water at p_c 240bar, before addition of heat. Once at process conditions the flowrate is verified. The moment the inlet is changed from deionized water to feed solution, the exit effluent is collected. This bottle contains the DI water that remains in the system until salt water replaces it, assuming plug flow in the reactor. The moment the exit TDS increases above DI water levels, the exit effluent is collected separately. This represents the process TDS, which is used to determine the salt removal efficiency. On test completion, the inlet feed is switched back to DI water while maintaining process conditions (temperature, pressure and flowrates). The resulting effluent stream is then collected to close the mass balance. Mass balance closures for the NaCl experiments are typically about 95%.

4.3   Part 2: Produced Water Experiment

In order to recycle Bakken produced water, it must be treated to a quality suitable for hydraulic fracturing. Since the objective is to reduce inorganic compounds, heavy metals, dissolved solids and foul causing organic compounds that can damage production equipment and decrease well performance. Produced water samples (Pierre Federal and Lindy34-10) obtained from two well locations are used in this experiment. As shown in **Table 4.4**, the percentage of dominant ions (Na^+, Cl^-, Ca^{2+}, Fe^{2+}/Fe^{3+}, K^+ and Mg^{2+}) present in Bakken produced water are consistent with those reported in the literature.

Other significant ions detected are barium, magnesium, potassium, strontium and sulfates.

A proof-of concept organic destruction experiment in the presence of the catalyst was performed. The experimental setup was configured to include a catalytic bed for oxidation reaction in the supercritical reactor. Two types of additives (X and Y) were used in this investigation. While 32 wt.% H_2O_2 solution was investigated as the oxygen source in the supercritical reactor. Varying wt.% ethanol solutions were employed as the organics fuel. Liquid effluent samples as well as gas samples were analyzed for organic and inorganic carbon. The gas sample was collected and analyzed using a Raman laser gas analyzer. Testing was done at 380°C and 240 bar, and performance at these conditions were evaluated based on reduction of the organic carbon in the effluent sample. The hypothesis is that internal heat supplied from the oxidation reaction will raise the temperature of the produced water to achieve maximum salt precipitation.

Ethanol is used for this experiment due to its simplicity. Since typical produced water streams have substantial amounts of organics. This makes ethanol applicable in this test, as evidenced by **Figure 4.4.** Hydrophilic acids (HPI) are represented by simple acids like acetic acid, acetone, and ethanol. Transphilic acids (TPIA) consist of aromatic compounds with acidic functional groups. Hydrophobic organic acids (HPOA) include less polar compounds such as phenol.
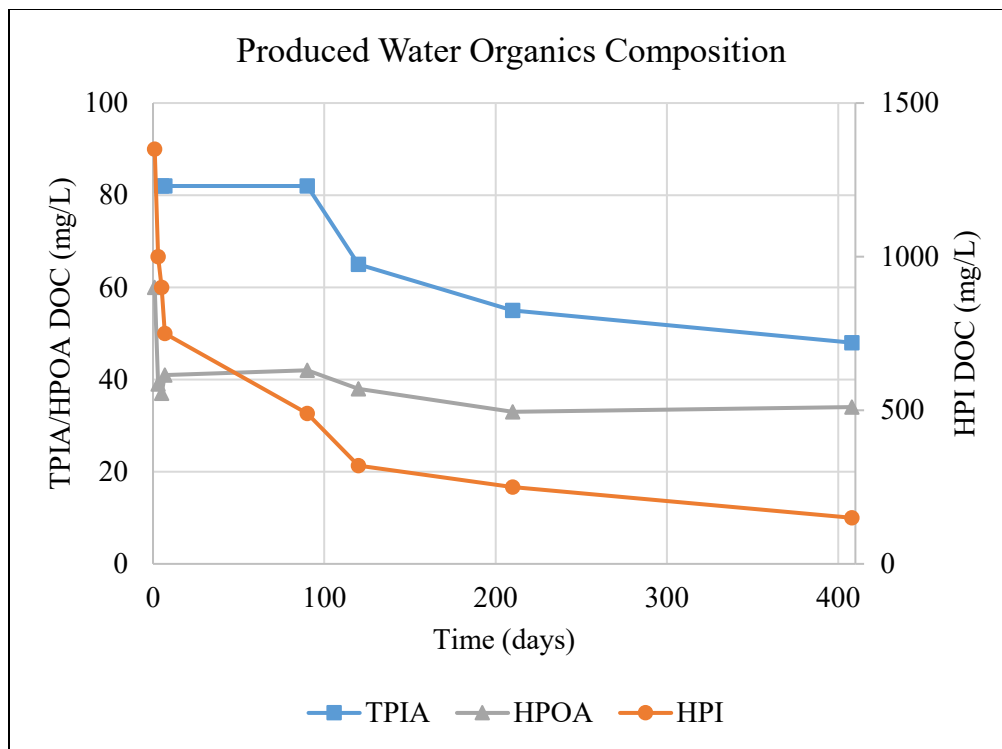
Figure 4.4: Concentrations of various classes of organics over time [70].

Literature data support the assumption that transition metal-oxides can improve the destruction of organics in supercritical water by reducing the time required for complete oxidation. Studies also suggest that a longer period for organics oxidation in the absence of a catalyst. **Figure 4.5** shows the drastically improved residence times for phenol conversion using catalysts.

Ding et al. showed important improvements in catalyzed organics destruction vs. non-catalyzed destruction [71]. Not only are reactions substantially faster when a catalyst is present, they also drive towards fully oxidized products such as CO_2.
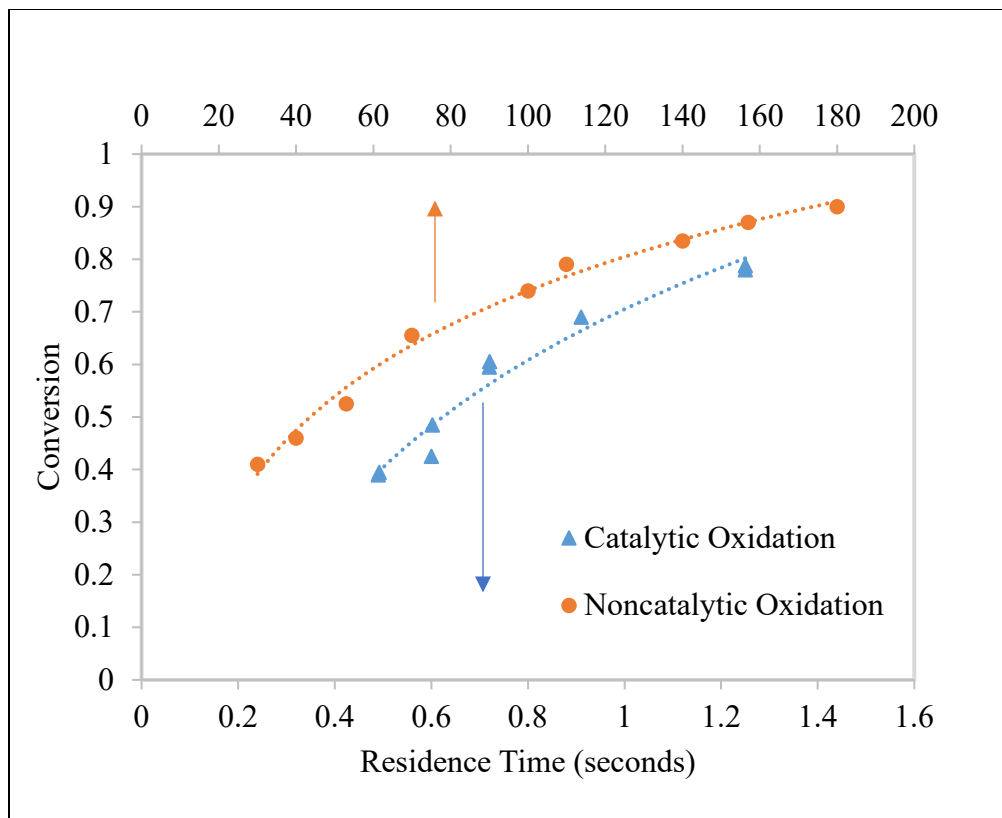
Figure 4.5: Oxidation of phenol under catalytic and non-catalytic conditions [72].

4.3.1   Organic Oxidation Methodology: SCWD system was modified to include a secondary feed location. Each inlet stream (the primary inlet and the new secondary inlet) is preheated separately to allow the ability of simultaneously introducing two feed streams into the reactor with the solutions meeting at the particle bed held within the reactor.

The system is heated externally to a steady state condition to a sub-critical bulk temperature of ~365-370°C and 240 bar. Heat from the ceramic heaters is applied to maintain the bulk fluid temperature. An ethanol/H_2O solution was fed through the

primary inlet (15-18mL/min). The primary inlet sends the solution through a preheater

and into a dip tube in the reactor where it meets the catalyst bed. A peroxide/H_2O

solution is fed through the secondary inlet (12-15 mL/min) passing through a second

preheater and enters the reactor below the catalyst bed. The two fluids meet in the

catalyst bed, a combined fluid flow of ~30mL/min (a flow rate that matches that used for

the "hot finger" tests). The heat of reaction from the oxidation of organics results in a

temperature increase in the lower reactor section and provides the heat that had been

previously supplied by the hot finger.

4.3.2   TOC Methodology

The effluent gas was collected and analyzed for composition and volume of gas

produced. The liquid effluent was collected and analyzed using SHIMADZU TOC-VcsN

Total Organic Carbon Analyzer. This data was used to determine the amount of organic

and inorganic carbon present in the effluent stream as well as characterize the efficiency

of ethanol oxidation. During produced water testing, liquid effluent streams were

analyzed using a benchtop conductivity meter (Hanna Instruments Model: 5522-01) to

determine the level of desalination that occurred in the reactor.

4.3.3　Produced Water Methodology

Based on the work done with the sodium chloride at varied temperatures, a similar approach was used to characterize produced water samples. Produced water samples were sourced from well-heads within the Bakken formation in North Dakota. A homogeneous mixture was prepared by stirring the produced water sample, without treating for organics and sulfates. A sample of 1200ml was measured in a beaker and filtered with a Buchner Funnel installed with a 0.45µm filter. **Figure 4.6** shows typical produced water sample before and after filtration. **Figure 4.7** shows the filter cake recovered after filtering with a 0.45µm filter. The conductivity and pH were recorded before and after testing.
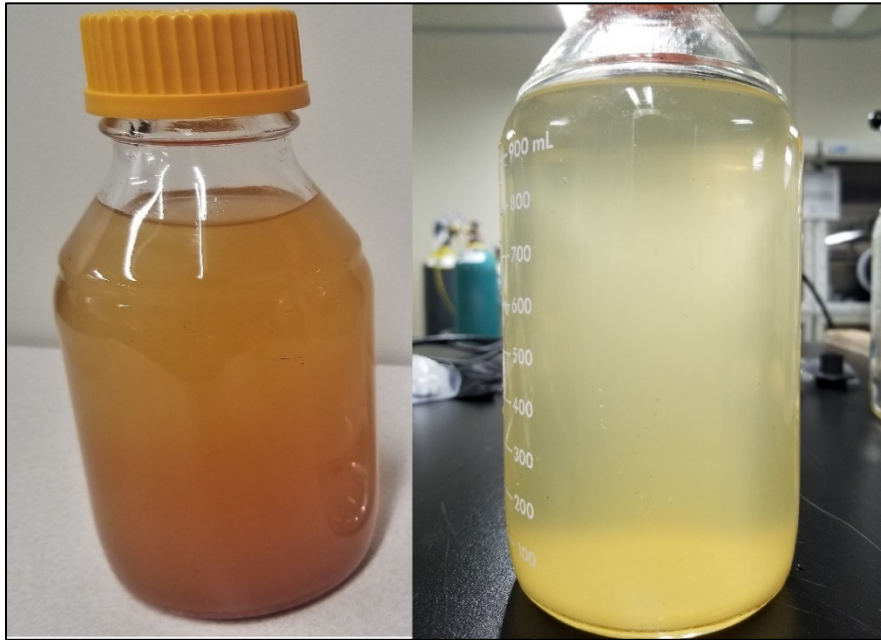
Figure 4.6: Typical produced water sample before and after filtration (from left to right).

The filtered produced water samples were prepared for testing. Samples used were diluted with deionized water by about 15 %, to provide protection for the high-pressure pump during testing. As a future study, this thesis would recommend further investigation of pretreatment methods that would be cost effective and offer protection for process equipment as needed.
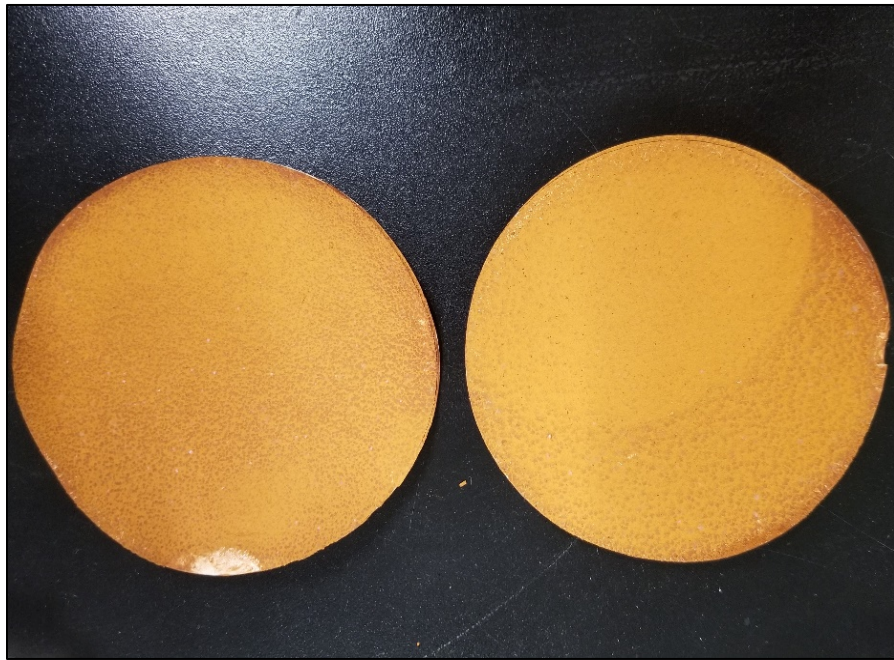
Figure 4.7: Filter cake recovered on 0.45μm filter.

With the current set-up and scale, this helps mitigate solids precipitation as the feed solution passes through the pump. The solution was also prepared with 1wt% Ethanol. The prepared solution composition is 84wt% Produced Water/1wt% Ethanol/15wt% DI-H_2O. Preparation of the PW feed solutions and diluted concentrations during testing are summarized in **Table 4.3**.

Table 4.3: Feed solution preparation and during test dilution, Ethanol/Produced water and H_2O_2.

Lab Prepared Produced Water Solutions		
Ethanol	**Produced Water**	**H_2O**
1 wt.%	~Salt Concentration: 20.8 wt.%	78.2 wt.%
Peroxide	--	**H_2O**
32 wt.%	--	68 wt.%

During Test - Diluted Solutions				Flow rates	
Ethanol	**Produced Water**	**Peroxide**	**H_2O**	**Primary Inlet**	**Secondary Inlet**
0.6 wt.%	~Salt concentration: 12.4 wt.%	13.2 wt.%	73.8 wt.%	17 mL/min	12 mL/min

The produced water samples Lindy34-10 and Pierre Federal were analyzed for their compositions before and after dilution using ICP-MS. Dissolved ions present in the produced water sample are shown in **Table 4.4**. The starting TDS prior to sample preparation and testing were determined at 262,358 mg/L and 237,860 mg/L for Lindy34-10 and Pierre Federal, respectively. In addition, dilution of the raw samples reduced the TDS concentration of Lindy34-10 and Pierre Federal by 17.8% and 23% respectively.

Table 4.4: Composition of the produced water samples.

