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for agricultural use in the state of Kansas**

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OIL AND GAS-PRODUCED WATER TREATMENT SYSTEM FOR AGRICULTURAL USE
IN THE STATE OF KANSAS

A Dissertation by

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Submitted to the Department of Mechanical Engineering
and the faculty of the Graduate School of
Wichita State University
in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy

May 2020

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OIL AND GAS-PRODUCED WATER TREATMENT SYSTEM FOR AGRICULTURAL USE
IN THE STATE OF KANSAS

The following faculty members have examined the final copy of this dissertation for form and content, and recommend that it be accepted in partial fulfillment of the requirement for the degree of Doctor of Philosophy with a major in Mechanical Engineering.

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DEDICATION

To my family

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and appreciation to my advisor, Dr. Eylem Asmatulu, who supported me throughout my research. This thesis would not have been possible without her recommendations and guidance. I would also like to extend gratitude to my committee members, Dr. Hamid Lankarani, Dr. Wei Wei, Dr. Yang-Sean Kim, and Dr. Wujun Si, for their helpful comment's suggestions on the research. A special thanks to Dr. Ramazan Asmatulu for his unlimited support and valuable suggestions in the experiments. I must thank Dr. Kevin Langenwalter for his help with conducting ICP-OES testing. I also thank Dr. Dennis Livesay and Dr. Kerry Wilks for their support, and Ms. Linda Young for her help allocating the produced water samples. Special thanks to Ms. Denecia Angleton, for her help and kindness. I also wish to thank Kristie Bixby for an extraordinary job at editing my dissertation.

I am writing this acknowledgment while under quarantine due to the coronavirus pandemic. I must mention and appreciate the support and encouragement I have received from my wife and children during this challenging and stressful time. I wish the end of this nightmare soon. Having said this, I pray for the health and safety of all the people mentioned in these acknowledgments.

ABSTRACT

Produced water (PW) is a term used to characterize water that is deposited over the course of a million years in the oil and gas reservoir rock formation and then flows to the surface along with the production of oil and gas as a by-product. Owing to the use of steam injection, water flooding, and other processes for enhanced oil recovery (EOR) to improve output flow and operations, the amount of produced water increases significantly based on the reservoir's age. At present, the water produced in the state of Kansas is disposed of in designated wells as defined by the state commission to reduce environmental issues and to discourage groundwater contamination. The research goal here is to pursue an innovative solution to existing practices by processing and reusing produced water for irrigation and generating new sources of revenue from 15.7 million acres of abandoned Kansas property owned by oil and gas corporations.

The water treatment system developed in this research focuses on integrating a state-of-the-art model with proven technologies. The sedimentation-media, adsorption, ceramic (S-MAC) system is a combination of sedimentation plus dissolved air flotation (DAF), media, adsorption, and microporous ceramic filtration. Produced water samples from Lario Oil & Gas Company (Kansas Mid-Continent Region) were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) to identify the produced water elements. Results show up to 80% water recovery and 95–99% oil removal, and that the water standard parameters of pH, total dissolved solid TDS, conductivity, hardness, and dissolved oxygen are within the limits of palatable water requirements for Kansas.

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LIST OF ABBREVIATIONS

| | |
|---------|---|
| AUFB | Aerobic Up Flow Fluidized Bed |
| AWWA | American Water Works Association |
| CCFF | Ceramic Cross Flow Filtration |
| CDI | Capacitive Deionization |
| CDT | Capacitive Deionization Technology |
| CNT | Carbon Nanotube |
| COD | Chemical Oxygen Demand |
| DAF | Dissolved Air Flootation |
| DI | Deionized |
| DO | Dissolved Oxygen |
| DWR | Division of Water Resources |
| EOR | Enhanced Oil Recovery |
| FO | Forward Osmosis |
| FTE | Freeze-Thaw Evaporation |
| GAC | Granular Activated Carbon |
| GW | Groundwater |
| HRH | High-Range Hydrocarbons |
| ICP-OES | Inductively Coupled Plasma Optical Emissions Spectroscopy |
| KDA | Kansas Department of Agriculture |
| KCC | Kansas Corporation Commission |
| KDHE | Kansas Department of Health and Environment |
| KGS | Kansas Geological Survey |

LIST OF ABBREVIATIONS (continued)

| | |
|-------|---|
| MF | Microfiltration |
| MPPE | Microporous Polymer Extraction |
| MRH | Medium-Range Hydrocarbons |
| NF | Nanofiltration |
| NOM | Natural Organic Matter |
| PAC | Powdered Activated Carbon |
| PVA | Polyvinyl Acetate |
| PVC | Polyvinyl Chloride |
| PVP | Polyvinylpyrrolidone |
| PW | Produced Water |
| RO | Reverse Osmosis |
| RSE | Rapid Spray Evaporation |
| SAR | Sodium Adsorption Ratio |
| SD | Standard Deviation |
| SEM | Scanning Electron Microscopy |
| S-MAC | Sedimentation, Media, Adsorption, Ceramic |
| SW | Surface Water |
| TCE | Trichloroethylene |
| TDS | Total Dissolved Solids |
| TOC | Total Organic Carbon |
| TPH | Total Petroleum Hydrocarbon |
| TSS | Total Suspended Solid |

LIST OF ABBREVIATIONS (continued)

| | |
|------|----------------------------------|
| UF | Ultrafiltration |
| UV | Ultraviolet |
| USDA | U.S. Department of Agriculture |
| WQCC | Water Quality Control Commission |

CHAPTER 1

INTRODUCTION

“The nation behaves well if it treats the natural resources as assets which it must turn over to the next generation increased, and not impaired in value. Conservation means development as much as it does protection” (Theodore Roosevelt, Denver, Colorado, August 29, 1910).

1.1 Benefits of Produced Water Treatment

This dissertation addresses the economic and environmental concerns regarding the increasing quantity of produced water (PW) in the state of Kansas. The amount of water produced increases annually because of aging production wells and the growing need for the steam injection technique for enhanced oil recovery (EOR) to boost oil and gas production. Also, to generate a new source of profit that utilizes more than 15 million acres of land in the state of Kansas owned by oil and gas companies and to develop a method that is environmentally friendly, it is essential to investigate the benefits of produced water treatment.

According to the current scenario, the state of Kansas is in urgent need of other water resources that can be used for irrigation. A new technology that is economically reasonable and reduces the risk to the environment and the cost of dumping the produced water back into disposal wells is needed. Implementing such a system is not an easy task because of federal restrictions and state regulations regarding managing and treating produced water. The water treatment system proposed here is a technology that has successfully provided results that are cost-effective, efficient, and environmentally friendly.

The laboratory-scale model developed here has confirmed that water produced through this system can be used safely for the irrigation of cotton crops in Kansas. The most crucial

conclusion is that the state of Kansas is in urgent need of another water resource that can be used for irrigation. The proposed system must be able to operate from any remote location with minimal maintenance requirements, and with Kansas Corporation Commission (KCC) approval to remove limitations so that companies can conveniently employ the system to reuse and recycle produced water.

Agencies such as the Environmental Protection Agency have determined protocols regarding the maximum contaminant level of some specific elements found in public drinking water supplies. The testing parameters are pH, alkalinity, hardness, turbidity, total dissolved solids (TDS), and electrical conductivities. These elements also include toxic elements such as sulfur, lead, nitrate, benzene, and others. At three testing sites on May 31, 2018, barium concentrations of 0.014 ppm, chlorine concentrations of 5 ppb, fluoride concentrations between 0.226 and 0.968 ppm, and lead concentrations up to 60 ppb were reported. The advantage of employing a water treatment system is that it can treat water at minimum cost, and this is fundamental in order for oil and gas companies to adopt and comply with state standards. This rules out the possible risk of earthquakes that are caused by frequent drilling of disposal wells within a five-mile radius [1].

As shown in Table 1.1, the produced water parameters include total organic carbon (TOC) values in the range of 0–1500 mg/l, total suspended solids (TSS) up to 1,000 mg/l, acceptable pH ranges from 4.3 to 10, and water density in the range of 1014–1140 kg/m³.

TABLE 1.1
PRODUCED WATER PARAMETERS

| Parameter | Value Range | Heavy Metal | Value Range (mg/L) |
|-------------------------------|--------------|-------------|--------------------|
| Density (kg/m ³) | 1014–1140 | Calcium | 13–25800 |
| Surface Tension | 43–78 | Sodium | 132–97000 |
| Total Organic Carbon (mg/L) | 0–1500 | Potassium | 24–4200 |
| Chemical Oxygen Demand (mg/L) | 1220 | Magnesium | 8–6000 |
| pH | 4.3–10 | Iron | 100 |
| Total Oil (mg/L) | 2–565 | Aluminum | 310–410 |
| Chloride (mg/L) | 80–200,000 | Boron | 5–9.5 |
| Bicarbonate (mg/L) | 77–3990 | Barium | 1.3–6.5 |
| Sulfite (mg/L) | 10 | Cadmium | 0.005–0.2 |
| Total Polar (mg/L) | 9.7–600 | Chromium | 0.02–1.1 |
| Higher Acids (mg/L) | <1–63 | Copper | 0.002–1.5 |
| Volatile Fatty Acids (mg/L) | 2–4900 | Lithium | 3–50 |
| Total Suspended Solids (mg/L) | 12–1000 | Manganese | 0.004–17.5 |
| Sulfate (mg/L) | <2 | Lead | 0.002–8.8 |
| Zinc (mg/L) | 0.01–35 | Arsenic | <0.005–0.3 |
| Mercury (mg/L) | <0.001–0.002 | Silver | 0.01–0.004 |

Source: A Comprehensive Determination of Produced Water Composition [1].

1.2 Research Objectives

The main purpose of this study was to analyze the constituents of produced water and to determine the capability of treating and reusing produced water according to specifications and Clean Water Act standards of surface water and safe groundwater in the state of Kansas [2]. To meet these goals, the objectives of this research are as follows:

- To study the elements of produced water in the state of Kansas to determine its qualification to be used for irrigation.
- To design and develop a multipurpose and efficient filtration system that can treat the produced water.
- To gather ample data by testing the system on different samples of produced water and the current water for performance measurement.

- To examine the results of experiments and models regarding agricultural use.
- To detect and discover noble and rare earth metals in the composition of produced water.

System criteria are as follows:

- Performance and stability.
- Percentage of water recovery.
- Standard parameter reduction percentages.
- Water quality.
- Effects on the environment.
- Flexibility and feasibility.
- Cost and energy efficiency.

1.3 Research Approach

This research indicates the study areas and requirements that need investigating regarding the state of Kansas and its water management. Furthermore, the proper method of water management will be discussed according to the appropriate selection criteria and after a thorough analysis of the available literature. The design of this new system was based on prime factors such as the reduction of cost on the disposal of water, and a reasonable and economical method of reusing produced water for irrigation.