Constituents	Lindy34-10 (mg/L)	After Dilution (mg/L)	Pierre federal (mg/L)	After Dilution (mg/L)
HCO_3^-	12.2	0	20	12.7
Br^-	694	535.1	848	597
Cl^-	178,000	141,000	159,000	107,000
F^-	NA	<10	NA	< 10
Al^{3+}	NA	<0.25	NA	< 2.5
Ca^{2+}	12,400	10,800	15,400	14,600
Fe^{2+}	87.6	3.77	112	3.14
K^+	4,370	3,840	5,510	5,160
Mg^{2+}	914	819	895	884
Mn^{2+}	9.02	7.85	105	110
Na^+	65,100	57,300	55,200	53,200
Ba^{2+}	6.32	8.05	9.43	11.7
Li^+	16.2	31.6	20.9	48.2
Pb^{2+}	97.4	0.202	0.312	0.679
Sr^{2+}	393	820	570	1340
NO_3^-	NA	<4	NA	< 4
SO_4^{2-}	258	301	169	127
TDS	262,358	215,467	237,860	183,094

4.3.4 Operating Procedures and Measurements

The equipment was set-up using the catalyst bed in the lower reactor section. The system was heated externally to a steady state condition at 240 bar and to a subcritical bulk temperature of ~365-370°C. An ethanol/H_2O solution was fed through the primary inlet (15-17 mL/min) and a peroxide/H_2O solution was fed through the secondary inlet (11-13/mL/min). The feed solution specifications are summarized below in **Table 4.5**

including the lab prepared feed solutions and the expected concentration of the solutions

as they mix in the reactor (diluted) at a combined average flow of ~28mL/min.

Table 4.5: Feed Solution preparation and during test dilution, Ethanol and H_2O_2.

Lab Prepared Organic and Oxidant Solutions	
Ethanol	**H₂O**
1 wt.%	99 wt.%
Peroxide	**H₂O**
32 wt.%	68 wt.%

During Test - Diluted Solutions			Flow rates	
Ethanol	**Peroxide**	**H₂O**	**Primary Inlet**	**Secondary Inlet**
0.6 wt.%	13.6 wt.%	85.8 wt.%	16 mL/min	12 mL/min

The two fluids meet in the catalyst bed and utilizing the heat of reaction of the

oxidation of the organics an increase in the lower reactor temperature of ~30-40°C is

expected. Hence achieving supercritical condition and consequently salt precipitation.

Once at steady state, the primary and secondary feed solutions are changed to

ethanol/PW/H_2O and H_2O_2. The desalination of the effluent stream is measured post-test

for conductivity and pH via samples collected. The oxidation of the organic is measured

via total carbon analysis of the liquids and collection/composition analysis of the exhaust

gas. The collected effluent streams are secured for compositional analysis using

inductively coupled plasma mass spectrometry (ICP-MS). The results of all experiments

performed are discussed in Chapter 5.

CHAPTER 5: RESULTS AND DISCUSSION

5.1 Hot Rod (NaCl-H$_2$O) Experiments

Table 5.1 shows a summary of the test conditions for 10 wt.% and 20 wt.% NaCl at which experiments were performed using the heated rod. As stated earlier the heated rod was used to create a localized supercritical zone for salt deposition. Therefore, the pressure and localized "Hot zone" represent the conditions of the bulk fluid at the lower reactor (supercritical zone). Two baseline tests for conductivities measurements were ran at 360°C and 240 bar, one for 10 wt.% NaCl and another for 20 wt.% NaCl. These was done with little to no desalination expected. These tests help establish that the reactor is operating under plug flow with minimal to no dilution.

Table 5.1: Summary of the test conditions for 10 wt.% and 20 wt.% NaCl.

Experiment	Salt Concentration	Pressure	Localized "Hot" Zone Temperature (°C)	Heated Rod Temperature (°C)	Flowrate (ml)
Condition-1	10 wt. % NaCl (100,000ppm)	~240 bar	360	365	13.8
Condition-2		~200 bar	380	440	9.0
Condition-3		~240 bar	400	490	9.7
Condition-4	20 wt. % NaCl (200,000ppm)	~240 bar	360	367	12.5
Condition-5			385	450	10.0
Condition-6			415	530	11.5
Condition-7			420	534	12.5
Condition-8			427	560	10.7
Condition-9			435	540	9.6

Results of the 10 wt.% and 20 wt.% are summarized in **Figure 5.4 and Figure 5.5,** respectively. At zero-milliliter mark, freshwater feed in the reactor was changed to a salt-water feed. The first slight increase noticed in conductivity occurred at the 150 ml/mark for most tests. Each test saw had a rise in conductivity before the 300 ml (32-minute) mark. The 280-330 ml volume range shows the exit conductivity is reflective of the salt stream that has passed through the reactor. This is believed to be representative of steady state conditions. A clear difference is established between tests above 400°C and those below 400°C.

The sub-400°C (360°C, 380°C and 385°C) tests show an increase in conductivity immediately after the saline stream begins to enter the reactor. This is reflected by the rise in conductivity in the 200 to 300 ml fed range (difference in time between the three sub-400°C tests are due to slight variations on how the test was performed). For the higher temperature tests, the outlet conductivity showed essentially complete removal of the salt (from the 300 to 500 ml fed range). **Table 5.2** shows the respective inlet and outlet conductivity of the influent and effluent stream for all experiments.

5.1.1   Results for 10 wt% NaCl concentration

As can be seen in **Figure 5.1**, at steady state temperature, the effluent TDS begins to increase after 15 minutes until it matches the conductivity of the influent stream. Although at supercritical pressure of 240 bar, this test was performed to show no desalination occurred at sub-critical temperature of 360°C. It is most likely that at this

temperature the solvation properties of water had not significantly diminished for complete salts precipitation. In **Figure 5.2**, the effluent TDS begins to rise after 30 minutes but does not completely match the conductivity of the influent stream. The wavy motion observed by the effluent conductivity is indicative of partial desalination at steady state conditions. However, lower pressure used at 380°C may account for minimal salt precipitation during this test. **Figure 5.5** shows 20 wt.% NaCl concentration at 240 bar and 380°C.
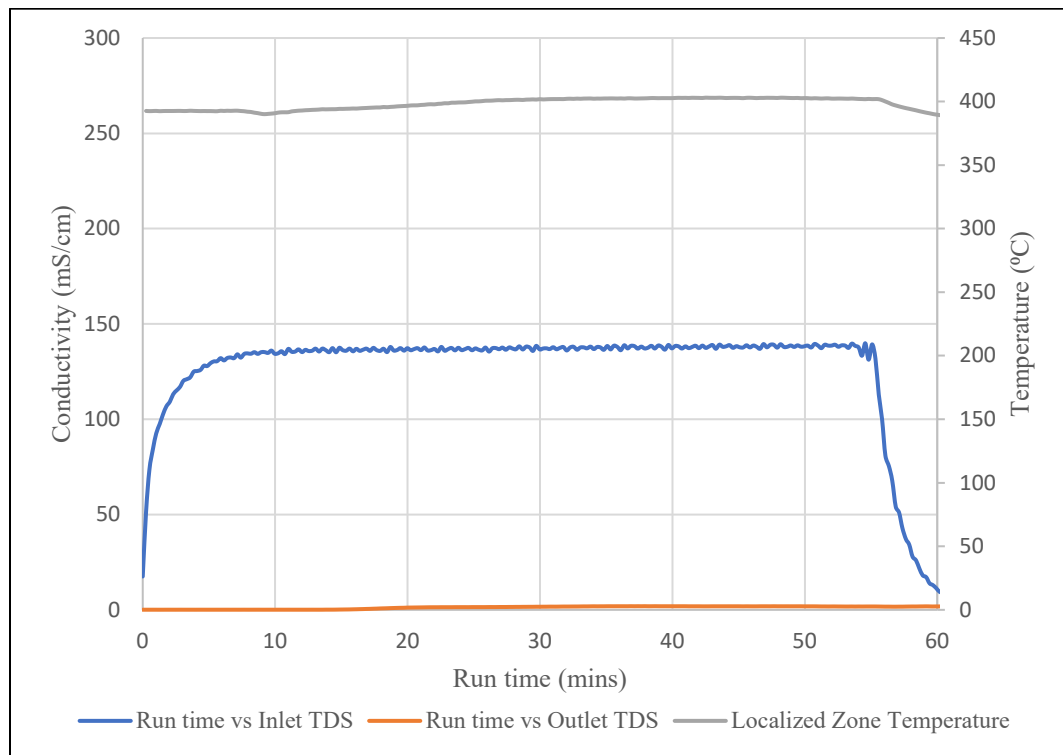
Figure 5.1: 10 wt% NaCl concentration at steady state 240 bar-360°C
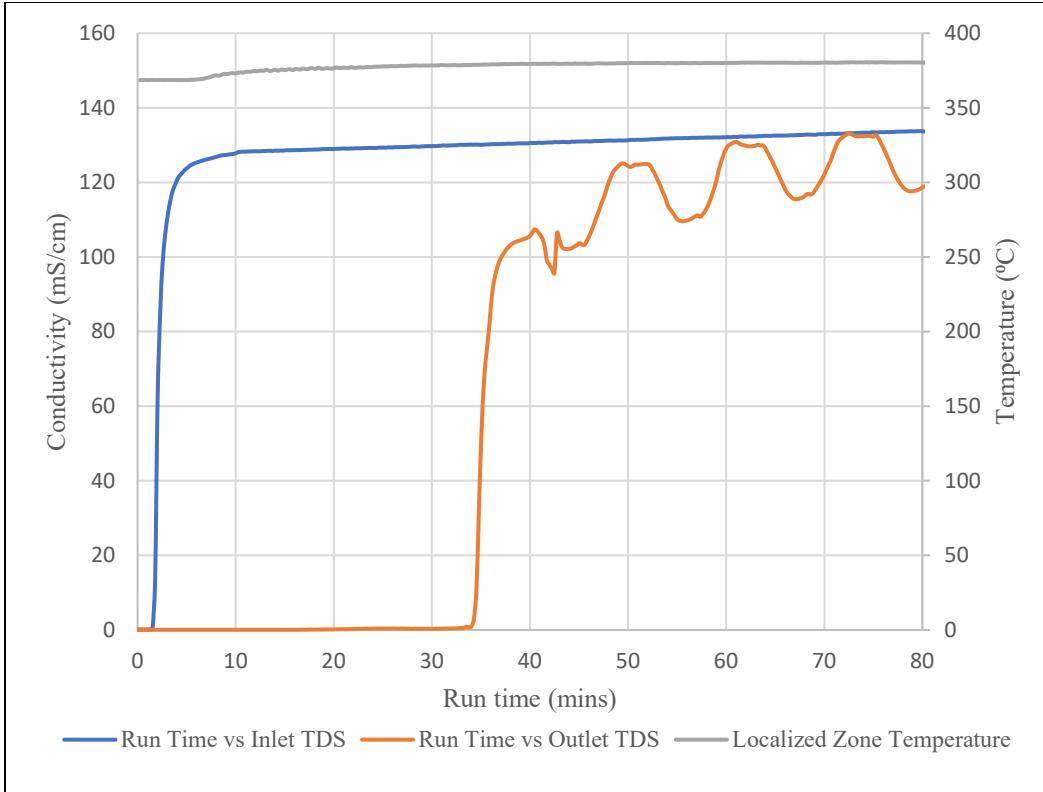
Figure 5.2: 10 wt% NaCl concentration at steady state 200 bar-380⁰C.

Unlike the first two tests, the effluent conductivity for 400⁰C was largely flat throughout the experiment (see **Figure 5.3**). This shows a greater amount of salt separation from the influent stream at these conditions.
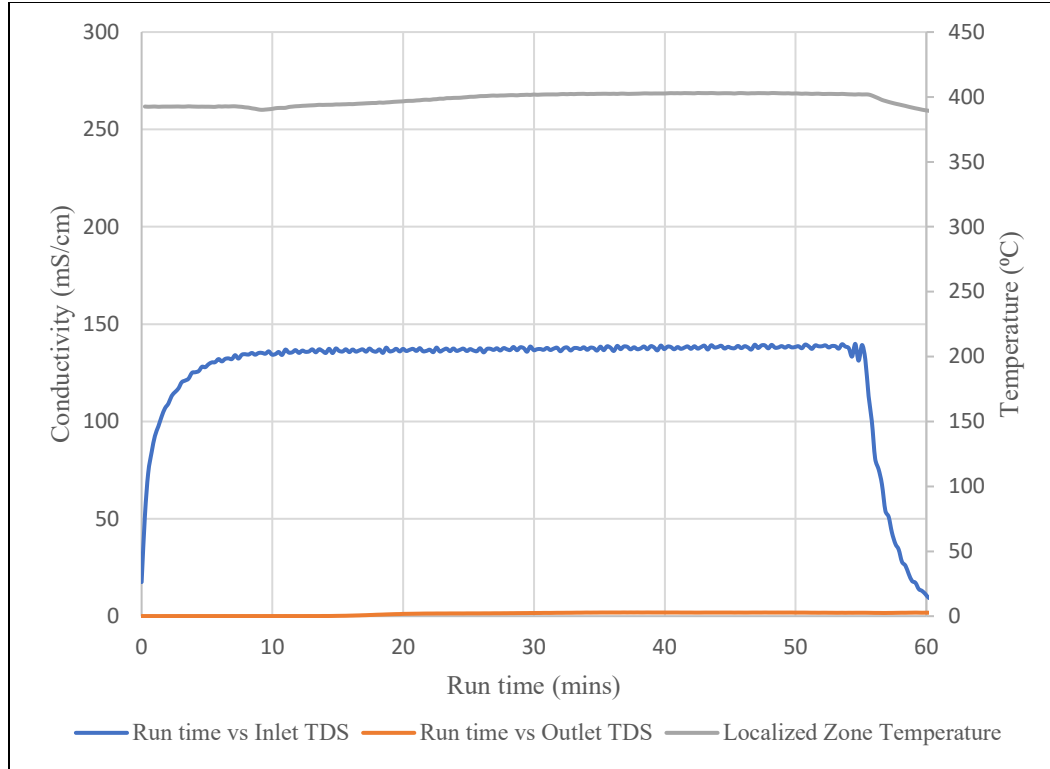
Figure 5.3: 10 wt% NaCl concentration at steady state 240bar-400ºC.

Figure 5.4 summarizes the three tests for 10 wt.% NaCl concentration. For the

360°C test, the exit salinity first increased at the 150 ml mark (after 15 minutes), before

matching the starting salinity at the 300 -350 ml mark (30-35 minutes). Thereby implying

no salt removal at this temperature. For the 380°C test, the exit salinity increased to a

steady state value of approximately 120 mS/cm, representing a removal efficiency of ~

10%. The test at 400°C showed no increase in salinity over the duration of the test,

suggesting a near 100% removal of salt for the entire test duration.
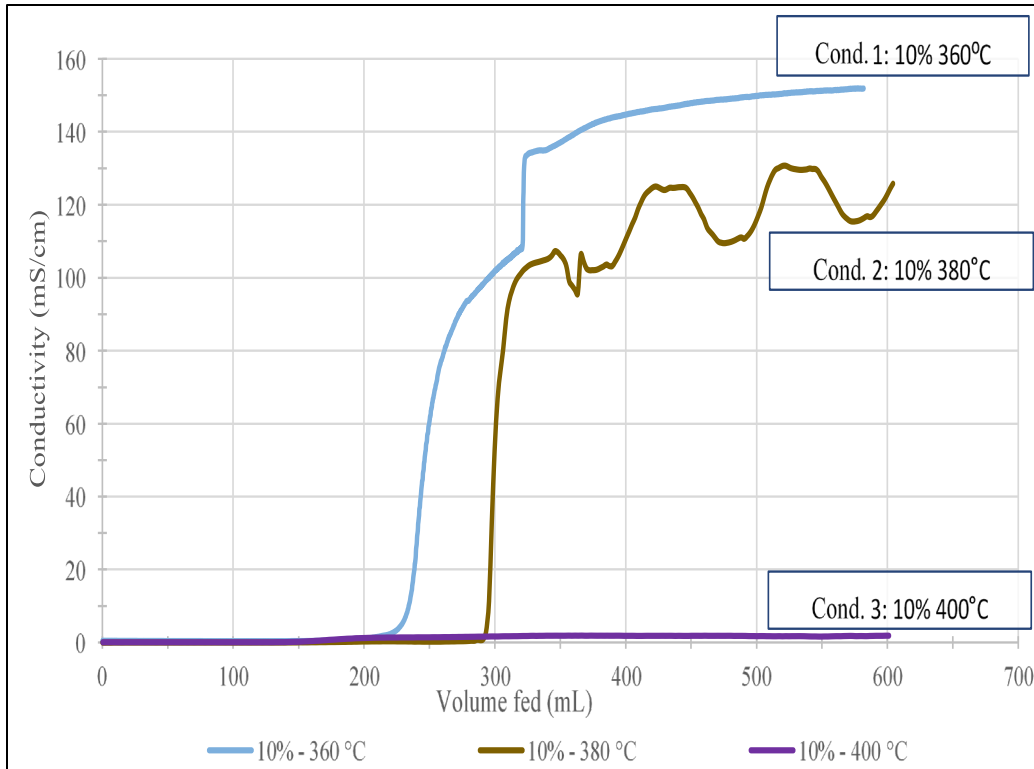
Figure 5.4: Conductivity vs. volume fed for 10 wt.% NaCl Concentration.

During the first set of tests the temperature profiles indicated a rather high heat loss through the bottom of the reactor. Modifications were made which included raising the reactor higher into the ceramic heaters and improving the insulation. Additionally, improvements to the hot rod were made by adding a protective sheath and placing it further into the reactor. The dip tube in the reactor was changed to a smaller diameter tube (1/4" from 3/8") to accommodate the larger hot rod. The 20 wt.% tests were performed with the improved temperature control.

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5.1.2   Results for 20 wt.% NaCl concentration

Figure 5.5 shows the results from the six tests performed with the 20 wt.% salt. The four tests above 400°C show 100% desalination up until the 500 ml mark. At this point the volume of salt deposited in the lower reactor covering the hot rod reaches capacity and the overall desalination efficiency decreases. The two tests below 400°C show minimal desalination at 360°C and 27% reduction for the 385°C test.
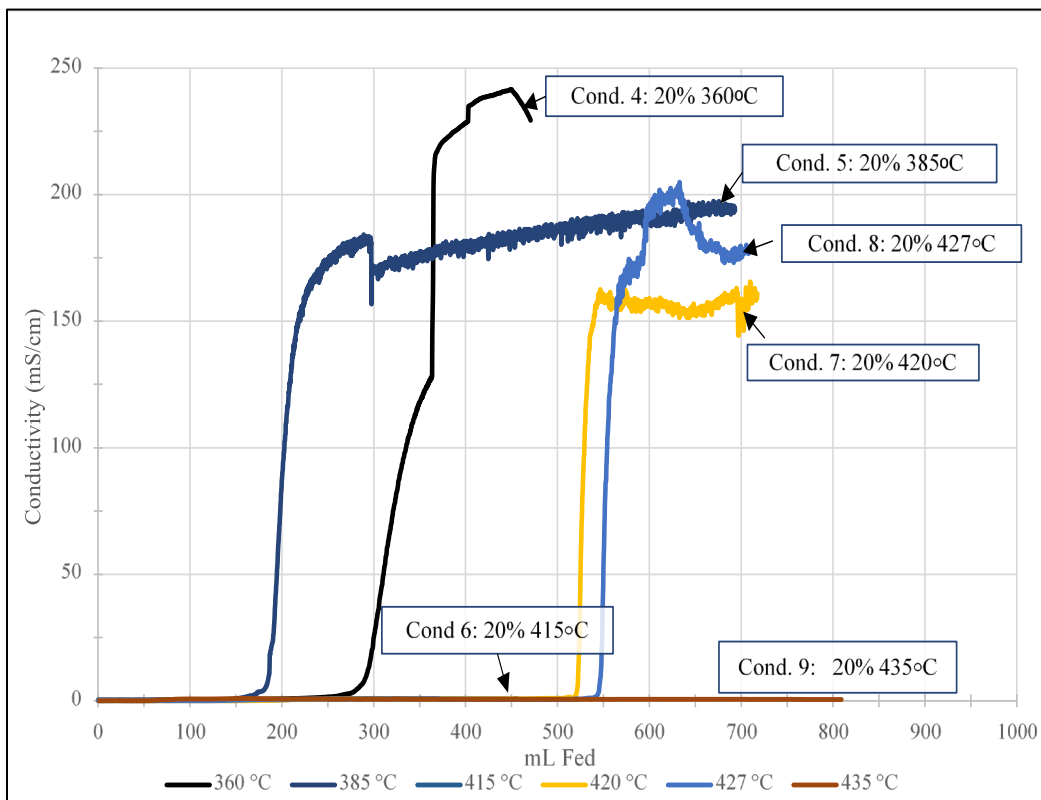
Figure 5.5: Conductivity vs. volume fed for 20 wt.% concentration.

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The data set reveals in all tests, salt brine had passed through the reactor and reached the outlet conductivity sensor by the 300 ml mark. The overall desalination/salt removal percentages for each condition are shown in **Table 5.2**. **Figure 5.6** and **5.7** suggest that increase in salt precipitation is directly propositional to increasing temperature. Thus, for conditions above 400°C, water recovery efficiency increased approaching 100%. The reactor begins to reach volume capacity beyond 500 ml mark for the 20 wt.% NaCl (i.e. 100 grams of NaCl deposited). This is indicated by the sudden increase in conductivity (except during 435°C testing).

<p align="center">Table 5.2: Summary of results from effluent analysis.</p>

Salt Concentration	Inlet Temperature (°C)	Inlet Conductivity (mS/cm)	Inlet TDS (ppm)	Outlet Conductivity (mS/cm)	Outlet TDS (ppm)	Removal Percentage (%)
10 wt. % NaCl (100,000ppm)	360	137.2	99000	131.9	98100	0.9
	380	135.1	97000	120.9	87000	10.3
	400	137.6	99000	1.206	840	99.3
20 wt. % NaCl (200,000ppm)	360	228.1	205000	228	205000	0
	385	228.9	206000	189.9	150000	27.2
	415	226.6	204000	0.721	490	99.7
	420	227.4	205000	0.650	420	99.8
	427	227.9	205000	0.98	660	99.7
	435	227.9	205000	0.956	600	99.8
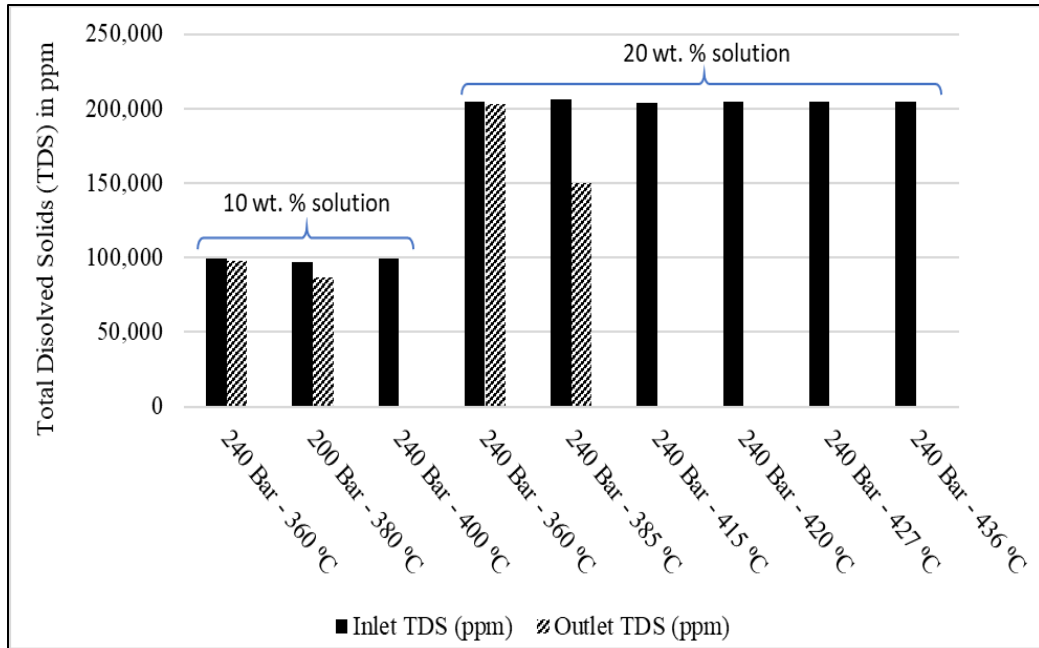
Figure 5.6: Inlet TDS vs Outlet TDS in ppm
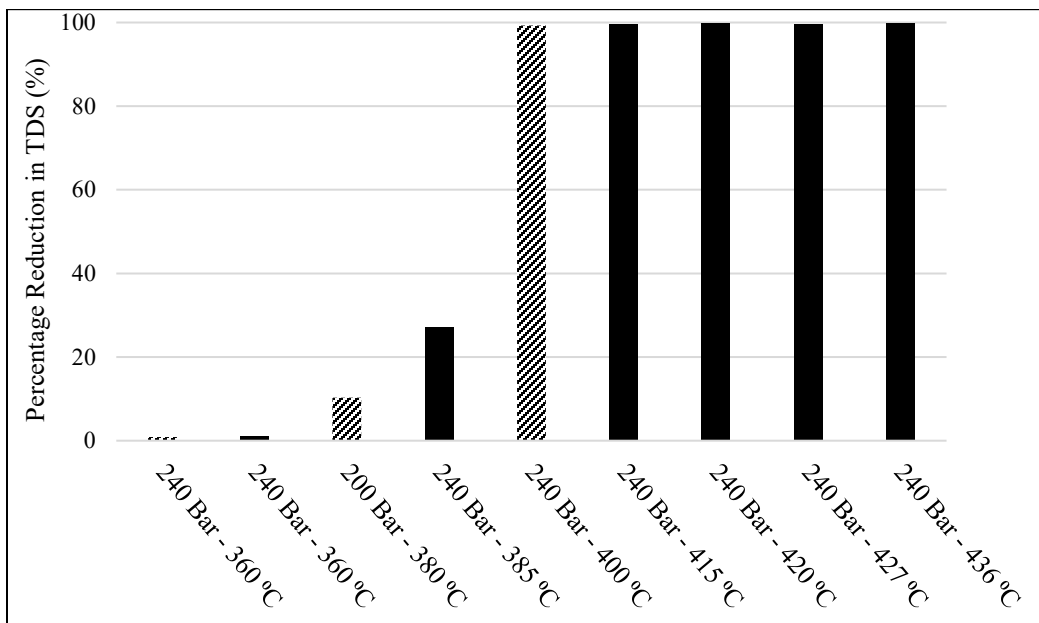
Figure 5.7: Percentage reduction in TDS, under varied concentrations and supercritical conditions. (Pattern = 10% NaCl, Solid = 20% NaCl)

5.2   Salt deposition

While later tests implemented a wash down to close the mass balance and clean the system. Earlier tests with near 100% desalination used a nitrogen purge to evacuate the system of liquids and identify areas of salt deposition. It was observed that areas of the system under subcritical temperatures (sub ~360°C) had no visible salt deposition. Although, methods for continuous removal of solids during operation were not investigated in this study, it was observed that majority of the salt deposition occurred on the heated rod surface, rather than in the cooler or reactor walls. This effect was not observed in the lower concentrations. **Figure 5.8** shows salt deposited on the heated rod with increasing temperature.

For the scale of this experimental setup, a major challenge encountered during operation was the volume limitation of the equipment for longer runs. Also, the above tests show removal of solid deposits is necessary for recovery of valuable salts and the sustainability of the equipment. This is an important consideration for the SCWD technology to be commercially profitable. For example, in a batch operation the volume and heated surface area available for deposition would be a critical design for consideration. In a continuous feed design, a method for the evacuation of the deposited solids would be necessary.
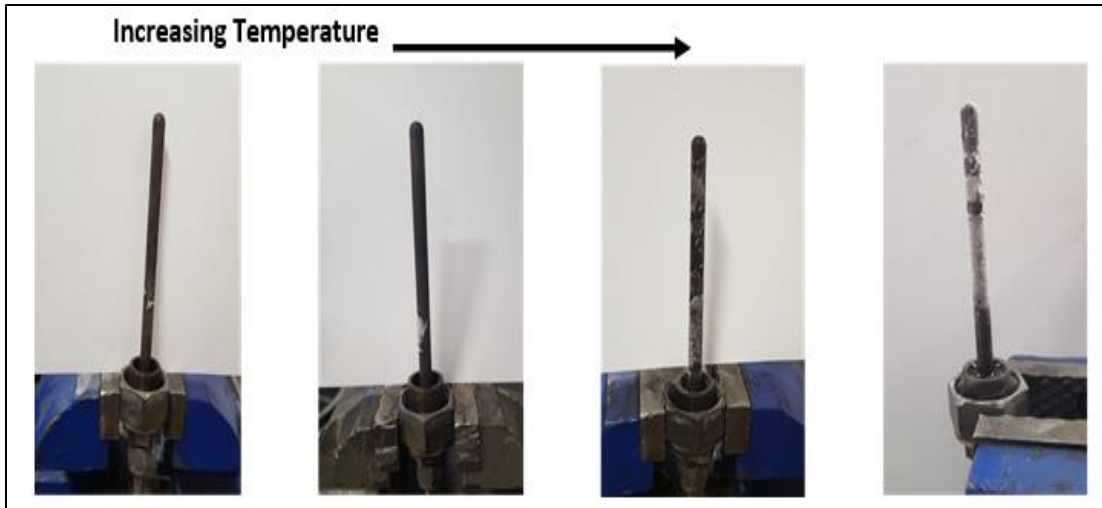
Figure 5.8: Salt deposition on the heated rod inside the reactor.

Preliminary results from the heated rod experiments reveal that the supercritical water desalination process can effectively reduce salt concentration in the brine. More importantly, the diminished solvation properties of water can be utilized by closely monitoring and tailoring supercritical conditions for efficient salt removal. In addition, it has demonstrated that temperatures above 400°C have a large impact on effluent TDS. This will be used as a starting temperature range during the produced water experiments. Also, organic oxidation and the addition of heat to achieve maximum salt separation in produced water will be discussed in the next section. Since the supercritical concept will be applied to recycle brine for hydraulic fracturing reuse. It is believed that SCWD operating conditions can be tailored to treat high TDS wastewater to an acceptable level.

5.3   Organic Oxidation and Additive experiment

Temperature increase as a result of the oxidation of organics was primarily

investigated in this section. 32 wt.% H_2O_2 served as the oxidant while ethanol

concentrations of 0.5 wt. % and 1 wt.% were used as organics and prepared for testing. In

addition, all experiments were performed at the supercritical pressure of 240 bar. **Table

5.3** shows the diluted ethanol and peroxide concentrations in flow as well as the

temperature difference (ΔT) achieved from the oxidation reaction. The results show

similar ΔT obtained in the presence of additive (catalyst bed) X and Y. For catalyst X,

ethanol was fed through the primary inlet to the reactor at ~15 mL/min while the

secondary inlet fed 32 wt.% H_2O_2 at ~15mL/min. At a combined flowrate of ~30mL/min,

ethanol was diluted to concentrations of low (0.3 wt.% ethanol) and (0.7 wt.% ethanol).

This process was repeated in the presence of additive Y, where ethanol was fed at

~15 mL/min while the secondary inlet fed 32 wt.% H_2O_2 at ~12 mL/min. At a combined

flowrate of ~27mL/min, the dilution concentration of ethanol remained the same as in the

case of catalyst X. However, due to lower flowrate at the secondary inlet, H_2O_2 was

diluted to 13 wt.% and 14 wt.% concentration for the low and high experiment,

respectively. The resulting increase in temperatures under supercritical conditions are

shown in **Figure 5.9 – 5.12** respectively.

Table 5.3: Summary of organics and oxidant testing.

Experiment	Additive	Ethanol Concentration (diluted flow)	Peroxide Concentration (diluted flow)	ΔT	Flowrate (mL/min)	
					Ethanol	H$_2$O$_2$
Low	X	0.3 wt.%	16 wt.%	16°	15	16
High	X	0.7 wt.%	14 wt.%	76°	16	13
Low	Y	0.3 wt.%	13 wt.%	61°	15	11
High	Y	0.7 wt.%	14 wt.%	76°	15	12

In all test performed, the zero-minute to 3-minute mark represents steady state temperature before the introduction of hydrogen peroxide and ethanol streams into the reactor. A drop in temperature is observed at the lower reactor and additive bed before the 8-minute mark. This can be attributed to the peroxide stream entering the reactor at a slightly lower temperature (~355°C). Although the ΔT generated differs in most tests, there is a clear rise in temperature before the 10 minutes in both additive X and Y experiment.