The main factors for selecting the best treatment method for wastewater are cost-effectiveness and environmental regulation: reducing the disposal of produced water without treatment to satisfy KCC regulation rules and reducing the expenditure of drilling of all pre-treatment processes. Samples of water were collected from various oil and gas fields located in Kansas, surface water, and groundwater during the past two years (2018–2020). The magnitude of operational, water conditions, and other factors that may have an impact on the research were

examined to decide the results. Testing provided excellent knowledge about the performance of the system concerning the safety and reliability of water sources for animal consumption, irrigation, and mixing with groundwater. Figure 1.1 shows a flow diagram that explains the treatment system for produced water that consists of a sedimentation tank along with three phases—media filtration, adsorption, and the last stage of microporous ceramic (S-MAC). This system design is unique and offers the capability of physical separation while being energy effective.

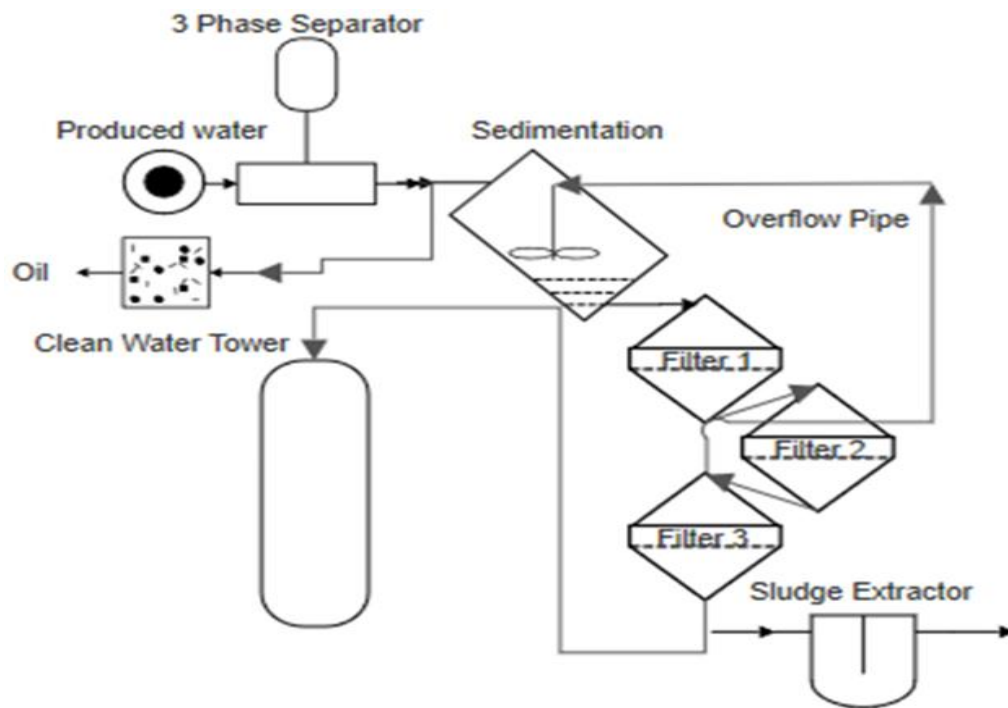


Figure 1.1. S-MAC System Flow Diagram.

1.4 Research Novelty

The novelty of water treatment involving physical separation will be the first advancement in the field of water treatment in the state of Kansas for many years. This cost-effective treatment process requires minimal maintenance and is environmentally friendly in order to benefit the water needs for irrigating cotton crops in Kansas. Moreover, it will be able to

add almost 10–15 acres of land for agricultural production. This research will also be able to solve the issue of how to handle and dispose of produced water. The research monitoring of water quality over the past two years has concluded that it contains no hazardous and harmful toxins; therefore, it can be treated and reused in the state of Kansas. It is critically important to determine the percentage of harmful toxins in water, generally known as hydrocarbon gases or (sweet gas), that are produced during the upstream production.

The presence of flammable gasses, vapors, and hydrogen sulfide in the produced water during operation in the oil and gas fields of Kansas were found to be at a low level. At the same time, there was no sulfur dioxide (SO₂) and nitrogen oxide (NO_x). This finding makes the treatment of produced water less complicated and also safer to handle. The filtration process becomes more manageable and flexible to operate with open storage and sedimentation tanks.

A complete filtration system will be able to treat and improve the quality of produced water in one compatible process dedicated to produced water. Moreover, the multifunctional design of this model will aid in a smooth flow of the physical separation. Additionally, the structure and composition of air exposure, dissolved air flotation (DAF), and stirring mechanism all enhance the quantities of dissolved oxygen (DO) during water treatment.

1.5 Thesis Organization

Chapter 1 provides an introduction to produced water treatment advantages and the benefits of a new source of water for the state of Kansas. Chapter 2 presents some background information regarding the oil and gas production along with the water resource quality and parameters. An up-to-date literature review, the latest technologies, and filtration theories of water treatment are presented in Chapter 3. Chapter 4 provides the technical assessment and description of water treatment. Chapter 5 covers the system design and selection of materials.

Chapter 6 presents the analysis and discussion of elements present in the produced water and the parameters involved. Lastly, Chapters 7 and 8 will present a discussion regarding the conclusion and future research areas, respectively.

CHAPTER 2

BACKGROUND

This chapter will provide background information relative to Kansas oil production, Kansas water resources, Kansas cotton production, and produced water management

2.1 Kansas Oil Production Background

Oil was discovered in Kansas on November 28, 1892, and the first well started to produce 12 barrels of oil per day. In 1904, Kansas was manufacturing more than 4 million barrels of oil per year, and in 1925, Kansas placed fifth in oil production in the United States [3].

One of the significant issues in oil and gas production is the presence of hydrogen sulfide (H_2S) gas, a great danger to life and health at the concentration level of 100 ppm, which is commonly found in crude oil production. However, Kansas oil fields are free of H_2S , which makes it easier to treat and reuse. In general, oil reservoirs contain layers of gas, oil, and water: gas on the top layer, oil in the middle, and water on the bottom layer. Sometimes gas and water are only found trapped in rock formations and thus become a gas-only reservoir, such as the gas production field in the Hugoton Gas area in southwestern Kansas.

The oil uplift flow depends on the internal reservoir pressure, rock formation, and oil properties. Internal pressure forces the oil up to the surface. After releasing the oil and gases, the pressure decreases. If there is no control measure to keep a reservoir pressure at a certain level, then the high-density (heavy) oil will still be trapped in the rock formation while the light oil will be pumped out. At that stage, enhanced oil recovery becomes the best method to ensure that the oil is flowing.

The oil and gas industry are responsible for the production of approximately 14 billion barrels of water annually. Since it is not possible to change the rock formations, enhanced oil

recovery is employed to increase the internal pressure and lower the oil viscosity to improve fluidity, using steam injection, CO₂, or any other method, depending upon the reservoir and rock types. In the past ten years, the number of Kansas oil wells has increased from 45,000 to 52,000, while production has decreased by more than 5 million barrels, as shown in Table 2.1. Produced water has increased because the wells are running out of oil, while the water level has remained the same.

TABLE 2.1
KANSAS OIL PRODUCTION 2008–2018

| Year | Oil | | |
|------|-------------------|--------|-------------------|
| | Production (bbls) | Wells | Cumulative (bbls) |
| 2008 | 39,658,170 | 45,128 | 6,273,955,224 |
| 2009 | 39,472,421 | 45,634 | 6,313,427,645 |
| 2010 | 40,469,726 | 46,109 | 6,353,897,371 |
| 2011 | 41,499,072 | 47,164 | 6,395,396,443 |
| 2012 | 43,750,558 | 49,480 | 6,439,147,001 |
| 2013 | 46,845,544 | 51,817 | 6,485,992,545 |
| 2014 | 49,504,847 | 53,628 | 6,535,497,392 |
| 2015 | 45,467,244 | 53,573 | 6,580,964,636 |
| 2016 | 37,941,819 | 52,877 | 6,618,906,455 |
| 2017 | 35,822,288 | 52,728 | 6,654,728,743 |
| 2018 | 34,707,978 | 52,185 | 6,689,436,721 |

Source: University of Kansas (bbls = barrels) [3].

In the year 2018, Kansas ranked tenth among the 50 states in the production of crude oil, with more than 6,000 oil and gas fields drilled in Kansas since 1860. The Hugoton Gas Field is one of the largest natural gas areas in the United States and covers most of southwestern Kansas. Gas production has decreased dramatically over the past ten years, as shown in Table 2.2.

TABLE 2.2

KANSAS GAS PRODUCTION 2008-2018

| Year | Gas | | |
|------|------------------|--------|------------------|
| | Production (mcf) | Wells | Cumulative (mcf) |
| 2008 | 378,718,724 | 25,613 | 38,364,591,951 |
| 2009 | 359,644,135 | 25,879 | 38,724,236,086 |
| 2010 | 334,365,998 | 25,319 | 39,058,602,084 |
| 2011 | 312,532,496 | 25,203 | 39,371,134,580 |
| 2012 | 299,051,000 | 24,866 | 39,670,185,580 |
| 2013 | 293,437,001 | 24,645 | 39,963,622,581 |
| 2014 | 288,090,641 | 24,764 | 40,251,713,222 |
| 2015 | 285,916,558 | 24,394 | 40,537,629,780 |
| 2016 | 246,630,371 | 23,434 | 40,784,260,151 |
| 2017 | 220,652,784 | 22,693 | 41,004,912,935 |
| 2018 | 202,139,702 | 21,949 | 41,207,052,637 |

Source: University of Kansas (mcf = 1,000 cubic feet) [3].

It is interesting to note that oil and gas production decreases regardless of the noticeable increase in the number of new oil wells drilled in the past ten years. The reservoirs are running out of easy to produce oil, and the remaining 60–70% of oil is in hard-to-reach areas, which requires more effort to extract. The produced water and water level have also increased due to the use of steam injection.

Oil fields in Kansas are spread over almost 30% of the surface area, which is equal to nearly 15.7 million acres of land. This land also includes the 3-million-acre Hugoton Gas Field and underlying Panoma gas area in southwest Kansas. These are one of the world's largest gas-producing regions, which have been responsible for the production of almost 21 trillion cubic feet of gas since 1922 (see Table 2.3). Steam injection is needed to enhance oil recovery, and with the increase in oil and gas production, the byproduct of produced water increases every year, forcing companies to drill more disposal wells.