For example, in low concentrations tests for additive X and Y, temperature increased by 16ºC and 61ºC at the 40-minute mark, respectively. This large ΔT may be a result of a lower flowrate at the secondary inlet during the low concentration experiment for additive Y (see **Table 5.3**). For the high concentration tests, similar gains in temperature was generated.

5.3.1 Additive X Test

Figure 5.9 shows temperature at the material bed slowly increase from subcritical to supercritical (370⁰C - 386⁰C). This in turn increases the lower reactor temperature from 364⁰C - 373⁰C. In the 1 wt.% organic test, the additive rises from 368⁰C - 444⁰C and increased temperature at the lower reactor by 72°C (see **Figure 5.10 and 5.13**). The magnitude of energy transfer from the liquid to additive bed and to the surrounding surface can be attributed to convection in the reaction and conductive ability of the catalyst.
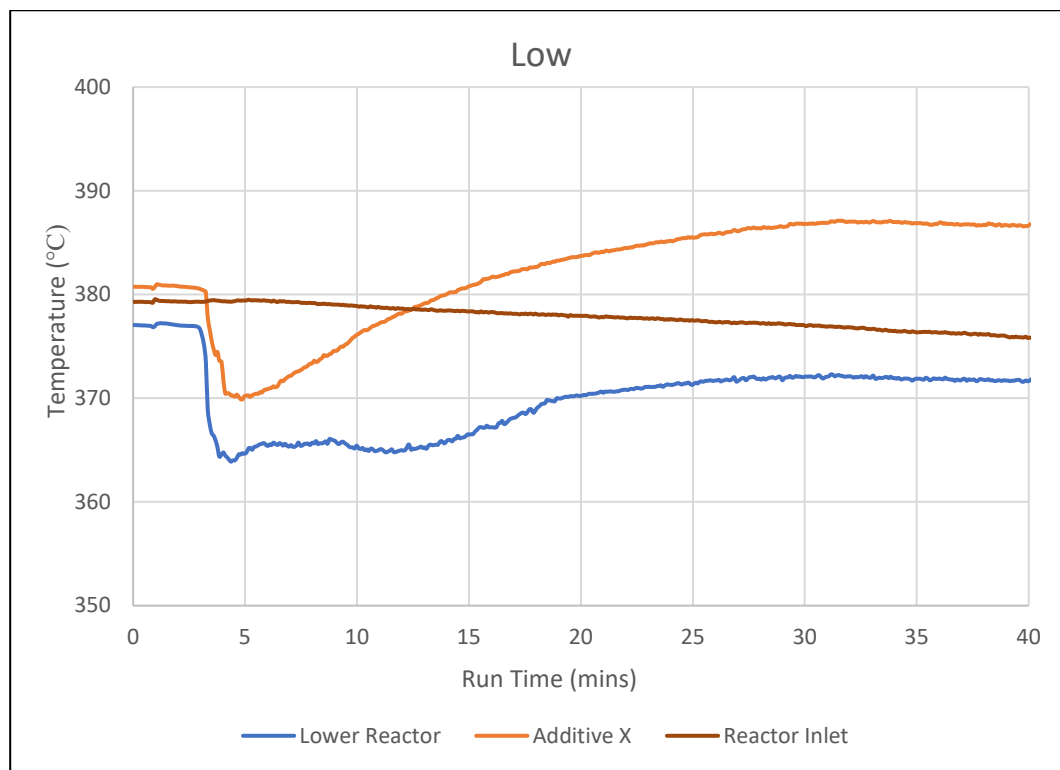
Figure 5.9: Temperatures profile for 0.5 wt.% ethanol in the presence of additive X.
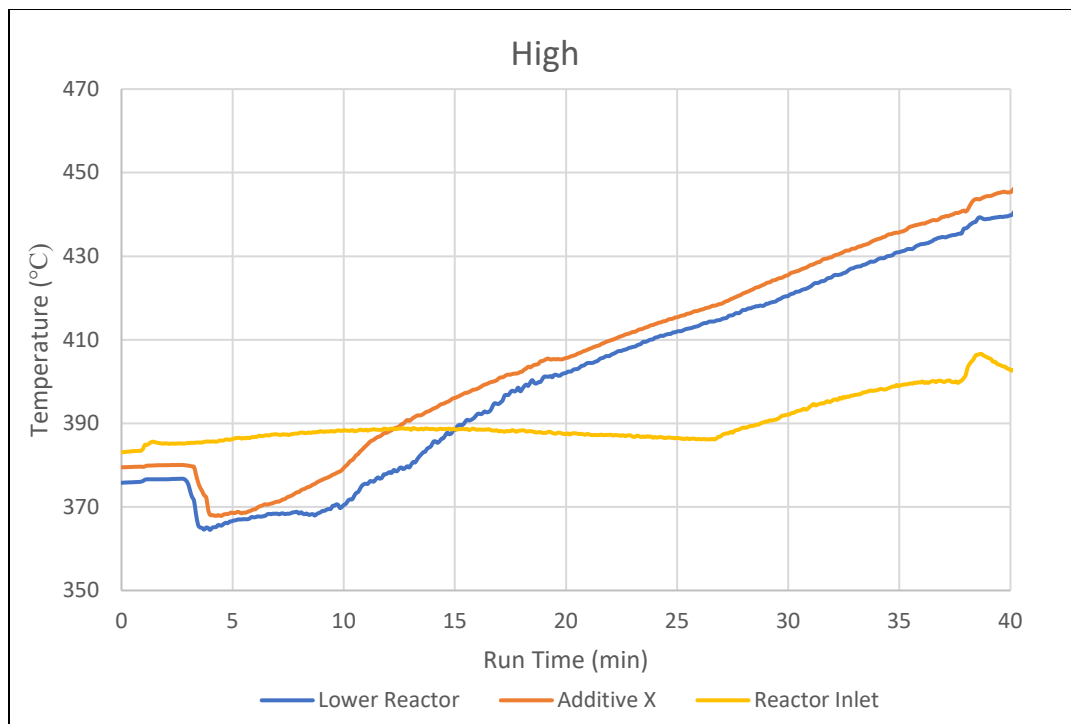
Figure 5.10: Temperatures profile at 1 wt.% ethanol in the presence of additive X.

5.3.2 Additive Y Test

In both low and high concentration test conducted using additive Y, the feed solutions were introduced when the system was at steady supercritical temperature. For low ethanol concentration, the additive temperature increases from 377⁰C - 438⁰C (see **Figure 5.11**). In **Figure 5.12,** the 1 wt.% organic test shows temperature of additive Y increased from 379⁰C - 455⁰C over a period of 40 minutes. This is similar to temperature increase under the same conditions for additive X. Thus, resulting in a substantial 68⁰C increase at the surrounding supercritical zone.

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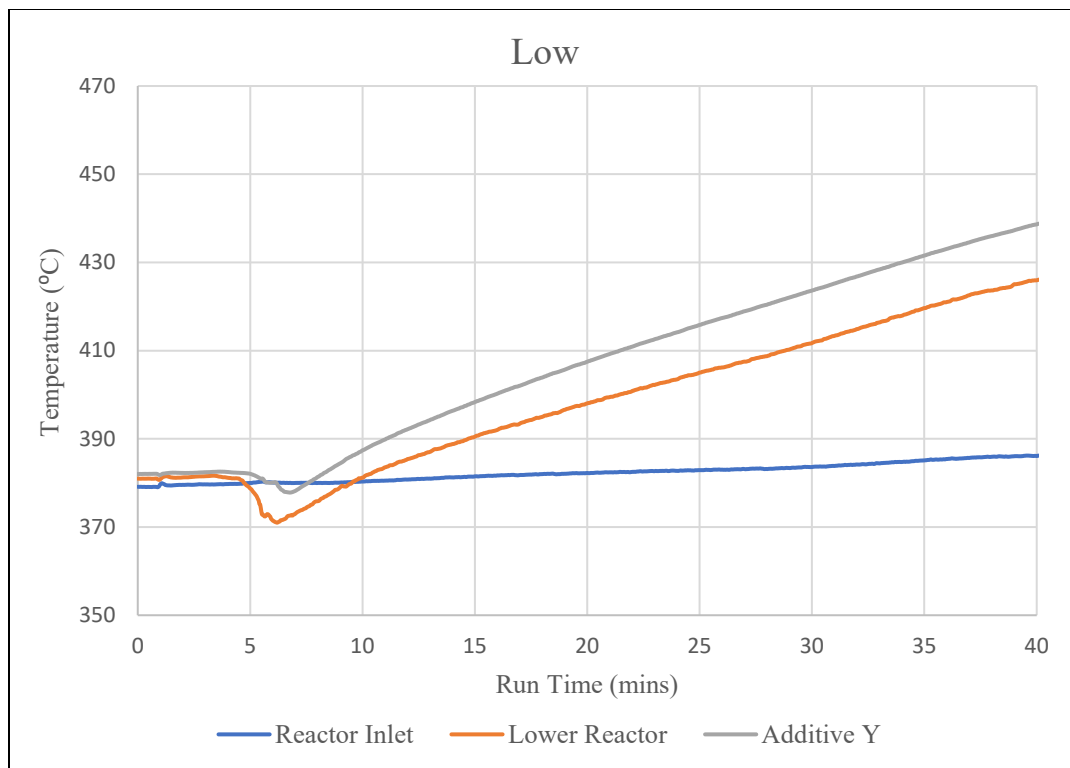
Figure 5.11: Temperatures profile at 0.5 wt.% ethanol in the presence of additive Y.

Figure 5.13 shows a comparison of change in temperature for additive and

reactor zone over an average of 40 minutes across all four tests. The result shows a 16°C

and 76°C temperature increase in additive X for 0.5 wt.% and 1 wt.% ethanol,

respectively. While additive Y temperature improved from 16°C to 61°C for 0.5 wt.%

and concentration. The thermal difference between 0.5 wt.% ethanol test for the two

materials may be a result of the lower hydrogen peroxide flowrate in the presence of

additive Y. Although energy requirement for the SCWD and SCWO process were not

investigated in this study, it is likely that the thermal properties of additive Y (such as

conduction) may have played a significant role in its temperature increase. Another point

of interest could be the external energy supplied from the heaters to maintain the temperature of the system. However, for this to be true the temperature of the inlet reactor will have increased relative to change in temperature observed at the lower reactor. This is not the case as shown in **Figure 5.11** and **5.12** where the inlet reactor is steady throughout the experiment.
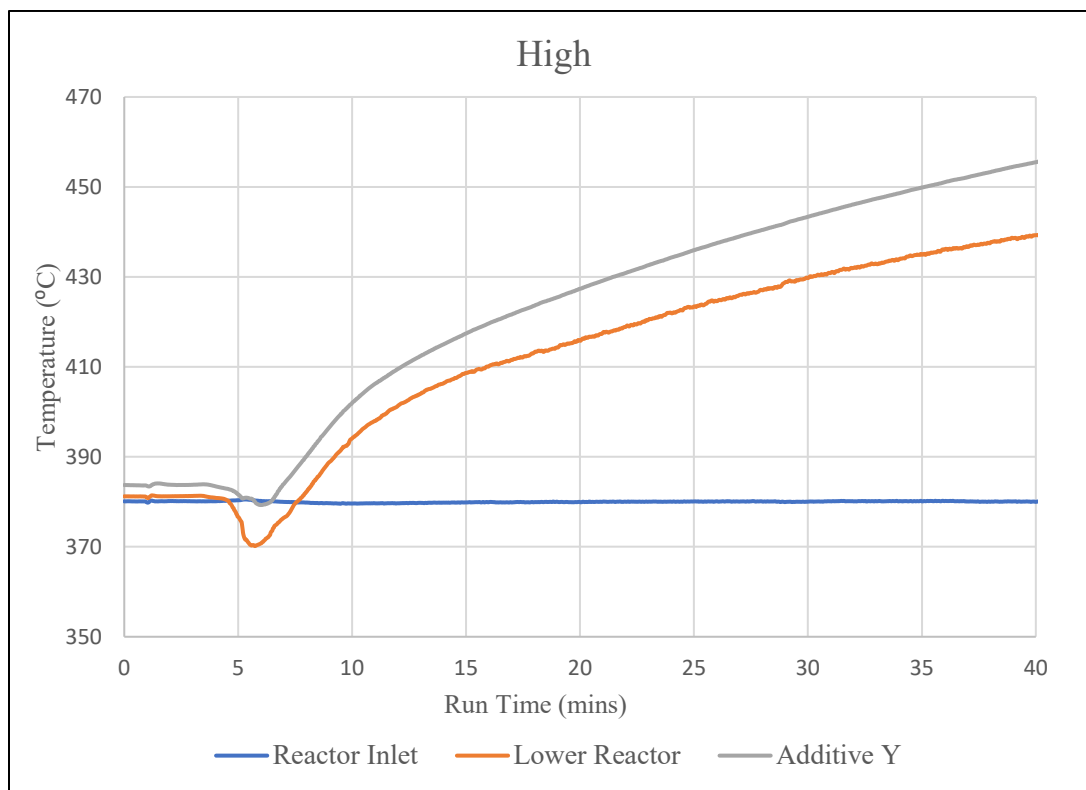
Figure 5.12: Temperatures profile at 1wt% ethanol in the presence of additive Y.
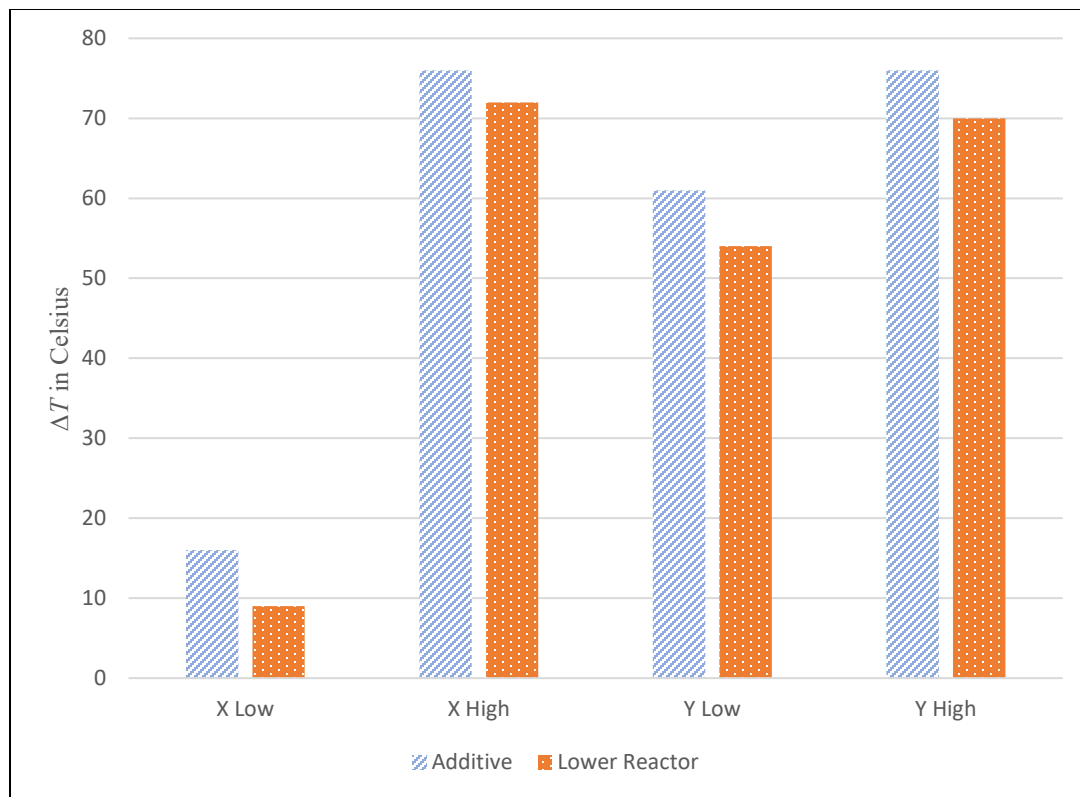
Figure 5.13: Change in additive and lower reactor temperature at low and high ethanol concentrations.

5.3.3 Carbon balance

Effluent samples collected during the test were analyzed for total organic carbon (TOC). Since gas bubbles were predominant during the oxidation process, gases were collected and analyzed for composition and volume. A summary of carbon content from the gas and liquid samples are presented in **Table 5.4.** The total organic carbon present in the liquid samples were considered unconverted during oxidation**.** While the carbon amount found in the gas samples represent the percentage volume converted during

oxidation. Since organics are majorly converted to CO_2 gas during oxidation reaction. Unsurprisingly, CO_2 gas was dominant in all gas samples collected.

Table 5.4: Carbon balance for the varied ethanol concentration in additives X and Y.

Ethanol Concentration	Additive	% Carbon to CO2	% Organic Carbon in Liquid
0.5wt%	X	93%	5%
1wt%	X	95%	2%
0.5wt%	Y	94%	3%
1wt%	Y	97%	2%

The results obtained from the experiments indicate that the additional energy supplied via organic oxidation process is enough to increase the temperature of the localized zone from subcritical to supercritical. Furthermore, the four experiments reveal that the energy generated is influenced by the concentration of organics present, which acts as a fuel during the oxidation process. The conducted organic oxidation experiment has provided information on the quantity of organics required to generate additional heat for desalination.

Since 1 wt.% ethanol in both additive X and Y experiment increased the temperature of the target localized zone in the reactor from about $370^\circ C - 450^\circ C$. Therefore, in combination with information gathered from the heated rod experiments showing supercritical temperature range at which salt precipitation begins. Organic oxidation and salts precipitation using additives at supercritical conditions were

implemented during the produced water experiments. Results of the experiments are discussed in the next section.

5.4   Results of produced water desalination

The equipment was set-up similar to the ethanol/peroxide testing described in the methodology and operating procedure in Chapter 4. The system was heated externally to a steady state condition at 240 bar and to a subcritical bulk temperature of ~365-370°C. The external heat was applied to maintain this bulk fluid temperature. Organic oxidation process using 1 wt.% ethanol (0.7 wt.% in diluted flow) was implemented to raise the temperature of the localized zone from subcritical to supercritical (~370°C – 480°C).

Once at steady state, the primary stream was changed to the prepared produced water feed solution (84 wt.% Produced Water/1 wt.% Ethanol/15 wt.% DI-H$_2$O). The preparation and dilution are summarized in the methodology. Three experiments were conducted using produced water samples Lindy34-10 and Pierre Federal. Pierre Federal PW sample was treated in two separate experiments using additive X and Y. Lindy34-10 PW sample was treated using only additive Y. Results for all three experiments are summarized in **Table 5.5**.

Table 5.5: summary of produced water experimentation.

Experiment	PFx	PFy	L34-10y
Additive	X	Y	Y
Temperature range (ºC)	380ºC - 410ºC	420ºC - 460ºC	430ºC - 480ºC
Influent Conductivity (mS/cm)	218.4	218.4	238.1
Average Effluent Conductivity (mS/cm)	43.7	7.0	9.0
% Change in conductivity	~80	~97	~96
Influent pH	5.8	5.5	5.5
Average Effluent pH (During test)	3.8	7.5	7.0

Results for Pierre Federal x, Pierre Federal y and Lindy34-10 y are shown in **Figure 5.14-5.19**. In all test performed, the zero-minute to 3-minute mark represents steady state before the oxidation process. The inlet stream was transitioned to the organics and oxidant feed before the 10-minute mark. This increased the temperature in the lower reactor to ~410°C, 420ºC and 430ºC for PFx, PFy and L34-10y, respectively. At this point produced water was introduced into the reactor for treatment.

In each experiment, samples were taken at intervals to determine the conductivity and pH of the effluent stream compared to that of the feed stream. In **Figure 5.15, 5.17** and **5.19,** the first pH value represents the influent stream and is not considered when determining the average effluent pH. Also, a treated product stream was collected to represent the temperature range during desalination. Test were conducted for an average

of 45 minutes. It should be noted that there is a time lag of about 10-15 minutes between the entry fluid and product stream. This is representative of the flowrate and the time taken for the feed stream to be transported through the system before coming out at the exit. After the 45 minutes marks the produced water feed stream was changed to DI water to wash and clean the system.

5.4.1 Pierre Federal using additive X (PFx)

Figure 5.14 shows the experiment performed using additive X during desalination of Pierre Federal produced water. Temperature increase at the lower reactor from ~370°C – 410°C, was a starting point above salt precipitation conditions (400°C and 240bar) previously determined in the heated rod experiment. The decrease in temperature at the 44-minute mark can be attributed to increasing flowrate (secondary inlet) that had a cooling effect on the lower reactor. The prepared produced water sample was introduced into the system.

Several samples taken at different periods during the test and examined using a benchtop conductivity meter showed an average of 80% decrease from 218.4 mS/cm in the feed stream. The reduction in conductivity from the effluent stream suggest desalination and salts removal. However, as shown in **Figure 5.15,** pH decline from 5.81 to about 2.36 suggests formation and presence of highly acidic solutions such as HCl in the product stream. The results are summarized in **Table 5.5**.

In addition, increasing conductivity and pH towards the end of the experiment (112-minute mark) indicates the reactor was at volume capacity and precipitated salt in the reactor were dissolving into the stream. This strongly implies efficiency of the additive to precipitate salts declined due to salts covering the surface area of the material. The author of this work recommends investigating the lifecycle of various additive materials and factors affecting the salt separation efficiency of an additive material, as a future study.
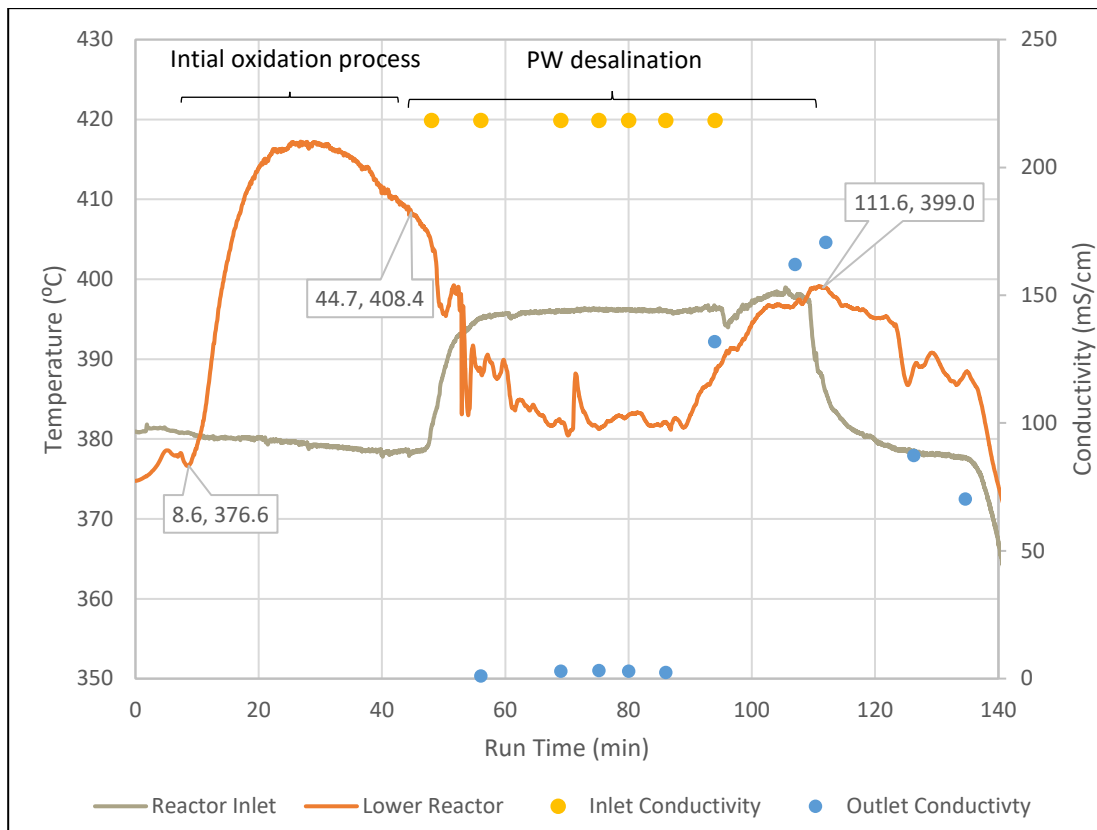
Figure 5.14: Conductivity of Pierre Federal (X) at 380⁰C - 410⁰C.

Subsequently, deionized water was fed to the reactor to clean and redissolve the deposited salts in solution. Hence the following effluent pH increased from 2.36 during test to an average of 6.12 "post-test". Finally, an overall product stream taken during the desalination period highlighted in **Figure 5.14** was analyzed for ions composition. The results are discussed in further section.
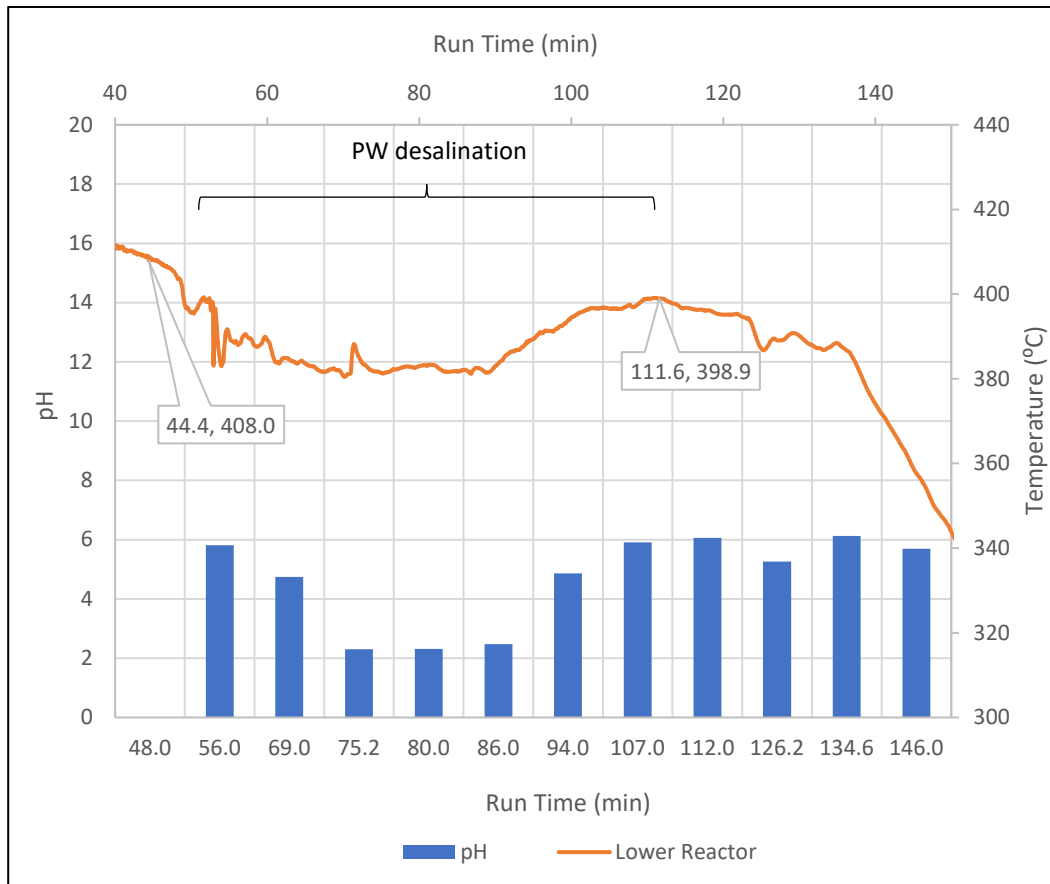
Figure 5.15: pH of Pierre Federal (X) at 380°C - 410°C.

5.4.2 Pierre Federal using additive Y (PFy)

Figure 5.16 shows the experiment performed using additive Y during the desalination of Pierre Federal produced water. Unlike the previous test, the influent stream was introduced at about 420°C. After some time, temperature increased from 420°C - 460°C (54 to 94-minute mark) likely due to heat transfer of thermal energy from the surrounding and reactor vessel. Initially heat is absorbed by fluids in the reactor until it reaches temperature above the critical point of water, where density then decreases drastically. As hot air in the enclosed heaters which surrounds the reactor expands, it supplies additional heat transferred to the fluids coupled with the heat of oxidation reaction with the reactor. This causes the overall temperature of the produced water to increase with minimum heat loss from the reactor to the surrounding.

The conductivity of effluent samples taken during the experiment revealed ~97% decrease from the feed stream across 35 minutes. This implies ~17% increase in desalination compared to conditions in PFx test. Consequently, **Figure 5.17** shows pH trends from 5.49 (feed solution) to about 7.5 during the same period, i.e. mildly acidic solution to neutral solution.

The conductivity measurements coupled with pH values of the effluent samples taken during test, strongly suggests a high rate of ion dissociation and salts separation from the aqueous stream. The results are summarized in **Table 5.5**. Finally, deionized water was re-introduced at the end of the test to redissolve the deposited salts in solution and prevent plugging of the equipment. pH value in the following effluent decreased

from an average of 7.5 to 2.16, becoming strongly acidic while conductivity in the same stream increased significantly.
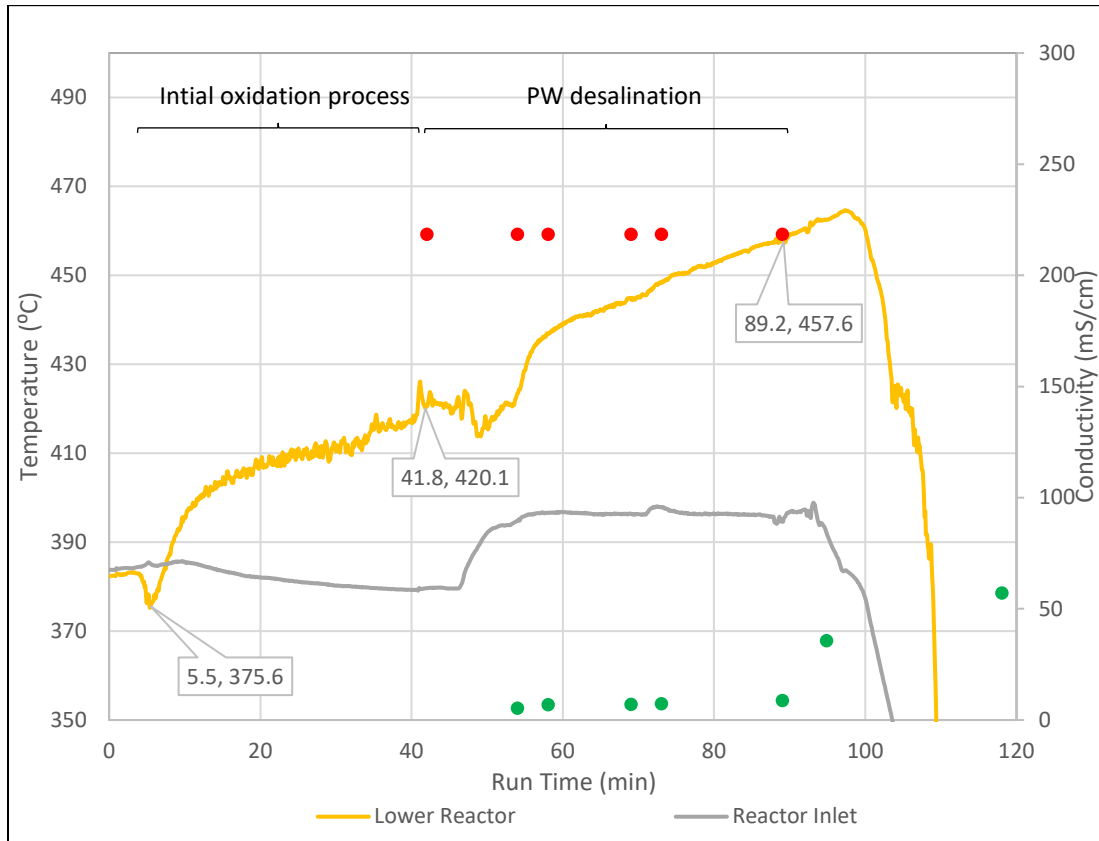
Figure 5.16: Conductivity of Pierre Federal (Y) at 420°C - 460°C.