TABLE 2.3

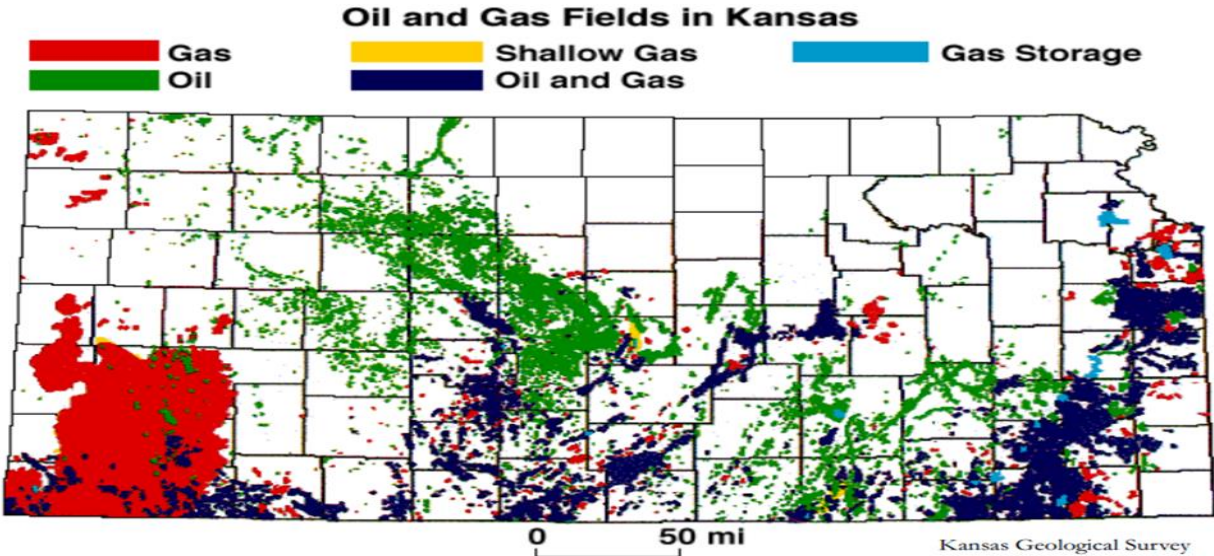
OIL FIELD DISCOVERY DATES IN KANSAS

| Oil Field/Area | Discovery Date | Oil Field/Area | Discovery Date |
|-----------------------|-----------------------|-----------------------|-----------------------|
| El Dorado | 1915 | Aetna | 1935 |
| Hugoton | 1922 | Trapp | 1936 |
| Gorham | 1926 | Kraft-Prusa | 1937 |
| Medicine Lodge-Boggs | 1927 | Bradshaw | 1937 |
| Bemis-Shutts | 1928 | Spivey-Grabs-Basil | 1949 |
| Ritz-Canton | 1929 | McKinney | 1950 |
| Chase-Silica | 1931 | Greenwood | 1952 |
| Hall-Gurney | 1931 | Hardtner | 1954 |
| Burrton | 1931 | Panoma | 1956 |
| Geneseo-Edwards | 1934 | Glick | 1957 |

Source: Kansas Geological Survey, Open-File Report 2018–18

The Kansas Corporation Commission Conservation Division regulates oil and natural gas production in the state. Its mission is to safeguard the public and natural resources with effective regulatory oversight of oil and natural gas exploration, storage, and transportation activities. Article 9 (Salt Water) of the KCC regulates the disposal of saltwater, stating that the owner or operator of any oil or gas field that may be generating produced water that holds an increased percentage of salt minerals, shall have the right to restore those waters to any horizon from which those salt waters may have been extracted, or to any other horizon containing or having extracted saltwater or waters containing minerals in satisfactory amount.

Article 10 (Disposal of Brines and Mineralized Water), Chapter 55, Sections 1003–1007, of the KCC establishes the minimum depths for disposal wells, stating that it is unlawful to dispose of certain waste such as saltwater, mineralized brine, or unwanted oil in disposal wells at excessive pressures, higher than the maximum pressure established by the state corporation commission. Section 55-1005 of the KCC clarifies the penalties and minimum depth of produced water [4]. Figure 2.1 shows the distribution of oil and gas production fields in Kansas.



Source: Kansas Corporation Commission (KCC) [4].

Figure 2.1. Kansas Oil and Gas Fields

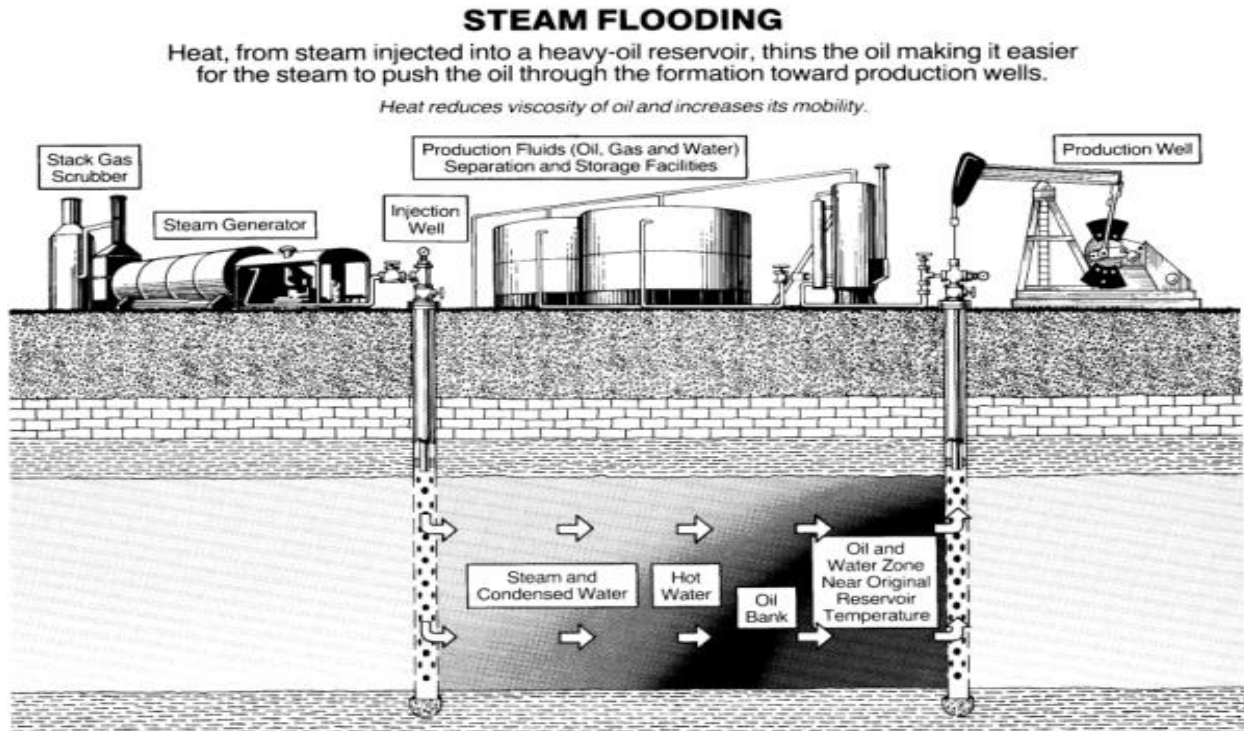
2.1.1 Oil and Gas Reservoir Recovery Stages

The first stage of hydrocarbon production for all-natural reservoir energy, such as gasoline drive, water drive, or gravity drainage, displaces hydrocarbons from the reservoir into the wellbore and up to the surface. Initially, the reservoir pressure is appreciably much higher than the bottom well pressure that is internally well boring. However, as the reservoir stress decreases owing to the production process, so does the differential pressure. To limit the bottom well stress or extend the differential strain to increase oil production, oil production companies must enforce an artificial carry system such as a rod pump, or gas to elevate installation.

The types of oil reservoir drive mechanisms in the principal stage are solution gas drive, gas cap drive, water drive, gravity drainage drive, or an aggregate of drives. In waterpower such as in the Kansas oil manufacturing field, the oil-water contact underlines the oil sector, pushing the oil up to the surface [5].

As oil production decreases, the main stage ends, and the secondary stage of enhanced oil recovery becomes the sole technique to improve production costs. It is also responsible for any

other case exploration regarding the new drilling area and the start of any new oil discipline production. Water is the preferred method to enhance oil production in the form of warm water flooding or steam injection. Steam flooding includes more heat than an equal weight of warm water and injects less water in the reservoir, consequently producing a considerable amount of water [6], as shown in Figure 2.2.



Source: Chevron Oil and Gas Company [6]

Figure 2.2. EOR Steam Injection

The third stage of enhanced oil recovery is referred to as “tertiary recovery.” In addition to retaining reservoir pressure, this kind of restoration aims to change the properties of the oil in such a way that it facilitates production increase. The three primary types of tertiary recovery are chemical flooding; thermal recovery, such as steam flooding and the displacement of carbon dioxide (CO₂) and hydrocarbon; and nitrogen injection. The first-time use of EOR techniques (thermal recovery) was in 1960 in Venezuela using steam injection, and in 1972 in the U.S. in Texas using CO₂ injection to improve oil flotation. Now more than 50% of EOR in the U.S.

involves thermal recovery. Thermal recovery or steam injection is the reuse of produced water after some form of filtration in a phase of steam to lower oil viscosity and improve flow [7].

2.1.2 Mississippian System

Kansas produces oil and gas at average depths of 4,375 ft or 1,334 m out of the Mississippian System shallow-water carbonates reservoir. This field commonly ranges from limestone to dolomite, or interlaminated limestone dolomite beds found in Franklin, Kansas, uplifted from the Petersilie oil field, also to the east of the Hugoton Embayment. Production peaked at nearly 378,000 barrels of oil per year in the 1960s, then started to decline rapidly. In the late 1990s, production began to increase again when water-flooding (steam injection) was successfully employed.

The steam injection technique was developed and widely used in other parts of the world as one of the most popular methods of enhanced oil recovery. It involves the injection of water in the form of steam into the reservoir to enhance the pressure of the reservoir and lower oil viscosity in order to increase production. The water injected is usually produced water that has been through the three-phase separator. Steam injection generally improves reservoir oil productivity by up to 20%. Before the use of the EOR technique, the Petersilie oil field, like many other southwestern Kansas field productions, had begun to decline [8]. In the 1990s, the Petersilie old wells were converted to injection wells, and the drilling of new oil production wells began. Figure 2.3 shows the geology of the oil and gas reservoir.

other plays of the U.S., the development and future of Kansas is difficult to predict based on results in areas with different geologic settings and properties.

2.2 Kansas Water Resources

Most Kansas groundwater wells draw water from three individual aquifers: the largest being the Ogallala Aquifer underneath the Rocky Mountains, which is shared by eight states from Texas to South Dakota; the Equus Beds between Wichita and Hutchinson; and the Great Bend Prairie aquifer in the center of Kansas.

Water levels in the aquifers correspond to the annual percentage of rain and the amount of water used for irrigation. Some studies have basically suggested that the Ogallala Aquifer could potentially dry out before the end of 2050. In Kansas, 90% of crop irrigation water is pumped from the Ogallala Aquifer, and if the aquifer is drained, then it may take up to 90 years to refill naturally. The level of groundwater has declined more than 150 feet, causing many farmers to close their wells [10]. Table 2.4 shows the number of water wells and depth of well to water, as reported by the Kansas Geology Survey (KGS) and Division of Water Resources (DWR).

TABLE 2.4

WELL WATER ANALYSIS 2018

| Type of Well | KGS | DWR | Total |
|-------------------------------------|------------|------------|--------------|
| Irrigation | 469 | 619 | 1,088 |
| Unused (monitor or abandoned) | 68 | 152 | 220 |
| Stock | 11 | 47 | 58 |
| Household | 6 | 2 | 8 |
| Depth of Well to Water (ft.) | | | |
| Less than 100 | 119 | 510 | 629 |
| 100 to 200 | 271 | 197 | 468 |
| 200 to 300 | 145 | 57 | 202 |
| More than 300 | 18 | 43 | 61 |

Source: Kansas Geological Survey [10]; Kansas Geological Survey (KGS), Division of Water Resources (DWR)

The Clean Water Act requires states to perform a water quality evaluation every two years to show the satisfactory status of surface waters in the state, which includes all rivers and lakes. Excessive sediment, nutrients, and poisonous metals prevent many Kansas waterways from aiding aquatic lifestyles or other uses. The University of Arkansas System Division of Agriculture's Public Policy Center has partnered with the Arkansas Natural Resources Commission to produce the 2018–2023 Nonpoint Source Pollution Management Plan, which includes water testing to decide alkalinity [10]

The determination of pH and fluoride concentration is related to particular ion electrodes. The approach used identifies concentrations of the ions of chloride and sulfate. The Kansas Geological Survey uses the Auto Analyzer to measure the nitrate concentration by using ultraviolet (UV) spectrophotometry. In the past, the instrument used for determining calcium, magnesium, sodium, potassium, silica, and boron concentrations was an argon plasma inductively coupled spectrophotometer.

2.2.1 Kansas Water Quality and Standards

Water quality is a common term used to refer to the quantity and type of dissolved or suspended solids in water. When water first contacts the ground as rain or snow, it is typically pure, very close to distilled water, in terms of its lack of dissolved materials. As it moves over soil, rocks, and sediments, it dissolves or picks up small portions of materials with which it comes in contact. These substances can be inorganic or organic, natural or human-made, or even bacteria and viruses. The total dissolved solids content (or TDS, and commonly measured in milligrams per liter or components per million) in a water sample is frequently used as an established indicator of water quality. Each kind of dissolved substance raises special problems with reference to the water quality, and scientists and fitness authorities have set up regulations

for drinking water. Some guidelines are the most permissible contaminant ranges (primary regulations) for public water supplies, while others are advocated stages (secondary regulations).

Table 2.5 lists some examples of the maximum and endorsed levels for selected natural and artificially added contaminants in Kansas. These are U.S. Environmental Protection Agency values that have also been adopted by the Kansas Department of Health and Environment (KDHE).

TABLE 2.5
MAXIMUM RECOMMENDED LEVELS OF CONTAMINANTS (KANSAS 2018)

| Contaminant | Source Concentration (mg/L) n = natural h = human | Maximum Contaminant Level Concentration (mg/L) | Recommended Contaminant Level (mg/L) |
|-------------------------|--|---|---|
| Arsenic | n, some h | 0.05 | |
| Lead | n, h | 0.015* | |
| Mercury | n, some h | 0.002 | |
| Nitrate (as N) | n, h | 10 | |
| Fluoride | N | 4 | |
| Sodium | n, some h | | 100 |
| Sulfate | n, some h | | 250 |
| Iron | n | | 0.3 |
| Benzene | h | 0.005 | |
| Trichloroethylene (TCE) | h | 0.005 | |
| Atrazine | h | 0.003 | |

Source: Kansas Department of Health and Environment [10].

Groundwater is inaccessible and has sources that are diffused or not properly known and migrate very slowly, in contrast to surface water. Water quality trouble may additionally be separated in both time and space from the activities that started the problem. One example of that is the incidence of extended nitrate concentrations in groundwater due to the application of agricultural fertilizer. Decades have elapsed between the first use of industrial fertilizers and the cognizance of a substantial problem. The result has been that massive volumes of soil and

groundwater now contain higher concentrations of nitrate for which there is no positive elimination technique [11].

The remediation of such problems can also be difficult or impossible. Under normal conditions, groundwater quality relies upon the nature of the materials with which the water has been in contact, and also on the amount of time it has been in contact. Other elements also play a role: evapotranspiration will increase TDS due to the dissolved solids that remain and become extra targeted as the volume of water is reduced by the loss of water vapor. Higher recharge at some point in wet periods can, in turn, dilute shallow mineralized waters.

Most salts are highly soluble, which is why salt deposits at the surface, or salt outcrops are discovered solely in very arid environments. Water flowing via salt deposits or salty soils regularly becomes saline very rapidly due to the fact the salt dissolves easily. Salt infection is a widespread problem in Kansas. Thick deposits of salt, deposited at some point during the Permian Period, underlie a great deal of central Kansas. Where the salts are near the surface, they can also be dissolved by way of freshwater and can naturally contaminate water supplies. Although most salts are not particularly toxic, human physiology cannot tolerate very saline water.

Since some of the brines in the salt-bearing formations of Kansas are incredibly concentrated, it is important to acknowledge why the mixing of distinctive waters can propose water quality problems. Freshwater is described as having much less than 500 mg/L chloride and less than 1,000 mg/L TDS. Carbonate minerals are no longer as soluble as the salts found in brines. However, water that stays in contact with carbonate rocks for long intervals tends to be hard.

Hardness is defined by the amount of dissolved calcium (40–100 ppm) and magnesium (30–50 ppm) carbonates, which are ideal for irrigation. The formation of scale deposits in pipelines and control valves is due to a higher level of hardness in water [12]. Hardness levels in the range of 100–150 mg/L are acceptable for crop irrigation. There is a crop-specific interpretation of the water quality for irrigation purposes. Crops vary in their resistance to salts and react differently to the water in which they are irrigated. The most important parameters of irrigation water analysis and the key elements that decide the suitability of irrigation water are TDS, hardness, and salt adsorption ratio (the ratio of magnesium plus calcium to sodium). Highly tolerant crops include cotton and wheatgrass, whereas crops that are highly sensitive to the salt adsorption ratio are beans, carrots, onions, and strawberries. Table 2.6 provides the stages of salt that are tolerable for consuming water, and some percentages of concentrations for comparison [13].

TABLE 2.6

SALT LEVELS FOR SURFACE WATER AND SOME NATURAL CONCENTRATIONS

| Type of Water | Chloride (mg/L) | TDS (mg/L) |
|---|----------------------------|-----------------------|
| Rain (typical) | 0.1–1 | 5–10 |
| Fresh surface water in Kansas | 3–500 | 100–1,000 |
| Fresh groundwater in Kansas | 3–500 | 160–1,000 |
| Drinking water, maximum recommended | 250 | 500 |
| Livestock consumption, satisfactory limit | | 3,000 |
| Saline to brine waters in Kansas | 500–190,000 | 1,000–330,000 |
| Seawater | 19,400 | 35,800 |

Source: Kansas Department of Health and Environment [13]

By contrast, rocks such as granite (common in the Rocky Mountains) are very unreactive and commonly have only a small impact on the TDS of water, even over lengthy durations of time. Water that flows through prosperous soils, is in contact with productive organic communities, or is found in buried organic deposits may also contain concentrations of natural organic materials. These are seldom a foremost problem in themselves; however, they may additionally co-occur with microbes or parasites that affect humans or different animal hosts.

Although these disease-producing elements have a natural origin, they are mentioned under the human effects and water treatment categories. When a large surface vicinity of water is exposed to the atmosphere, either as free water or as moist soil, evapotranspiration affects the water loss and amplifies the TDS of the water.

Static reservoirs enhance the ability of turning small flowing streams into larger ones. However, they are not able to pose greater problems, at least in Kansas. Irrigation, however, can have major effects.

Most irrigation water applied to crops is lost to evapotranspiration, leaving only salts that were contained in the water from the beginning. This can result in a buildup of salts in the soil, and when irrigation returns the water or vegetation floats, the resulting water may be high in TDS.

2.2.2 Characteristics of Kansas Surface Water

The chemical properties of water are decided by the major chemical characteristics and the relative concentrations of specific dissolved constituents. The essential dissolved components in Kansas surface water are mainly the dissolved inorganic resources that have always been found to be more than 10 mg/L. The fundamental dissolved cations in river water in

southwestern Kansas are sodium (Na), calcium (Ca), and magnesium (Mg). The essential anions are sulfate (SO_4), chloride (Cl), and bicarbonate (HCO_3).

Most of the cations and anions exist as character ions dissolved in the river water (as Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , and HCO_3^-). Massive concentrations of selected ions are related to one another, particularly calcium, magnesium, and sulfate, which form the dissolved ion pairs CaSO_4 and MgSO_4 . Therefore, the percentage of the constituents is referred to as the total amount dissolved in the water. The addition of dissolved silica, which is suggested as SiO_2 , generally varies between 10 and 24 mg/L in most Kansas water bodies. Most of the silica dissolved in the river water appears as dissociated silicic acid (H_4SiO_4).

The saline water in southwest Kansas holds much greater quantities of sulfate than chloride. The relative order of mass concentrations (mg/L) of the important dissolved components in most lakes and rivers in Kansas is sulfate: sodium, calcium, bicarbonate, magnesium, chloride, and silica [14].

Salinities are smaller in high flows, and mass calcium concentrations typically exceed that of bicarbonate and sodium. Low flows contain increased dissolved solids, and the mass density of calcium exceeds that of bicarbonate. Based on equal concentrations (that consider the cost of the dissolved ions), the river waters are characterized as made up of sodium-sulfate chemical types.

Equivalent concentrations and masses of sulfate are the best of any dissolved constituents. Both sodium/chloride and sulfate/chloride ratios remain in a relatively slender variation for each low and excessive flow. Mass ratios are almost usually between 3.2 and 3.8 for sodium/chloride and between 13 and 17 for sulfate/chloride [15].

The electrical conductivity of water is a chemical property that is proportional to the TDS concentration. Conductivity is the most important factor for irrigation water used for crops, and it is one of the easiest ways to measure the quality of water. Therefore, the conductivity of water is frequently referenced and used as a measure of salinity. For example, conductivity, as an alternative for the dissolved solids concentration, is often employed for identifying the salinity hazard of water for field crops.

Conductivity is measured with a cup or dip-type tube with electrode surfaces that are configured in such a way that an electric-powered conductor will only allow a particular quantity of water to pass through. The electrical conductivity of a substance is the reciprocal of resistance. The units of electrical conductance are described as the reciprocal of the resistance of a cubic centimeter of solution. The International System of Units for current scientific use expresses conductance as siemens (S), which is equal to the mho. In older publications, the expression mho was derived as the reverse spelling of the resistance unit, ohm.

The units most usually used for particular electrical conductance of water are micro siemen per centimeter ($\mu\text{S}/\text{cm}$), which is identified as the device's micromho/centimeter ($\mu\text{mho}/\text{cm}$). Soil scientists typically use the unit desi siemen per centimeter (dS/cm), which is identified as the millimho per centimeter (mmho/cm). The electrical conductivity of surface water varies proportionally with temperature.

The total dissolved solids concentration against specific conductance for Arkansas River water in southwest Kansas can be used to estimate the TDS content, given a unique conductance measurement. The accuracy of the estimation relies upon the accuracy of the conductance measurement. However, the error in the TDS determination was used to prepare the plot (Figure 2.4) by the U.S. EPA. This plot represents Arkansas River water near Coolidge and is based on

the electrical conductance reported as 1,540-6,010 $\mu\text{S}/\text{cm}$, and the variance in dissolved solids reported as 1,160–4,460 mg/L (sum-of-constituent values).