Ion composition from the product water representing the temperature range 420°C - 460°C are examined and discussed in a future section.
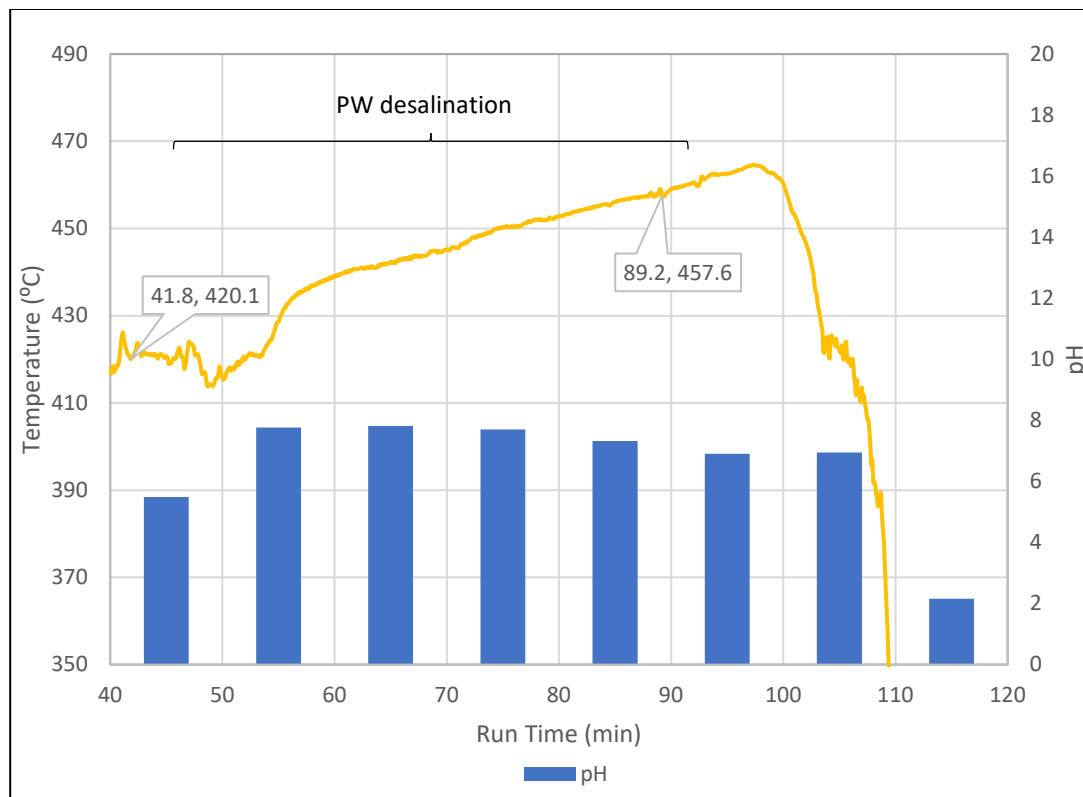
Figure 5.17: pH of Pierre Federal (Y) at 420°C - 460°C.

5.4.3 Lindy34-10 using additive Y (L34-10y)

Lindy34-10 was treated using additive Y like the PFy experiment but at a wider temperature range. Temperature of the supercritical reactor was raised by nearly 60°C prior to feeding the aqueous stream through the inlet. **Figure 5.18** shows treatment started at about 430°C and increased over time to 480°C (62 to 105-minute mark). An average of 96% decline in conductivity was discovered from the effluent samples taken during experiment. 7 samples investigated were spread across approximately 33 minutes (72 to 105-minute mark). **Figure 5.19** shows the trend of the pH has it increases from

5.81 (aqueous feed) until it peaked at 7.66 mid-experiment and gradually decreased into a strong acidic solution at the end of the test.
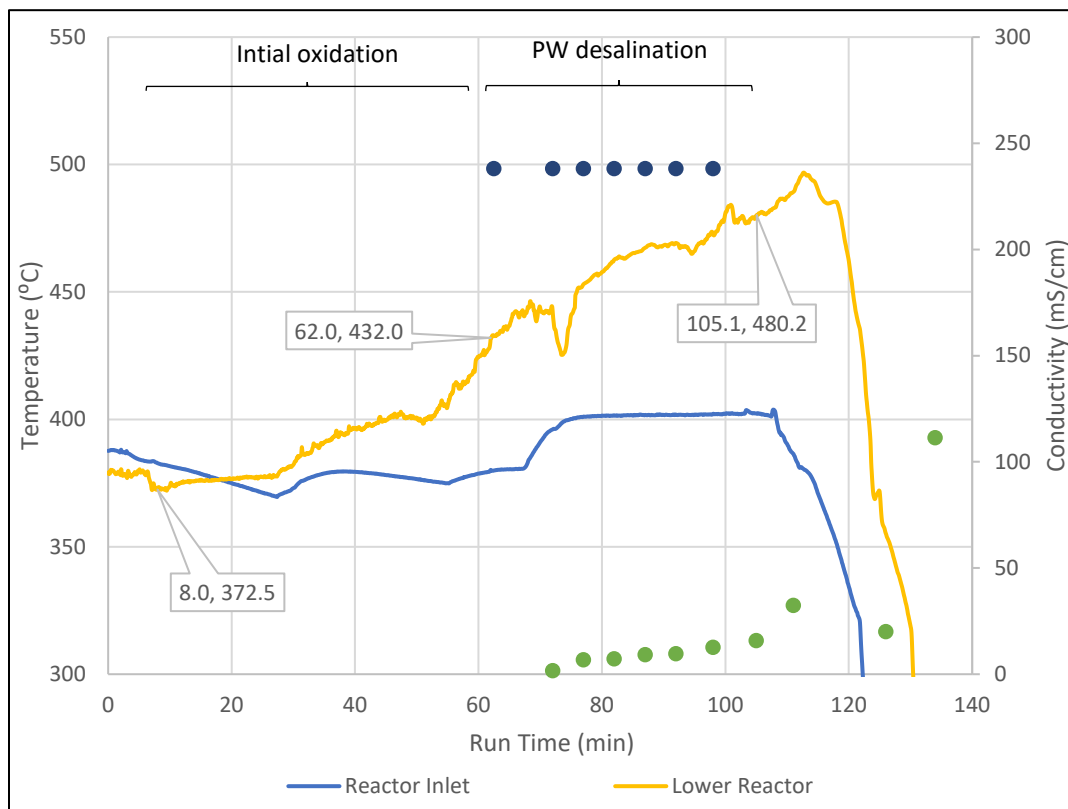
Figure 5.18: Conductivity of Lindy34-10 (Y) at 430⁰C - 480⁰C.

The collected data suggest a high level of salt precipitation within the supercritical reactor. Although solid salts recovery was not fully investigated in this study, **Figure 5.20** shows salts precipitates obtained from this experiment. Since, experiment L34-10y occurred over a wide range of supercritical temperature. Subsequently, two effluent samples were collected to represent separate conditions and analyzed for ion

composition. For the purpose of identification, the two streams are called L34-10y and
L34-10yy.
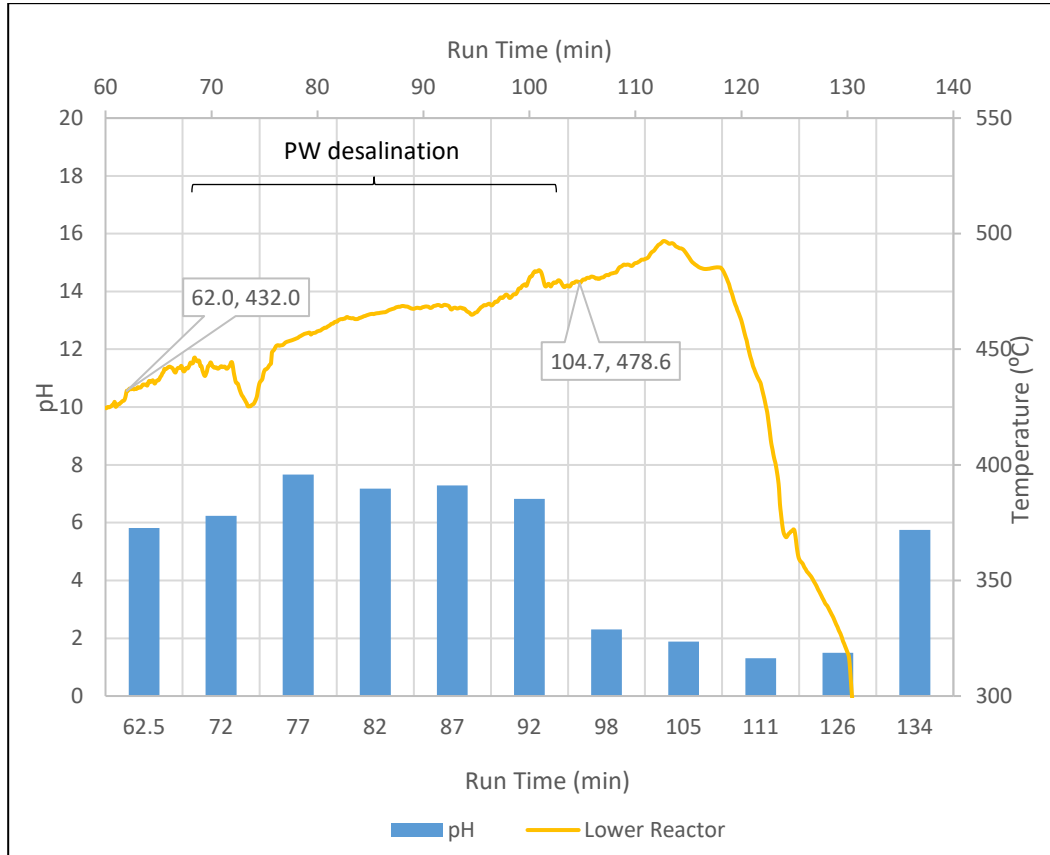
Figure 5.19: pH of Lindy34-10 (Y) at 430°C - 480°C.

Figure 5.20: Salt precipitates of Lindy34-10 (Y) at 430°C - 480°C.

5.5   Ion analysis of treated product water

Effluents samples obtained from the produced water experiments represent different temperature limits. Samples were analyzed for ion composition along with their respective feed solution (see **Table 5.7).** As shown in **Figure 5.21** there is a clear difference between the feed solution (left) and the product stream (right) obtained from all experiments. However, the effluent stream from PFx which was slightly blueish in color. The examined product streams and their temperatures are presented in **Table 5.6.**

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Figure 5.21: SCWD feed solution and desalinated product water (left to right).

Table 5.6: Temperature range of desalinated product water

Experiment	PFx	PFy	L34-10y	L34-10yy
Temperature range (°C)	380°C - 410°C	420°C - 460°C	440°C - 465°C	465°C - 480°C
Effluent Conductivity (mS/cm)	79.9	8.6	7.3	15.8
Effluent pH	5.5	6.9	7.2	1.9

As shown in **Table 5.7** desalinated product water samples were examined for inorganic composition using inductively coupled plasma-mass spectroscopy (ICP-MS).

Results of the treated streams are shown in **Figure 5.22 – 5.25.** It was revealed that the overall percentage reduction in inorganic constituents increased with temperature.

Table 5.7: Inorganic ion concentration of SCWD product water and feed solution.

Constituents	Pierre Federal Concentration (mg/L)	PFx (mg/L)	PFy (mg/L)	Lindy34-10 Concentration (mg/L)	L34-10y (mg/L)	L34-10yy (mg/L)
HCO_3^-	20	305	778	12.2	1,250	0
Br^-	848	157	0.37	694	0.23	0.76
Cl^-	159,000	29,900	2,250	178,000	1,440	3,540
F^-	NA	< 10	<0.2	NA	<0.2	<0.2
Al^{3+}	NA	< 2.5	< 0.25	NA	< 0.25	<0.25
Ca^{2+}	15,400	3,620	0.814	12,400	2.68	2.76
Fe^{2+}/Fe^{3+}	112	1.33	0.083	87.6	0.139	73.5
K^+	5,510	1,260	1.58	4,370	14.7	0.55
Mg^{2+}	895	76.3	2.83	914	0.484	1.69
Mn^{2+}	105	330	13.4	9.02	3	15.7
Na^+	55,200	13,600	50.3	65,100	36.01	36.3
Ba^{2+}	9.43	2.33	0.0126	6.32	0.0152	0.0181
Li^{2+}	20.9	11.8	0.095	16.2	0.038	0.085
Pb^{2+}	0.312	< 0.07	<0.007	97.4	<0.007	0.104
Sr^{2+}	570	315	<0.1	393	0.24	0.147
NO_3^-	NA	< 4	0.44	NA	0.26	0.56
SO_4^{2-}	169	35.6	1.2	258	1.6	1.7
TDS	237,860	49,614	3,099	262,358	2,749	3,674

Figure 5.26 shows the water recovery efficiency for PFx, PFy, L34-10y and L34-10yy of approximately 73%, 98%, 99 and 98% respectively. However, some divalent and monovalent ions like bicarbonates, iron and manganese increased to more than 3 times the amount found in the feed stream.

The increase in bicarbonate is most likely a result of organic oxidation in the produced water. Oxidation of organics will produce CO_2 as demonstrated in the oxidation experiment. Which would then form more carbonates with positive hydrogen ions present in the supercritical water. In addition, corrosion caused by acids formed during oxidation would explain the increase in iron and manganese at different experimental conditions.

5.5.1 PFx Inorganic compositions

It is commonly known that the salt concentration (salinity) of hypersaline brine is greater than seawater. Inorganic ions responsible for the salinity of brine in order of relative abundance include, sodium, chloride, calcium, magnesium, potassium, sulfate, bromide, and bicarbonate [74]. In this study, treatment of PFx under the supercritical temperature of 380ºC - 410ºC reduced the most abundant inorganic constituents by an average of 72%. Although, the concentration of bicarbonate and manganese in the effluent stream was 24 and 3 times more than that present in the feed solution. Increase in bicarbonate is a result of the supercritical water oxidation process during desalination.

Sodium and chloride ions which form the predominant salts in produced water (e.g. NaCl) reduced by 4 and 5 times the original concentration, respectively. As shown

in **Figure 5.22**, barium and calcium which tend to form insoluble sulfates and sulfides are in low concentrations, reducing by 80% and 75% respectively, compared to the feed stream. It is mostly likely that barium and calcium salts together with sulfates precipitated out of solution within the supercritical temperature range employed for this experiment. For example, the concentration of sulfates which promote barium and calcium scale formation in production pipes is noticeably lower than that from the Hibernia oil field produced water (about 248 to 339 mg/L) in Canada and seawater (~2712 mg/L) [73].
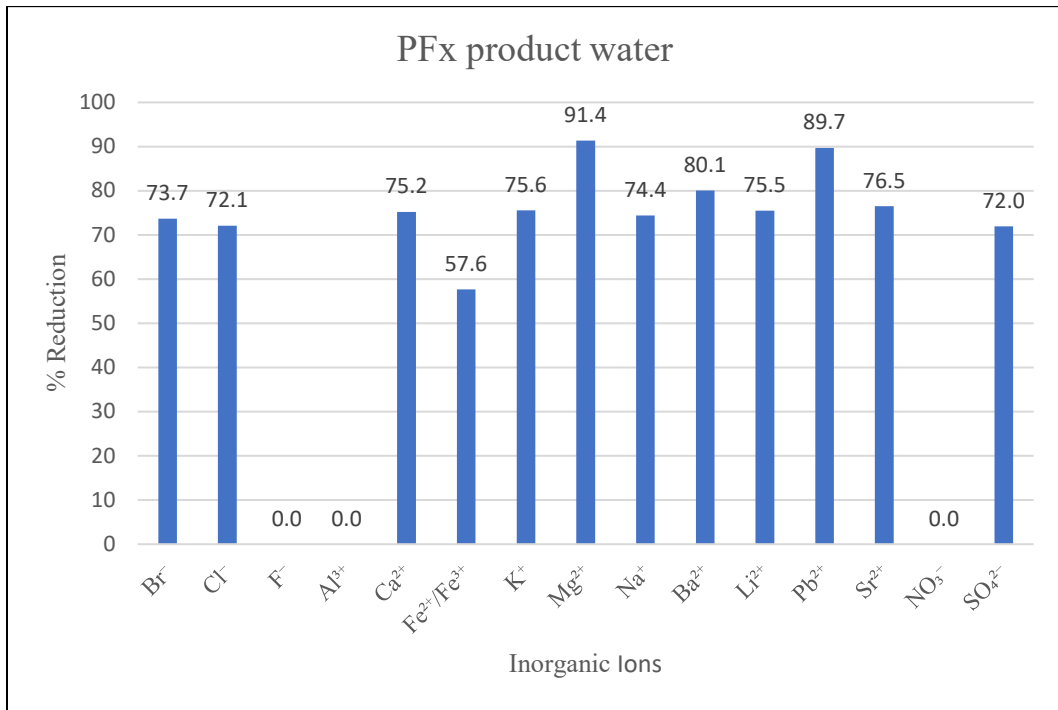
Figure 5.22: Percentage reduction of inorganic ions in PFx effluent.