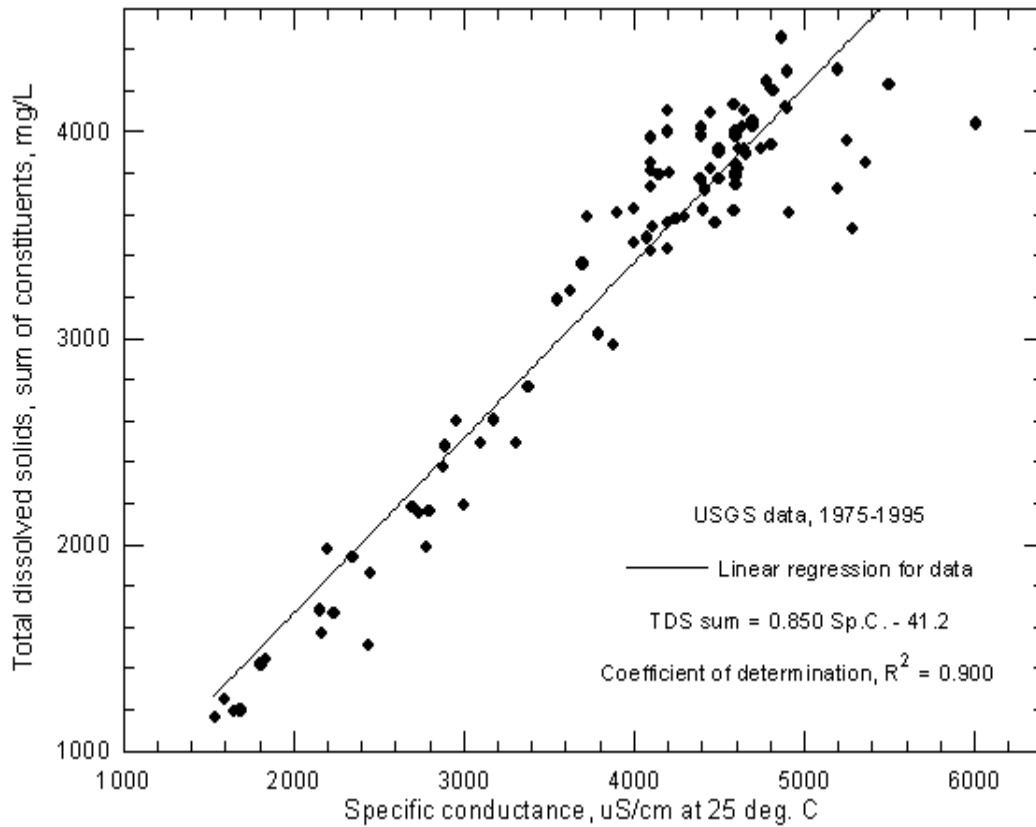


Figure 2.4. U.S. Geological Survey Data of TDS vs. Specific Conductance of Arkansas River

Electrical conductivity meters, without temperature compensation tools, need accurate temperature measurements for corrections. The temperature correction of a meter can be another source of error: the farther the water temperature is from the 25°C calibration reference, the larger the temperature correction error of the meter.

The reason behind most of the sulfate and dissolved solid content throughout low flows is mainly related to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) solubility. Gypsum precipitates in soil and sediments, and water further concentrates the dissolved solids. Kansas has become white in the course of dry intervals as a result of mineral precipitation from the water.

The expected composition of most of the precipitated salts is an aggregate of gypsum and calcium carbonate (CaCO_3). Some magnesium is also integrated into the calcium carbonate and, as a result, is restricted to calcium alone. The chloride concentration is not constrained by means of mineral solubility unless and until it exists in higher concentrations. The increase in sodium content is normally parallel to chloride, through cation trade with calcium and magnesium. The clay in river sediments and soils should barely alter the chemical concentration. Small quantities of chloride salts would exist in the mineral precipitates if all of the river water evaporated. Thus, the chloride concentration does not restrict the lowering of water flow in rivers as does sulfate and other dissolved solids. It can continue to extend the lowering discharge below 100 cubic feet per second. Therefore, chloride-content material is more critical than dissolved salts in river water as a result of consumptive losses [16].

The salinity of the Arkansas River water started to expand over the natural levels once sizable consumptive losses took place as a result of massive river diversions and ditch irrigation. In addition, the extra water applied to soil could have leached additional salts from the subsoils that had been weathered from bedrock [17].

In 1990, Professor Sherow [17], described the exacerbation of the salinity hassle from the invasion of the salt cedar. The salt cedar increased the consumption of water in the valley, mainly causing extended salinity in the water. Dissolved salts taken up into the leaves of the phreatophytes had been recycled into the soil after the leaves fell from the trees and decomposed.

Regarding the uranium level in surface water, especially in the Arkansas River, the state has required that the uranium level in surface waters shall be maintained at the lowest possible level.

2.2.3 Irrigation Water Quality

The sulfate concentration of the Arkansas River water entering Kansas generally exceeds the KDHE criterion of 1,000 mg/L for water substances for livestock. The same limit for livestock water is included in suggestions by the Canada government. However, sulfate concentrations of more than 1,500 mg/L have been observed to cause problems for young livestock. Thus, water in the Arkansas River is not normally used for livestock watering. River water must have less than 1,000 mg/L sulfate concentration.

The vast amounts of dissolved solids in the river are enough to limit yields of vegetation when used as irrigation water in comparison to the use of fresh water, according to information from the U.S. Department of Agriculture (USDA). The salinity hazard for field vegetation is excessive to very high, relying on soil type and dissolved solids content for most flows. However, many studies of the danger of salinity to crops are based totally on irrigation waters, which are high in chloride or high in both chloride and sulfate concentrations.

The effect of high sulfate waters used for irrigation will enable higher assessment of the salinity hazard of Arkansas River waters. These river waters have high fluoride, boron, and selenium concentrations that can exceed limitations permissible by the KDHE standards for irrigation use. Both fluoride and boron contents in the saline water of low flows of the Arkansas River in southwest Kansas can exceed the maximum endorsed limit of 1.0 mg/L and 0.75 mg/L, respectively. The precise conductance of the river water must exceed about 3,000 and 4,000 $\mu\text{S}/\text{cm}$, respectively, in order to enable these fluoride and boron concentration limits to be larger. The error in this estimation from conductance is less for boron and more for fluoride concentrations. Selenium concentrations can occasionally exceed the 20 $\mu\text{g}/\text{L}$ degree advocated for irrigation in low-saline flows [16].

2.2.4 Kansas State Regulations

The Kansas Water Quality Control Commission (WQCC) is in charge of protecting and improving bodies of water in the state. Similarly, it is empowered and directed to classify state waters and to promulgate high-quality water standards for any measurable water attribute. This is done to defend each of the uses in location and those that can be reasonably predicted in the future. The classifications and requirements for state waters are in accordance with “basic regulations” that were adopted on May 22, 1979.

The WQCC finds that Kansas is a water-short state, experiencing extensively increased usage of water, which places other burdens on already-scarce water supplies. These concerns mandate choosing a conservative method for projecting future water supplies. The Kansas Administrative Regulations have authorized the KDHE to set up minimum wastewater standards and design onsite treatment systems. The management of wastewater covers the following:

- Quality of surface and groundwater to protect aquatic life.
- Hazards associated with wastewater exposure and treatments.
- Local regulations governing water disposal and waste pollution.
- Obnoxious odors and nuisance conditions.

Industrial wastewater treatment facilities, such as the one located in southwest Wichita (see Figure 2.5), treat and discharge treated water into the Arkansas River in a subtle way. This Wichita wastewater plant was approved by local city codes and permits based on sanitary regulations adopted through the Sedgwick County Health Department.



Figure 2.5. Wichita Wastewater Treatment Facility in 2018

2.3 Kansas Cotton Production Background

Cotton farming in Kansas began in 1995 when the Farm Bill allowed cotton to be grown in the state. Starting in the spring of 1996, producers started to farm and gin cotton in Sumner and Cowley Counties [18]. In 2018, farmers grew almost 100,000 acres more of cotton than the amount grown in 2016, according to the USDA. While Kansas is part of a larger trend towards cotton acreage, it is expected to grow 7% per year. Cotton became popular in Kansas in the early 2000s due to groundwater levels declining in the Ogallala Aquifer. This is because cotton takes less water than other crops. According to Jerry Stuckey, a cotton farmer and manager at Northwest Cotton Growers Co-Op Gin, “Cotton takes about a third of the water as corn to produce the same amount of revenue in most years. It’s pretty much more water-efficient, as far as dollars per inch of water.” Figure 2.6 shows a cotton field used to grow cotton in the past 18 years. Based on estimates and with the aid of the Kansas Department of Agriculture (KDA), the cotton enterprise in Kansas has a direct output of more than \$24.8 million. Through indirect impacts, the industry contributes approximately \$43.6 million per year.

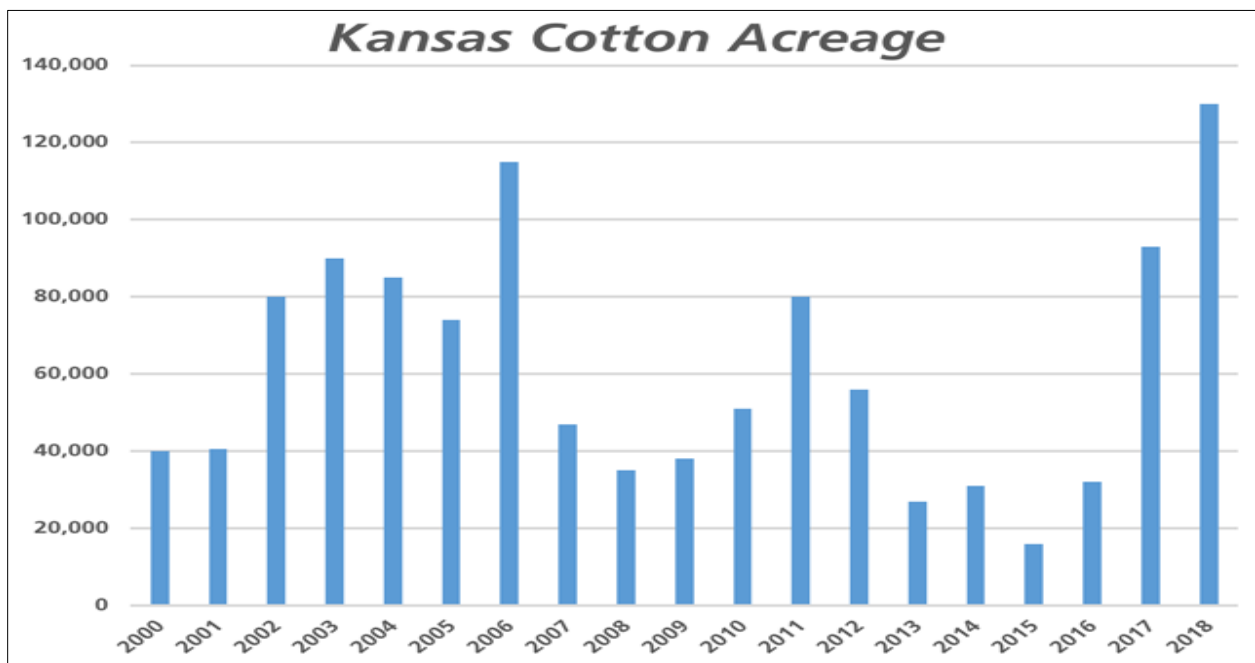


Figure 2.6. Cotton Field in Sedgwick County, Kansas, 2020

Cotton production and ginning in Kansas has exceeded 1.6 million bales. Significant infrastructure investments exceeding \$44 million have been made in Kansas. Cotton, As many as four cotton gins positioned in Moscow, Pratt, Anthony, and Winfield, and a 100,000-bale cotton warehouse in Liberal are used in the Kansas cotton industry. More than \$4.2 million cash investments have been made in the Plains Cotton Cooperative Association. The quantity of acres planted in cotton has multiplied from 16,000 acres in 2015 to 165,000 acres in 2018, corresponding to a tenfold increase. Cotton produces greater farm-level financial value per inch of water than any other crop in southwest Kansas.

Compared to corn, alfalfa, and soybeans, profitable cotton yields can be reached using irrigation that is roughly one-half to one-third of the water of these crops. As a result, farmers are primarily interested in growing cotton on land that has restricted water capacity. Kansas is recognized nationwide for its proactive practices of conserving water for future generations in a major way. Kansas has current accessible water rights and is enforcing proactive water conservation practices by restricting farmers and ranchers from controlling their personal water in order to retain the aquifer for generations to come, contrary to popular belief.

Kansas has developed a 50-Year Vision for the Future of Water Supply in Kansas, which aligns with the priority of developing the economy through strategies and movements that are fundamental to ensuring that a dependable water supply is available to guide that growth. Several objectives within the Kansas Water Vision call for possibilities to address the policy and investigate challenges related to increasing cotton acres in Kansas. Even with the centered implementation of the Kansas Water Vision, declines in the Ogallala Aquifer will continue to be an issue for all agriculture production in Kansas [19]. See Figure 2.7 for the average Kansas cotton production.



Source: Kansas Department of Agriculture [19]

Figure 2.7. Average Kansas Cotton Production

2.4 Produced Water Management

Current options available to oil and gas companies in dealing with the growing problem of produced water are as follows:

- Use polymer gels to block the produced water from reaching the surface of the ground.

The three-phase gravitational water separation occurs underground, and then the

downhole water separation re-injects water back into the bedrock formation. This solution is sophisticated but not always available due to variance in the rock formation of each unique oil field and reservoir formation, and it is not economically feasible for most oil and gas companies.

- Re-inject produced water into the reservoir by drilling new injecting wells, a practice that is currently being used in the state of Kansas and regulated by the KCC.
- Treat and reuse the produced water to reuse for drilling and workover operations.
- Treat and discharge the produced water for animal consumption and agriculture.

These options will enable environmentally sustainable and economically possible natural fuel extraction. This is fundamental for the improvement of this significant power source [20]. The unconventional, onshore natural fuel sources in deep shales are unexpectedly increasing to meet world power needs. Water administration has emerged as an essential problem in the improvement of these inland gas reservoirs, where hydraulic fracturing is used to liberate the gas. Following hydraulic fracturing, giant volumes of water containing very excessive concentrations of whole dissolved solids return to the surface. The TDS concentration in this wastewater, also recognized as “flow back,” can be five times that of seawater.

Wastewaters that include excessive TDS levels are difficult and expensive to treat. Economical production of shale gas sources will require innovative management of flow back to protect groundwater and surface water resources. Currently, deep-well injection is the major means of management. However, in many areas where shale gasoline production will be abundant, deep-well injection sites are not available.

2.4.1 Produced Water De-Oiling

The removal of oil droplets dispersed and emulsified from produced water depends on the oil concentration, droplet size, and other elements present, such as total dissolved solids and salt concentration. Temperature, flow discharge, and pressure all affect the removal rate. The most popular method used by oil and gas companies to remove oil droplets from produced water is the three-phase separator. Other methods and treatments, as shown in Table 2.7, display how droplet size affects the removal processes.

TABLE 2.7

OIL REMOVAL TECHNOLOGIES BASED ON PARTICLE SIZE

| Oil Removal Technology | Minimum Size of Removed Particles (microns) |
|--|--|
| API Gravity Separator | 150 |
| Corrugated Plate Separator | 40 |
| Induced Gas Flootation (Without Flocculants) | 25 |
| Induced Gas Flootation (With Flocculants) | 3–5 |
| Hydroclone | 10–15 |
| Mesh Coalescer | 5 |
| Media Filter | 5 |
| Centrifuge | 2 |
| Membrane Filter | 0.1 |

Source: Argonne National Laboratory [20]

2.4.2 Soluble Organic Removal

Adsorption technology has been widely used to remove soluble hydrocarbons from wastewater. Highly porous solid materials with high surface areas, known as adsorbents, are used for the treatment of produced water. Activated carbon, nutshell media, and zeolite materials are some of the popular adsorbents for water treatment.

Oxidation is another way to remove soluble organic material and contaminants found in produced water. As shown in Figure 2.8, the mobile packed-bed adsorption system is used in

limited quantities for drilling operations [21]. Air stripping and UV lights, normally follow any oxidation process in order to deionize the water and eliminate microorganisms, including bacteria. The system presented in this research shows adsorption employed in the second stage of water filtration.



Source: ET Ventures Inc.[21]

Figure 2.8. Mobile Packed-Bed Adsorption System

2.4.3 Disinfection and Desalination

Disinfection is the removal of bacteria and microorganisms from wastewater to avoid contamination. Microorganisms and bacteria occur naturally in produced water and are generated during storage and de-oiling treatments. Ceramic filtration is an effective technique used to remove microorganisms.

Desalination is the removal of total dissolved solids, and salts are the most abundant TDS in any water treatment systems. The average TDS in produced water is approximately 2000–15,000 ppm. The selection of desalination methods depends on the percentage level of TDS, and in the case of produced water treatment for agricultural use, the salt concentration is more

important than the TDS concentration, especially in cotton production. Multistage filtration systems, as shown in Figure 2.9, have more potential than other methods.

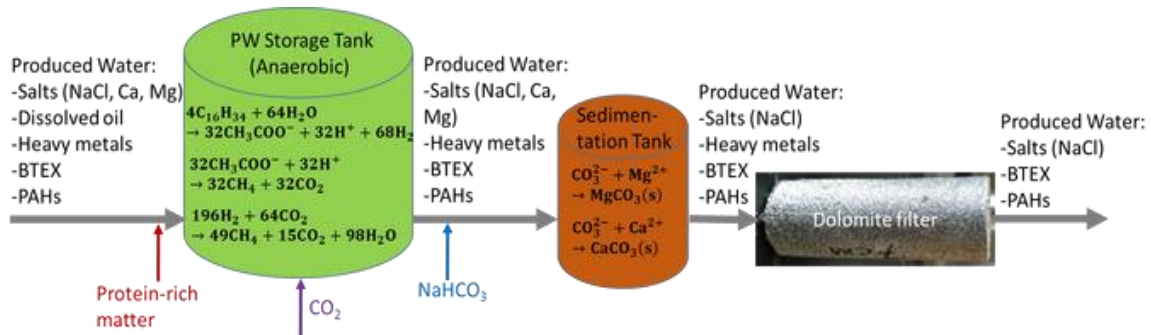


Figure 2.9. Multistage Filtration Treatment of Produced Water for Dissolved Oil and Heavy Metals.

Multistage flash distillation uses the evaporation process, which evaporates water by reducing the pressure. This is done by heating the produced water to the boiling point, then allowing the flow into the low-pressure chamber to condensate. Evaporation, membrane filtration, and chemical treatments are the most known treatment methods to remove TDS from wastewater [22].

CHAPTER 3

LITERATURE REVIEW

In 2017, Malekizadeh and Schenk studied the use of aluminum hydroxide hydrate gels for high-flux water purification. This study reports on a new ultra-filtration-range separation technology using a gelatinous layer of aluminum hydroxide polyhydrate as a secondary membrane on a retaining fabric, which enables a simple and cost-effective production of filtered water. Properties include at least fourfold higher flux rates than currently available membranes, pressure resistance, impenetrability to filtered particles, easy cleaning by backwashing, and simple, cost-effective replacement by gel injection. The amount of filtration achieved depends on the substrate and is accomplished through a packed bed of 1–2 nm hydrate gel globules, partly by mechanical straining with a size exclusion of approximately 10 nm, and partly by physical adsorption. As a result, the filtration of water contaminated with colloids and microorganisms including viruses yields clean water that is free of solid particles or detectable organics. However, small water-soluble molecules (salts, sugars, proteins) remain in the filtrate. The findings demonstrate the potential for broad applicability of hydrate gels in high-flux and low-cost water purification devices [23].

In 2013, Maphutha et al. conducted an experiment to treat oil-containing wastewater using a carbon nanotube (CNT)-infused polysulfone membrane with a polyvinyl alcohol layer. They researched the fabrication and testing of a CNT-infused polymer composite membrane with polyvinyl acetate (PVA) as a barrier layer and witnessed the effectiveness of the membrane in removing oil from wastewater. Several types of research have proven successful in transferring thermal, electrical, and mechanical properties of CNTs to polymer composites. They used a PVA composite membrane to eliminate NaCl (22.8% removal) and MgSO₄ (83.8% removal) from the

solution. The researchers tried to show that CNTs infused with a polymer composite membrane (using PVA as a barrier layer) are capable of amplifying the mechanical strength of the membrane for oil-water separation [24].

The treated produced water from oil fields can be enhanced for use in irrigation operations or subsequently discharged to the receiving aquatic systems. In produced water containing elevated levels of salt, the ability to decrease the conductivity of the produced water may influence the potential reuse of the water for irrigation purposes. The objective of this type of research is to assess the quality of treated water in terms of physicochemical characteristics and toxicity influencing the reuse of water for irrigation or other designated uses [25].

In July of 2016, the Total Oil Company developed and validated an oxidation process with an ultra-fine filtration method using a ceramic membrane, i.e., ceramic cross-flow filtration (CCFU) to filter produced water containing polymers at the Matzen oilfield in Australia. The main objective of the pilot test was to industrialize the process. The company started testing and experimenting from 2008 to 2012 at the offshore Angola Dalia oilfield, and then in 2013 and 2014 at Wyoming's Rocky Mountain Oilfield Testing Center and the ABK oilfield in Abu Dhabi. Their work confirmed the effectiveness of surfactants formulated in laboratories in order to extend the field of chemical enhanced oil recovery EOR to the challenging context of a hot and highly saline reservoir in the Middle East [26].

In 2004, Sirivedhin and Dallbauman investigated the organic matrix in produced water from the Osage-Skiatook Petroleum Environmental Research site in Osage County, Oklahoma. Their research involved characterization of discrete organic compounds and non-volatile, macromolecular organic compounds, i.e., natural organic matter (NOM) from three produced water samples from the site. The specific chemical fragments linked to polysaccharide sources

were found to be potential identifiers that distinguish produced water from newer oil wells from produced water from older oil wells. However, these identifiers were only suggested for this preliminary study. The researchers determined the need for more samples to be included in order to build a substantial database on produced water NOM to confirm and identify more markers [27].

In 2009, Ahmad provided an overall review of up-to-date technologies for treating oil and gas produced water. They confirmed that current methods (at that time) cannot altogether remove suspended soil particles and toxic components. They concluded that numerous treatments have potentially high running expenses and produce risky waste. The organic pretreatment of produced water can be a financially doable and environmentally safe technique. Because high salt percentages and varieties of influent qualities have a direct impact on the turbidity of the water, it is appropriate to join physical treatment with other types of treatment to remedy produced water. Therefore, future research endeavors could concentrate on creating a treatment that includes all physical, chemical, and biological methods required to make advancements in the field of water treatment [28].