5.5.2   PFy Inorganic compositions

Inorganic ions present in effluents from PFy experiment reduced overall by 97%. This indicates high water recovery efficiency and TDS level removal from the

hypersaline solution. It is reflective of the effectiveness of the supercritical water desalination process and conditions under which the experiment was performed. All inorganic ion concentrations were reduced by more than 85%, except bicarbonates. **Table 5.7** and **Figure 5.23** show the most abundant constituents, chloride (107,000 – 2,250mg/L), sulfate (127 – 1.2mg/L), magnesium (884 – 2.83mg/L), sodium (53,200 – 50.3mg/L), bromide (597 – 0.37mg/L), potassium (5,160 – 1.58mg/L) and calcium (14,600 – 0.814mg/L), diminish by 97.9%, 99.1%, 99.7%, 99.9%, 99.9%, 100%, and 100%, respectively.

The concentration of the treated product water at 420ºC - 460ºC supercritical temperature is several times lower than seawater (35,151mg/L). It is evident that the reduction of sulfates largely affects precipitation of barium and calcium scale. It further proves SCWD capability as a standalone treatment to reduce TDS to levels beyond the feed concentration limits for conventional desalination technologies. Unlike PFy product water, barium, and calcium concentration at PFy test conditions declined by more than 2 order of magnitudes. Also, TDS in PFy effluent reduced by an additional 93% compared to PFx effluent composition. The concentration of PFy compared with the required limit for livestock watering and hydraulic fracturing would be discussed in the next sections.
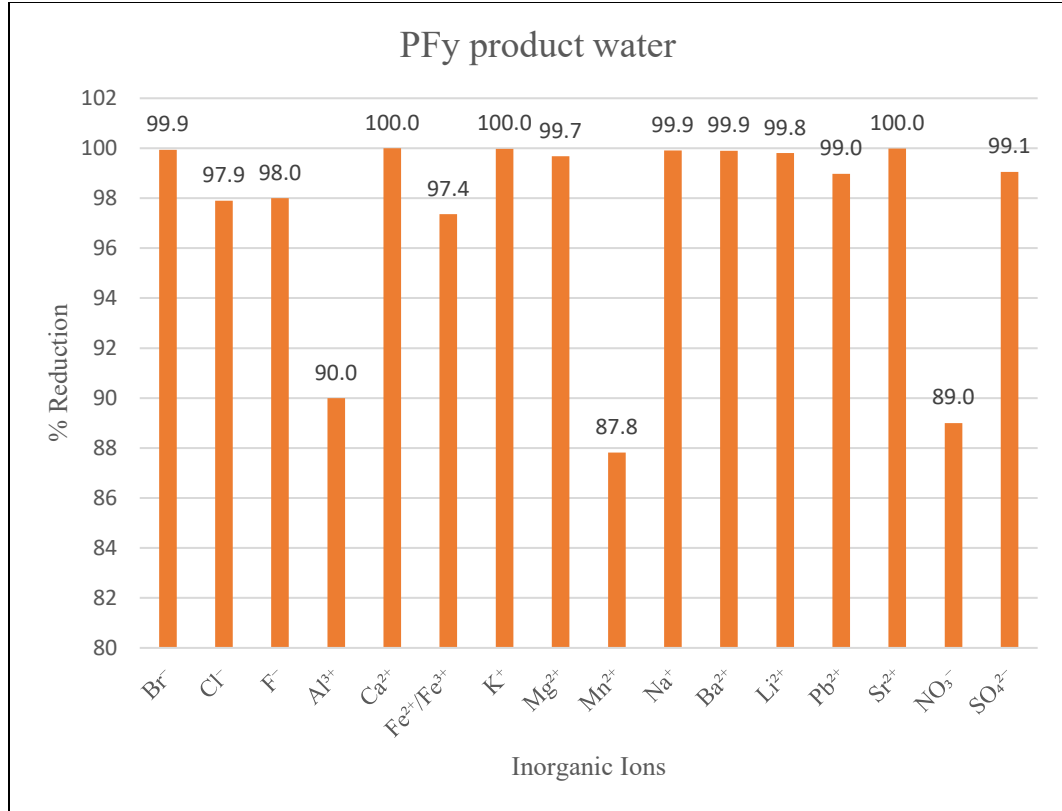
Figure 5.23: Percentage reduction of inorganic ions in PFy effluent.

5.5.3 L34-10y Inorganic Compositions

The test results for supercritical temperature 440°C - 465°C, represented in **Figure 5.24,** show the highest overall inorganic ion reduction across all four effluent samples. It suggests very high quality of water with a recovery efficiency of 98.7% from the hypersaline solution. Like PFy, it demonstrates the effectiveness of the supercritical water desalination process to precipitate majority of inorganics salts out of solution except bicarbonates and aluminum.
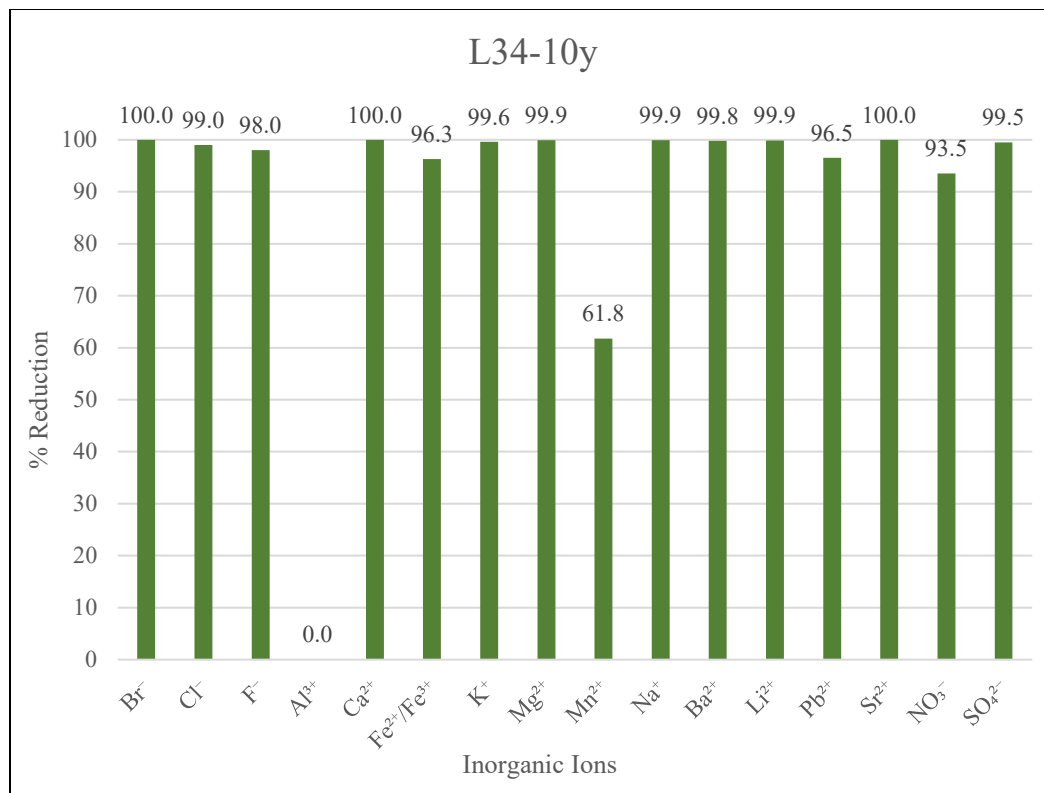
Figure 5.24: Percentage reduction of inorganic ions in L34-10y effluent.

In addition, **Table 5.7** and **Figure 5.**24 imply that unlike PFy which had lower TDS feed concentration (183,111mg/L) and a wider temperature range, the L34-10y process condition was able to achieve a greater percentage of salt separation with higher TDS brine feed (215,481mg/L) under shorter temperature limits. A closer look at the individual ions show chloride, sulfate, magnesium, sodium, bromide, and nitrate diminished by a larger percentage while barium and calcium were similar.

5.5.4 L34-10yy Inorganic Compositions

The investigated sample for Lindy34-10yy process temperature at 465⁰C - 480⁰C shows the second highest reduction efficiency among all four effluent samples. Despite having higher concentrations of chloride, bromide, nitrate, and lead more than the PFy and L34-10y product stream. There are no bicarbonate ions detected in the solution. In addition, concentrations of manganese and iron increased from 7.85mg/L – 15.7mg/L and 3.77mg/L – 73.5mg/L, respectively.
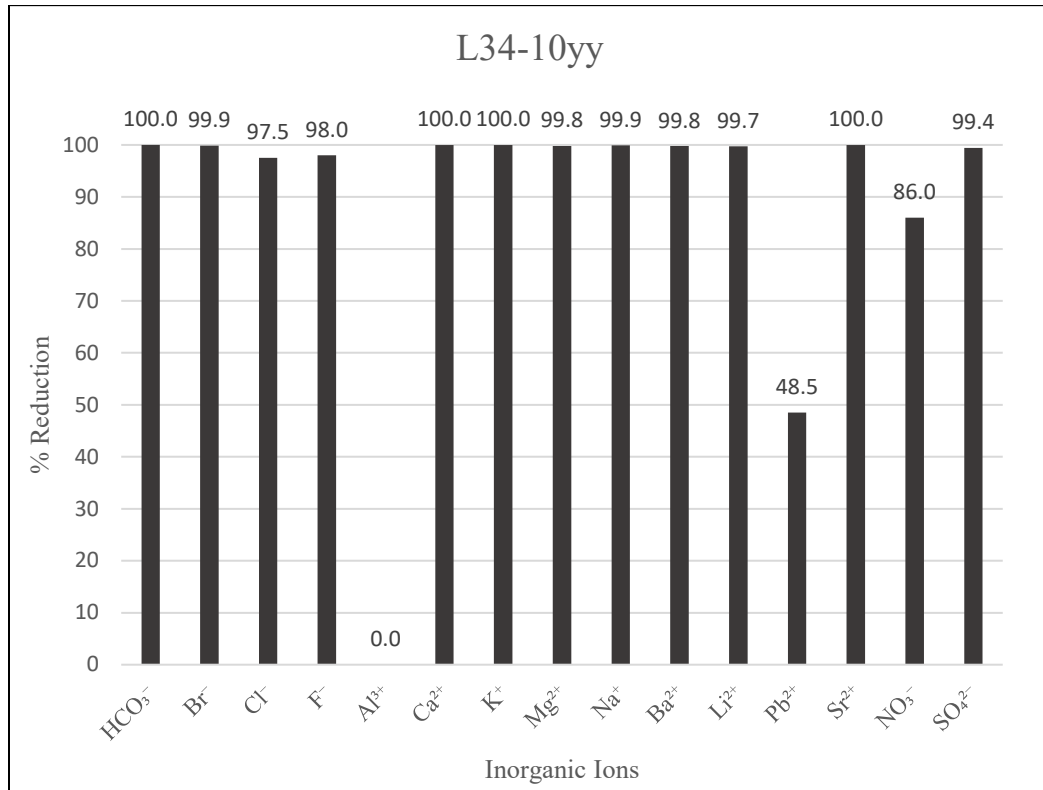
Figure 5.25: Percentage reduction of inorganic ions in L34-10yy effluent.

The presence of high iron concentration coupled with pH value of 1.88 (see **Table 5.6** and **5.7**) suggest corrosion from a strong acidic solution. This could account for the absence of bicarbonates with the hydrogen atoms possibly forming strong acids with anions such as chloride (hydrochloric acid), nitrite (nitric acid) and/or bromide (hydrobromic acid), etc. Overall, the TDS discovered in L34-20yy effluent is lower than the concentration reported for conventional desalination technologies as well as that of seawater. Finally, **Figure 5.26** summarizes the efficiency of water recovered from high TDS Bakken brine for all experimental conditions.
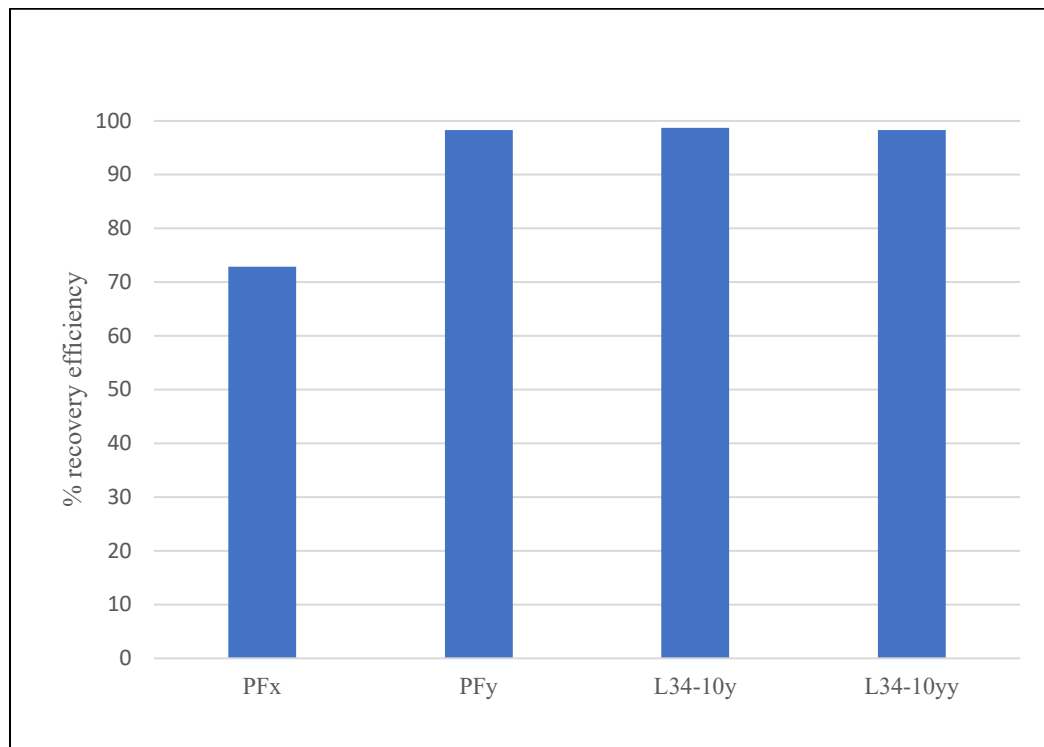
Figure 5.26 Water recovery efficiency for PFx, PFy, L34-10y and L34-10yy.

CHAPTER 6: APPLICATION FOR BENEFICIAL USE

This study outlined treatment of produced water for hydraulic fracturing as the primary beneficial use. However, the following application scenarios are discussed due to the water quality achieved. The effluent compositions are compared to lower limits of specific constituents available in the literature for livestock drinking, irrigation, and hydraulic fracturing water quality.

6.1   Livestock watering

Water quality is essential for livestock watering and varies depending on the species. While livestock water quality is lower than the requirement for human consumption, the impact of highly saline water for livestock consumption can vary with species susceptibility. Therefore, requirements such as concentration of inorganic constituents, salinity and pH should be considered based on the recommended limits. **Table 6.1** compares the effluents samples treated in this study to the lowest expected concentration for constituents in livestock watering based on The National Academy of Sciences guidelines [75].

Although, concentration limits for chlorine, iron and manganese are not provided, the total dissolved solids (TDS) for PFx is beyond level 6 category of recommended use described by Lardy and Stoltenow et al [74] [75].

Table 6.1: Comparison of effluents samples from this study to recommended livestock watering concentration limits.