In 2009, Mang and Zhang suggested a biological method for treating oilfield-produced water. A field test was conducted on a hydrolysis acidification/biocontact oxidation (HA/BCO) system to treat oilfield-produced water with high salinity. By operating the biodegradation system for three months with a hydraulic retention time of 32 h and a volumetric load of 0.28 kg chemical oxygen demand (COD) m³/d, the treatment process achieved a mean removal efficiency of 63.5% for COD, 45% for NH₃, 79.5% for TSS, and 68.0% for total petroleum hydrocarbon (TPH). The researchers concluded that the use of maize powder would enhance the

environmental adaptability of microorganisms. The biodegradation abilities work as a nutrient stabilizer to maintain the treatment performance [29].

In 2003, Salehizadeh and Shojaosadati suggested a metal ions removal method using an aqueous solution of polysaccharide produced from bacteria known as *Bacillus firmus*. This research deals with the adsorption of Pb, Cu, and Zn on a polysaccharide produced by *Bacillus firmus*. The adsorption of metal ions was significantly affected by the initial pH of the solution, initial metal ion and polysaccharide concentrations, and the presence of other ions in solution. At the optimum pH, the uptakes of Pb, Cu, and Zn were 98.3%, 74.9%, and 61.8%, respectively. Removal of the metal ions was lower at neutral, and generally, the initial adsorption rate was rapid and reached equilibrium after 10 min. The process of uptake follows both Langmuir and Freundlich isotherms [30].

In 2013, Satoshi and Nagano described the characterization of nitrifying granules produced in an anaerobic upflow fluidized bed (AUFB) reactor. This research investigated the granulation of nitrifying bacteria in an AUFB reactor using a nitrification process for inorganic wastewater containing 500 g/m³ of NH₄⁺-N. Results suggested that the use of granules realizes the retention of a large number of nitrifying bacteria in the reactor, which guarantees highly efficient nitrification [31].

In 2009, Shpiner and Stuckey studied the dissolved metal treatment of oil-well produced water close to waste stabilization ponds. This research evaluated the potential of removing cadmium (II), chromium (III), and nickel (II) from produced water by chemical precipitation using biological treatment. They found that the use of chemical precipitation, such as a sulfide salt, is an advantageous mechanism to remove toxic metals. They used biosorption, organic

metal uptake, precipitation as hydroxides, and carbonates to remove heavy metals down to below the irrigation standards [32].

In 2011, Muppalla experimented with filters of highly hydrophilic electrospinning fiber to treat micro- and nanosize particles with coagulants. At 5%, the polyvinylpyrrolidone (PVP) membranes exhibited a superhydrophilic nature. The membranes produced at 4% PVP showed the desired hydrophilic nature and were utilized for the filtration process. To overcome the fouling property of the membrane, coagulation, which enhances the efficiency of the membrane in the removal of colloidal particles, was used as a pretreatment process. Two coagulants, Tanfloc and alum were used during the coagulation process. These coagulants measure the removal efficiency of the suspended particles in the liquid in terms of turbidity, pH, and TDS. They observed that the coagulation/filtration experiments exhibited a higher efficiency in the removal of turbidity in comparison with the direct filtration process [33].

Nanoflotation technology was deployed at the Jinan refinery in China to demonstrate its ability to remove oil in a 24/7 operation on a commercial scale. Testing occurred on site over six weeks. Backwashing of the replaceable skin layer membranes happened at least once a day. The researchers developed a water treatment technology to replace the existing filtration and oil-separation technology resulting in a 90% reduction in energy. This technology was a finalist in the 2017 California-based Katerva awards as the most sustainable technology in the world. Also, after a third-party peer review, the Chinese Ministry of Environmental Protection selected nanoflotation as one of the top 100 environmental technologies in the world [34].

In 2011, Stewart and Arnold produced a water treatment field manual. Their review of current technologies for the management of produced water examines how electrochemical techniques may be used in these areas and compares the prospects for future development. They

suggest that treatment technologies based on electrochemistry could be the future of produced water management since produced water is a potential electrolyte with relatively good conductivity. They also evaluate the application of photoelectrochemistry and electrodeposition to recover valuable metals from produced water with minimal or no negative impact on the environment [35].

In 2017, McEachern claimed that rare earth elements such as lithium are easily recovered from oilfield-produced water treatment, contrary to popular belief. A theoretical approach to lithium recovery from oilfields drew heavily from existing methods and more importantly from the sequential precipitation methods deployed with solar evaporation in a significant way. This method requires the drying of 98% of the water from the brine, an energy-intensive and fairly costly approach. He evaluated other processes for possible efficiencies with the pellucid ultrafiltration (UF) technology, which is significant [36].

In 2018, The University of Wyoming Center of Excellence researched the management of produced water containing a myriad of valuable resources, such as minerals, precious metals, and rare earth elements, in addition to the water itself. They were working towards developing a technology to extract these resources or refine the elements in an economically viable manner. The pilot-scale model covered the evaluations of chemical and physical extraction of evaporation/crystallization, co-precipitation, and liquid-to-liquid extraction [37].

In 1995, Tellez et al. evaluated the biokinetic coefficients in the degradation of oilfield-produced water under varying salt concentrations and achieved a total of *n*-alkane removal efficiencies greater than 99%. They used respirometric techniques for determining the biokinetic constants, obtaining values of 1.37 mg/l and 0.136 h⁻¹ for *K*_s and *M*_{max}, respectively.

Evaluation of specific growth rates at various levels of TDS concentrations exhibited a distinct reduction from 0.131 to 0.047 h⁻¹ when TDS concentrations exceeded 90,000 mg/L [38].

In 2014, Faisal researched the removal of oil from produced water after a three-phase separation treatment involving a sedimentation tank with a stirring mechanism, a bubble generator as the dissolved air floatation, and adsorption treatment. The system was able to remove an average of 94% of oil constituents [39].

In 2016, Waisi used the electrospinning method on a polymeric solution and activated carbon to create an activated carbon nanofiber nonwoven (ACNFN) to remove oil from produced water. The adsorption process based on the high specific surface area, porosity, and hydrophobicity was also studied. This method works for produced water with very low oil percentages. Otherwise, the researcher encountered subsequent clogging due to oil deposited on the top side of the first layer of the filter. Also, this is not a complete water treatment method, but rather one for the removal of low oil concentrations from wastewater [40].

In 2008, Xu et al. treated produced water using carbon aerogel-based capacitive deionization (CDI) technology. CDI together with carbon-aerogel electrodes represents a novel process in desalination of brackish water and has merit due to its low fouling/scaling potential, ambient operational conditions, electrostatic regeneration, and low-voltage requirements. The researchers investigated the viability of CDI to efficiently recover iodide from produced water, as a one-step method of produced water treatment. They suggested further improvements regarding design and operation, modification of aerogel pore-size distribution, development of a low-cost electrode, high capacitance materials, minimizing the dead volume after regeneration, and rinsing [41].

Adsorption is the most common method used for the treatment of produced water, because it can remove more than 75% of heavy metals and results in a very high percentage of product water recovery. Materials used for adsorption, such as activated carbon, zeolites, organoclays, and activated alumina, can remove many contaminants, including iron, manganese, and others. The use of a chemical is minimal, but the overloading of large concentrations of organics is the main issue with an adsorbent method. Due to many limitations, this type of treatment cannot be used as a primary treatment.

Oxidants such as chlorine and chlorine dioxide are also used to treat produced water to remove organics and some inorganic compounds like iron and manganese by sedimentation. A pretreatment of solid separation is necessary to remove oxidized and other particles. This method is time-consuming and is dependent on the end uses of the treated water [42].

Ceramic microfiltration is currently used in Colorado and other states on a smaller scale to treat produced water. Ceramic ultra-filtration tools are made from aluminum oxides, titanium oxides, or zirconium carbides. Ceramic membranes are more resilient and mechanically strong, and chemically and thermally stable [43].

Other research covered the use of compressed filters made of powdered dolomites for treating produced water. This application is important because of its superior adsorption capacity for removing heavy metals and because of the abundant quantity of dolomites in Kansas [44].

In 2002, Tellez et al. evaluated an activated sludge system for removing oil from produced water. They assessed the performance of a field (continuous flow)-activated sludge treatment system for removing petroleum hydrocarbons from a southwestern U.S. oilfield-generated produced water [45]. Table 3.1 shown the latest research and technologies on produced water treatments.

TABLE 3.1

PRODUCED WATER TREATMENT TECHNOLOGIES

| Project Title | Treatment Methods | Advantages | Disadvantages/ Limitations | Reference Number |
|--|--|---|---|-------------------------|
| High-Flux Water Purification Using Aluminum Hydroxide Hydrate Gels (2017) | Filtration is achieved through a packed bed of 1–2 nm hydrate gel globules, partly by mechanical straining with a size exclusion of approx. 10 nm and partly by physical adsorption. Layers of aluminum hydroxide polyhydrate as a secondary membrane on a retaining fabric. | Easy cleaning by backwashing and simple, cost-effective replacement by gel injection. | Small water-soluble molecules (salts, sugars, proteins) remain in the filtrate. | [23] |
| Highly Hydrophilic Electrospun Fibers for the Filtration of Micro and Nanosize Particles Treated with Coagulant (2011) | Hydrophilic electrospinning fiber to treat micro and nanosize particles with coagulants. At 5%, PVP membranes exhibited that of a super-hydrophilic nature. | Higher efficiency in the removal of turbidity in comparison with the direct filtration process. | Pre-treatment required, not an effective method for high turbidity water, and not a complete water treatment system. | [33] |
| Produced Water Treatment by Organoclay Adsorption (2014) | Sedimentation tank with stirring mechanism, bubble generator as dissolved air floatation, and adsorption treatment. | System is able to remove an average of 94% of oil constituents. | Not designed for complete water treatment. | [39] |
| Produced Water Treatment for Beneficial Use: Emulsified oil Removal (2016) | Electrospinning method on polymeric solution and activated carbon to create an activated carbon nanofiber nonwoven (ACNFN) to remove oil from produced water. | Cost-effective, up to 90% oil removal. | Produced water with very low oil percentages; otherwise, subsequent clogging due to oil deposited on the topside of the first layer of the filter. Not designed for complete water treatment. | [40] |
| Assessing the Corrosivity of Field Produced Water Obtained from In-situ Oil Sands Water Treatment Systems (2017) | In-situ oil sands water treatment systems used to treat and recycle produced water to ultimately supply steam to the steam-assisted gravity drainage (SAGD) and cyclic steam stimulation (CSS) processes. | Very effective method to remove TDS and reduce electrical conductivities up to 80%. | Failure associated with erosion-corrosion. Treatment used for reinjecting produced water back into oil sands reservoir to lower the viscosity. | [46] |