Constituents	Concentration limit (mg/L) [76]	PFx (mg/L)	PFy (mg/L)	L34-10y (mg/L)	L34-10yy (mg/L)
Aluminum	5	<2.5	<0.25	<0.25	<0.25
Fluorine	2	<10	<0.2	<0.2	<0.2
Chlorine	N/A	29,900	2,250	1,440	3,540
Iron	N/A	1.33	0.083	0.139	73.5
Lead	0.1	< 0.07	<0.007	<0.007	0.104
Manganese	N/A	330	13.4	3	15.7
Nitrate + Nitrite	100	< 4	0.44	0.26	0.56
Sulfates	1,000	35.6	1.2	1.6	1.7
pH	5.5-8.5	5.47	6.91	7.18	1.88
TDS	3000	49,614	3,099	2,749	3,674

TDS within the range <1,000 – 4,999mg/L was categorized from level 1 – level 3 and defined as satisfactory while 5,000 – 10,000mg/L (level 4 – level 6) were termed "reasonable to unfit" for use. Also, it will require additional treatment to reduce the chloride, fluorine, and TDS concentration for PFx effluent to be considered reusable.

More importantly, **Table 6.1** implies that the quality of PFy, L34-10y and L34-10yy product water meet the requirement for livestock watering. However, the pH of L34-10yy effluent would need to be adjusted to reduce its acidity. Furthermore, it provides evidence that supercritical water desalination can be tailored to treat high TDS

produced water for livestock use in states with large ranching areas and access to oilfield brine such as, North Dakota, Wyoming, California, Oklahoma, Wyoming, and Texas.

6.2   Irrigation water

In most States, irrigation represents majority of fresh-water use. For example, In 2014 North Dakota State Water Commission reported that irrigation accounts for over 54% of water used in the state and is distributed based on soil types and availability [77]. The percentage of water use has grown with increasing population and demand. Since irrigation water is less recoverable than water for municipal use, this section aims to provide evidence that treated produced water using supercritical water desalination is beneficial for North Dakota's agricultural economy. Like livestock watering, irrigation water quality criteria require considerations to prevent crop damage and protect soil sustainability. **Table 6.2** compares the effluents samples treated in this study to essential criteria for evaluating irrigation water quality. Important parameters used in this study include sodium adsorption ratio (SAR), water salinity (EC), pH and ion toxicity.

The sodium absorption ratio (SAR), determines the sodicity (amount of sodium in a soil) hazard and indicates the suitability of water for irrigation. It is a measure of the concentrations of sodium (Na^+) relative to calcium (Ca^{2+}), and magnesium (Mg^{2+}) in water. It is calculated with the formula [78];

$$SAR = \frac{N_a^{(+)}}{\sqrt{\frac{1}{2}\left(C_a^{(2+)}+M_g^{(2+)}\right)}}$$

Where Na^+, Ca^{2+} and magnesium Mg^{2+} are expressed in milliequivalents per liter (mEq/L). While irrigation water with a SAR value between 1 -10 mEq/L (sodium hazard class 1) is typically considered safe for long term use, water with SAR of 10 – 18 mEq/L (sodium hazard class 2) is deemed unsafe and require some level of SAR adjustment using gypsum [79] [80].

The salinity of the water which determines the total soluble salt (TSS) is measured in electrical conductivity (EC). EC is expressed in micro Siemens per centimeter (μS/cm). It is generally used in conjunction with the SAR value to determine the effect of irrigation water quality on soil. Though at low SAR value, high salinity promotes drought and reduces water penetration into the soil. This can cause crop damage as a result of plants being unable to replenish lost water. The recommended salinity level for safe long-term irrigation water is < 250 μS/cm. Water between 250 – 750 μS/cm may be used with moderate leaching and careful management [79] [80] [81].

In addition to salinity and sodium absorption ratio, high concentrations of specific ions such as boron, chloride, and sodium are harmful to plants. The tolerance of elements present in irrigation water varies with crops. **Table 6.2** shows guidelines for specific ion concentration limits, pH, SAR, and electrical conductivity. Since, boron is not readily detected in Bakken produced water. It will not be included in this evaluation.

Table 6.2: Evaluation of effluents samples from this study with guidelines for irrigation watering

Parameters [76] [79] [81] [80].	Concentration limit (mg/L)	PFx (mg/L)	PFy (mg/L)	L34-10y (mg/L)	L34-10yy (mg/L)
SAR (mEq/L)	<10	61.1	5.9	5.3	4.2
EC (µS/cm)	<250	798	86	73	158
pH	6.5 – 8.5	5.47	6.91	7.18	1.88
Aluminum	5	<2.5	<0.25	<0.25	<0.25
Fluorine	1	<10	<0.2	<0.2	<0.2
Chlorine	<70	29,900	2,250	1,440	3,540
Iron	5	1.33	0.083	0.139	73.5
Lead	5	< 0.07	<0.007	<0.007	0.104
Lithium	2.5	11.8	0.095	0.038	0.085
Nitrate + Nitrite	<55	< 4	0.44	0.26	0.56
Sulfates	250	35.6	1.2	1.6	1.7

The results indicate that chlorine concentration in PFy, L34-10y and L34-10yy effluent solutions must diminish to meet the required water quality for long-term irrigation use. L34-10yy could be used regardless of the pH value since most crops can tolerate a wide range of pH. For example, organic matter, humic acids and clay minerals in soils tend to adjust the pH overtime by absorption [80]. PFx effluent solutions may be usable for short term but additional treatment is recommended to prevent crop and soil damage. Due to sensitivity of some crops like lemon, grapefruit, garlic, pepper, etc., a

drastic reduction of chlorine concentration in the desalinated product water is necessary to prevent crop damage.

6.3   Water for Hydraulic Fracturing

Recent developments in hydraulic fracturing fluid chemistry have facilitated economic reuse of minimally treated oilfield wastewater. In 2015, The Energy Water Initiative detailed trends in the oil and gas industry using low quality saline water for exploration and production operations to reduce cost and potential risk associated with spillage [82]. The quality of water required during fracturing varies by play and the type of method employed.

Generally, slickwater hydraulic fracturing is less sensitive to water quality than crosslinked gel since it operates by supplying enormous volumes of water at high velocity [32] [82]. While crosslinked fracturing involves high quality water with less volume due to provide fluid properties such as conductivity and viscosity. Nonetheless, research and advances are being made to develop gels that accommodate low quality water for fracturing. **Table 6.3** shows important considerations to limit the TDS in brine suitable for hydraulic fracturing reuse.

The hydraulic fracturing water requirements utilized here are associated with Halliburton and was presented in a water resources investigation conducted by North Dakota State Water Commission (NDSWC) [83]. Since each oil and gas company

operate specific fracture system, water quality may differ by plays and oilfield operators.

Effluents samples treated in this study were evaluated against the quality for frack water.

Table 6.3: Evaluation of effluents samples from this study with guidelines for frack water.

Parameters	Concentration limit (mg/L) [83].	PFx (mg/L)	PFy (mg/L)	L34-10y (mg/L)	L34-10yy (mg/L)
pH	6-8.5	5.47	6.91	7.18	1.88
Chlorine	<40,000	29900	2250	1440	3540
Calcium	<2,000	3620	0.81	2.68	2.76
Magnesium	<2,000	76.3	2.83	0.48	1.69
Iron	<10	1.33	0.08	0.14	73.5
Barium	<5	2.33	0.013	0.015	0.018
Strontium	<5	315	<0.1	0.24	0.15
Bicarbonate	<300	305	778	1250	0
Sulfates	<500	35.6	1.2	1.6	1.7
TDS	44,000	49,614	3,099	2,749	3,674

Table 6.3 indicates the potential for PFx reuse is limited due to substantial

amount of calcium, strontium, magnesium, and sulfates depreciation. The results show

low solubility salts like calcium, iron, magnesium, barium, and strontium in PFy and

L34-10y are significantly reduced beyond the limit. Although high bicarbonate

concentration may affect crosslink gels and promote precipitation of magnesium

carbonate ($MgCO_3$), strontium carbonate ($SrCO_3$), barium carbonate ($BaCO_3$) and

calcium carbonate ($CaCO_3$) scales in fractures, scale inhibition and control can be utilized depending on water quality requirement.

L34-10yy best fits the guidelines with zero bicarbonates, extremely low sulfates, strontium, magnesium, and calcium concentration. Chemical precipitation can adequately reduce iron which would most likely influence a change in pH. In addition, the low sulfates concentration (<200mg/L) coupled with high efficiency organics destruction in all cases implies limited interference with crosslink gels and prevents sulfur reducing bacteria from causing souring of the crude oil. Finally, from experiment PFy, L34-10y and L3410yy, the results reveal the capability of SCWD to produce high quality hydraulic fracturing water with less augmentation for beneficial reuse.

6.4   Evaluation of Supercritical Water Desalination

The section contains a summary of the supercritical water desalination technology developed based on the results derived from this study. The effectiveness and performance of SCWD is also compared to various desalination technologies. The evaluation is determined using an approach devised by the author and described in this section. The criteria used for the evaluation and comparison between the technologies were selected based on the robustness of a treatment method to treat high TDS produced water. **Table 6.4** shows the summary of the supercritical water desalination technology used in this study. While **Table 6.5** compares its performance criteria with current desalination technologies.

Table 6.4: Summary of Supercritical water desalination technology from this study.

Technology	Characteristics	Advantages	Limitations	Influent (mg/L)	Product water efficiency
Supercritical Water Desalination	Removal of organic acids, phenols, divalent ions, metal ions, acids, sugars, aqueous salts, natural resins, monovalent salts, BOD, COD, NORM, dissolved oil, dissolved gases, water softening etc	• Tolerates high pH. • Little to no pre-treatment required • High product water quality. • High organics destruction efficiency • High rate of salt removal near 100% • Suitable as a standalone treatment technology • Suitable for high TDS > 200,000 mg/L produced water • Applicable to a wide range of TDS	• Requires filtration of suspended solids. • Sensitive to corrosion. • Difficulty separating valuable solid materials. • High energy requirement.	> 200,000	> 99.5%

From **Table 6.4**, it is evident the supercritical water desalination technology developed exhibits characteristics necessary to treat hypersaline water. Its applicability in a wide range of TDS also makes it advantageous compared to conventional technologies. Although, scaling and plugging of flow paths may pose a challenge if appropriate liquid-solid separation methods are not utilized, the wide treatment applicability and high-water recovery rate proves the supercritical water desalination technology developed is a highly efficient standalone treatment method. While supercritical water desalination system requires high grade corrosion resistant equipment for sustainability and durability, its

targeted constituent approach coupled with organic destruction makes it reliable to treat water for beneficial use. Furthermore, the salt deposits obtained from this study show its ability recover valuable minerals that would offset the operational cost and energy penalty. At the same time, it reveals the capability to reduce environmental impact associated with reject concentrate disposal.

6.4.1   Comparison with Current Desalination Technologies

In this section, considerations for comparing the supercritical water desalination technology developed to other conventional techniques are determined using criteria with robust practical significance for treating high TDS wastewater. Performance of the treatment technologies are expressed using pre-treatment, post-treatment, influent concentration limits, organic destruction and product water quality.

While some treatment methods are not equipped for removing/destroying organics due to the damage caused to the equipment, most desalination technologies become more susceptible to fouling and scaling as the organic concentration of feed water increases. Consequently, their separation efficiency and product water quality diminish, thus requiring pre-treatment and/or post-treatments to achieve better efficiency and product water quality. Another common approach is to combine treatment methods thereby adding to capital cost, operational cost and the overall complexity of the technology. However, the capital cost, operational cost and energy requirements were not considered in this analysis.

The criteria used for comparison are defined as follows

• Pre-treatment – No/Light/Heavy

• Post-treatment – Yes/No

• Influent TDS – Low (< 50,000 mg/L)/Median (50,000 – 100,000 mg/L)/ High (> 100,000 mg/L)

• Organic destruction – Yes/No

• Product water quality – Low (< 40%)/Moderate (40% – 70%)/High (> 70%)

The result suggests little or no pretreatment is required in SCWD to produce high water quality compared its counterpart technologies. It also shows its flexibility with high feed concentration as demonstrated with high TDS Bakken produced water examined in this work.

Table 6.5: Comparison of current desalination technologies with SCWD from this study.

Criteria	SCWD	RO	MED	MSF	VCD
Pre-treatment	No	No	Yes	Yes	Yes
Post-treatment	No	Yes	Yes	Yes	Yes
Influent TDS	High	Low	Low	Low	Low
Organics destruction	Yes	No	No	No	No
Product water quality	High	High	Moderate	Low	Low

From the comparison in **Table 6.5**, it is clear the supercritical water desalination technology developed in this study is the most efficient and reliable treatment for all ranges of TDS. Unlike other desalination techniques, SCWD's capability to destroy

organics proves it is less susceptible to fouling and does not require chemical cleaning like in other technologies. In addition, the ability for targeted salt precipitation produces a high quality of product water without rigorous post-treatment that can be distributed for various purposes. Finally, if deployed on a large scale, SCWD has the potential to recover large tons of valuable material needed for reuse which makes it a "go to" technology for brackish water, seawater and produced water treatment.

CHAPTER 7: CONCLUSION

7.1   Summary and Conclusion

A supercritical water desalination technology has been developed in this study to treat high TDS brine under critical pressure of 240 bar with varying temperature. In this work, SCWO was combined with SCWD for the oxidation of organics and salt precipitation present in Bakken oil field brine. The process analysis of single component brine under varying critical temperatures confirmed that T_c above 400°C is significantly efficient with a near 100% salt removal. In addition, salt deposition on the "hot rod" and reactor vessel provide evidence of potential for zero liquid discharge given appropriate liquid-solid separation system is utilized. Thus, in a continuous mode of operation, important considerations are required to systematically remove precipitated solids to reduce fouling or plugging in the reactor for the technology to be commercially viable.

A novel approach was developed using additive materials with excellent conductivity and chemical stability to increase the efficiency of organics oxidation in the supercritical reactor. The additives proved to be an excellent catalyst in the destruction of organics with ~ 98% reduction efficiency. Furthermore, analysis confirmed the hypothesis that heat addition within a localized zone can raise the temperature in that localized zone from subcritical to supercritical. Although, flow variation and energy from external heaters used to maintain the bulk fluid temperature were not fully examined, the effect of temperature and observed TOC results prove higher concentration of organics

significantly influence greater energy input. This work demonstrated that heat addition from supercritical water oxidation is sufficient for salt separation in produced water.

Data obtained from the hot-rod and oxidation experiments were utilized for treating two samples (Lindy34-10 and Pierre Federal) of high TDS produced water with varying concentration. Three experiments PFx, PFy and Lindy34-10y conducted at 380°C - 410°C, 420°C - 460°C and 430°C - 480°C, respectively. Analysis of effluent samples show ~89%, ~97% and ~96% reduction in conductivity. At the same time, pH increased from a strongly acidic position of 5.81, 5.49 and 5.54 to 2.36, 7.50 and 7.04, respectively, thus demonstrating effective salt precipitation with increasing temperature. Additionally, the product water quality for PFx, PFy, L34-10y and Lindy34-10yy proves the author's earlier hypothesis that removal of dissolved solids and oxidation efficiency increased with temperature. Moreover, solid deposits acquired during brine experiment provide evidence that valuable materials can be obtained with zero liquid discharge (ZLD).

Subsequently, evaluation for practical application using composite requirements for livestock watering, irrigation and hydraulic fracturing reveal PFy, L34-10y and Lindy34-10yy product water have exceptionally high quality. Also, since requirements vary by location and purpose of use, limited augmentation is expected for the three cases. Reuse of PFx product water for any of the examined areas will require some form of blending or treatment to be considered safe. This demonstrates the ability for SCWD to achieve targeted precipitation of high TDS wastewater and produce extremely high-

quality product water for various purposes. Finally, assessment of SCWD and comparison with conventional desalination technologies reveal the proposed technology as the most robust method to treat high TDS saline water and accomplish a greater water recovery efficiency.

7.2   Future Work

The author recommends that future work to further develop the technology should include:

- Characterizing the rate of deposition of salts onto the catalysts.
- Determining the impact of deposition on the reduction of effective oxidation of the organics.
- Understanding the lifetime of the catalyst in the system.
- Further development on the following components will better shape the overall process design.
- Moving from the current packed bed configuration to one that moves the catalyst in the flow path.
- Allowing for continuous removal and replacement of coated/fouled particles.
- Investigating other sources of oxidation, organics, as well as other catalyst materials.

DISCLAIMER

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