TABLE 3.1 (continued)

| Project Title | Treatment Methods | Advantages | Disadvantages/ Limitations | Reference Number |
|--|--|--|---|-------------------------|
| Evaluation of Integrated Microfiltration and Membrane Distillation/Crystallization Processes for Produced Water Treatment (2018) | Integrated microfiltration and direct contact membrane distillation (DCMD)/membrane crystallization (Mcr) system for freshwater and minerals recovery from produced water. | High efficiency of oil removal. | High cost, and intensive maintenance requirements, high energy consumption. | [47] |
| Integrating Membrane Distillation with Waste Heat from Natural Gas Compressor Stations for Produced Water Treatment in Pennsylvania (2017) | DCMD using hydrophobic porous membrane by water evaporation across the membrane, then condensed in a cold permeate. | Uses waste heat source generated by exhaust stream from natural gas compressor station (NGCS) during gas production to operate DCMD, providing economically feasible option to treat produced water. | Up to 30% reduction of standard parameters from its initial salinity. Not a complete treatment system and required pre-treatment. Very expensive treatment. | [48] |
| Novel Produced Water Treatment Using Micro-emulsion Systems to Remove Oil Content (2020) | Chemical process by dispersions stabilized with added surfactants having two or more immiscible or partially miscible fluids. | Effective technology for oil/water separation. | EOR method to reduce oil/water interfacial tension. Not known for water treatment as primary method. | [49] |
| Osmotically Enhanced Dewatering-Reverse Osmosis (OED-RO) Hybrid System: Implications for Shale Gas Produced Water Treatment (2018) | Produced water moving across permeable membrane due to osmotic pressure differences. | Higher water recovery over forward osmosis (FO) and ability to extract up to 28.5 g/l of TDS. | Water recovery up to 67%. Required high hydraulic pressure and high energy consumption based on water turbidity and density. | [50] |

3.1 Media Filtration Theory

The scientific equation of Darcy's law that was uncovered in 1856 by French engineer Henri Darcy dealt with regulating the movement of liquids through granular media or other fluids. The regulation of granular media through porous materials such as the regulation of crude oil through sandstone or calcareous stone was studied. The rate equation for this process is

$$\frac{dV}{dt} = K \frac{A \Delta P}{\eta L} \quad (3.1)$$

where $V (m^3)$ is the volume of fluid (total discharge is m^3/s), t (s) is the time, ΔP (Pa) is the pressure drop across the porous media surface, L (m) is the porous media thickness, A (m^2) is the cross-sectional area of the media, η (Pa.s) is the viscosity of water, and K is the rate constant known as permeability. Due to fluid flow from high to low pressure a negative sign might be needed.

Dividing the equation on both sides by area and using more common terminology yields

$$Q = \frac{-K}{\mu} \Delta P \quad (3.2)$$

where Q is the flux discharge (m/s) per unit area, and ΔP (Pa/m) is the length of units per time. That value, referred to as Darcy flux, is not the velocity experienced by the fluid passing through the pores. Rather, the fluid velocity (v) is related to the Darcy flux (q) by the porosity (ϕ). The flux is divided by porosity, so that only a portion of the total volume of formation is available for flow. The fluid velocity is that which is encountered by a conservative tracer if the fluid is carried through the structure [51]:

$$v = \frac{q}{\phi} \quad (3.3)$$

Darcy's law is a fundamental mathematical principle that sums up neatly some common properties demonstrated by water flowing into reservoirs, including the following:

- Those are hydrostatic conditions, if there is no pressure gradient over a distance.
- If the pressure gradient is present, then the flow will be from high pressure to low pressure, opposing from the direction of increasing gradient, hence, the negative sign in Darcy's law.

- The higher the pressure gradient, the greater the discharge rate through the same forming material.
- The fluid discharge intensity can always be different, either through different forming materials or through the same material in different directions, even though the same pressure gradient is present in both cases.

Darcy's law is applicable only for the law of viscous flow; luckily, this research framework falls in that category. Usually, any low flow with a Reynolds number is simply laminar, and Darcy's rule would be applicable. The Reynolds number for a porous media flow (a dimensionless parameter) is generally presented as

$$Re = \frac{\rho v d}{\mu} \quad (3.4)$$

where ρ (kg/m³) is the density of water, v (m/s) is the specific discharge, d is the grain diameter for the porous media, and μ (Pa.s) is the viscosity of the fluid.

The filtration method is often associated with the flow of liquid through a series of capillary tubes. In this case, one could use Ponselle's equation (1846):

$$\frac{dV}{dt} = \frac{\pi r^4}{8\eta} \frac{\Delta P}{L} \quad (3.5)$$

where η is coefficient of viscosity, and r is the radius of the capillary.

By combining equations (3.1) and (3.2), Kozeny (1927) acquired the following equation:

$$\frac{dV}{dt} = \frac{A\varepsilon^3}{kS(1-\varepsilon)^2} \frac{\Delta P}{L} \quad (3.6)$$

where ε is the media porosity, S is the specific surface area of the particles, and k is the Kozeny constant [52].

From equations (3.1) and (3.6), the following relationship is possible:

$$\begin{aligned} K &= \frac{\varepsilon^3}{kS^2(1-\varepsilon)^2} \\ &= 1/\alpha \end{aligned} \quad (3.7)$$

where α is the specific media resistance. Equation (3.7) implies that both media permeability and S decrease as the particle size decreases. Thus, the rate equation based on Darcy's law, shown previously in equation (3.1), provides an explanation that the flow of fluid versus time should be linear, regardless of the distribution of pore sizes.

However, it can be concluded that the volume of pores determines the flow rate and the efficacy of the filtration. The level of reduction of moisture in the porous media is referred to as S irreducible saturation. This value varies depending on the pressure applied, substrate, media size, basic gravity, media porosity, particle form, surface oxidation, viscosity, surface hydrophobicity, and water density:

$$S_{\infty} = 0.155(1+0.031 N_{\text{cap}}^{-0.49}) \quad (3.8)$$

where N_{cap} is the capillary number. In this research, the filtration process is governed by equation (3.9), whereas the capillary number depends on the gravitational acceleration g , filter depth L , particle diameter d , and surface tension γ :

$$N_{\text{cap}} = \frac{\varepsilon^3 d^2 (\rho g L + \Delta P)}{(1-\varepsilon)^2 L \gamma}, \quad (10^{-5} < N_{\text{cap}} < 0.14) \quad (3.9)$$

Darcy's law is well known for relating the decrease in pressure and velocity in an unbounded porous medium. The pressure drops caused by the frictional drag is directly proportional to the velocity for the fluxes of a viscous Newtonian fluid at low speed through a porous medium. [53]

3.2 Sedimentation Theory

The rising velocity of an oil droplet is proportional to the square of the droplet diameter and viscosity of the fluid [54]. Based on Stokes' principle of spheres moving in fluids, the force

that slows down a sphere moving in a viscous fluid is directly proportional to the velocity of the sphere, the radius of the sphere, and the viscosity of the fluid. Other than oil droplets, oil exists in the form of semi-solids, as shown in Figure 3.1.



Figure 31. Oil Particles in Produced Water

The ability to separate oil droplets from water will decrease as the size of droplets decreases. Also, the distribution of oil droplets in the produced water is an important factor for the separation process. The distribution of oil droplets mainly depends on three conditions of produced water:

- Tension forces between the hosting fluid and the sphere oil droplet surface.
- Storage and transportation through various diameter pipes.
- Produced water temperature and pressure.

The high energy rate during the process influences the size and distribution of the oil droplets. Decreasing the size and spreading the oil droplets almost evenly into the produced water results in an energy rate decrease during storage, and the oil droplets colliding with each other and creating larger droplets, called coalescence.

The buoyant force is resisted by the drag force caused by the vertical movement of droplets through water. The droplet rising velocity becomes constant when the two forces are equal to each other [55]:

$$V_r = 1.78 \times 10^{-6} (SG_w - SG_o) d_o^2 / \mu_w \quad (3.10)$$

where V_r , is the velocity of the oil droplets, SG is the specific gravity, μ_w is the viscosity of the produced water, and d_o is the oil droplet diameter.

When a body falls into a viscous medium it instantly drags when in contact with the substrate of the fluid. This induces relative motion between the different layers of the liquid [56]. The drag force is proportional to the sphere size, traveling velocity, and the host fluid viscosity:

$$F = 6 \pi \eta r v \quad (3.11)$$

where r is the sphere radius, v is the terminal velocity, and η is the coefficient of viscosity [57].

3.3 Dissolved Air Flotation Theory

Dissolved air flotation is the method of removing stable and immiscible liquid particles from liquid segment with the aid of the injection of gas microbubbles. Particles are attached to the bubbles and glide at the surface due to the reduced density. Flootation is an effective approach for separating particles that have a low settling speed. DAF is a commonly used commercial technology for treating oily wastewater and is known for its ability to separate low-density particles from water [58].

DAF advances the sedimentation process of small and low-density particles that take a longer time to settle down. It works by pressurizing air with the help of a pump or compressor in the formation of microbubbles (about 10–100 μm in size). Some bubbles are so small that they appear as white clouds in water; these are referred to as whitewater [59].

Microbubbles rise and encounter oil droplets and suspended particles during their way to the surface; the fine oil droplets and micro solid particles collide with the air bubbles and float to the surface. The average time for the bubbles to reach the surface is 15–30 min. According to the whitewater blanket model, the collision of particles with bubbles occurs by Brownian diffusion, interception, and settling [60]. Other than the advantages of speeding up the process of solid/liquid separation, some of the air bubbles will dissolve in water and improve the oxygen saturation of water.

The concentration of dissolved oxygen is one of the most important parameters for higher quality water. Coagulation improves the settling velocity, and 50–60% of the removal efficiency of suspended solids is expected to be achieved in the primary sedimentation tank along with the achievement of almost 95% oil-free produced water just after 6–8 hours of processing time.

By comparing the sphere weight to the total of the thrust up and the drag forces in equation (3.11), velocity becomes

$$v = \frac{2}{9} (\sigma - \rho) a^2 \frac{g}{\mu} \quad (3.12)$$

where σ is the density of the sphere (kg/m³), a is the radius of the sphere (m), and ρ is the density of the liquid (kg/m³)

Haarhoff and Edzwald suggested that the rising rate of particles in the water is in the range of 20–35 mm/s [61]. The rising velocity is even greater than the settling speed (<0.5 mm/s) of a floc of iron found in water treatment works. Theoretically, at smaller Reynolds numbers, gas bubbles move like solid spheres. For air bubbles to behave like solid spheres in water, the bubble surface has must sustain finite shear stress. When the tangential velocity of the surface is zero compared to the center of the bubble, the Stokes' equation relates, and the force balance equation will be

$$v = \frac{2\rho g a^2}{9\mu} \quad (3.13)$$

Equation 3.13 shows that the rising velocity of air bubbles is affected by bubble size and the hosting fluid viscosity. On the other hand, viscosity is controlled by the temperature and the specific density of the fluid. Viscosity decreases when the temperature increases, and so does the rising velocity of the air bubbles. The force equilibrium in terms of drag coefficient, C_D , is [62]

$$C_D = \frac{4gd}{3v^2} \quad (3.14)$$

There were no major variations in the average turbidity readings between different tank depths in terms of turbidity elimination. Comparison of turbidity at various tank lengths revealed that the overall turbidity values were the same between three-quarters of the tank length and the lower end of the tank. Figure 3.2 shows adhesion of the air bubbles (a) and the rising air bubbles attaching to the suspended solids structure (b) [63].

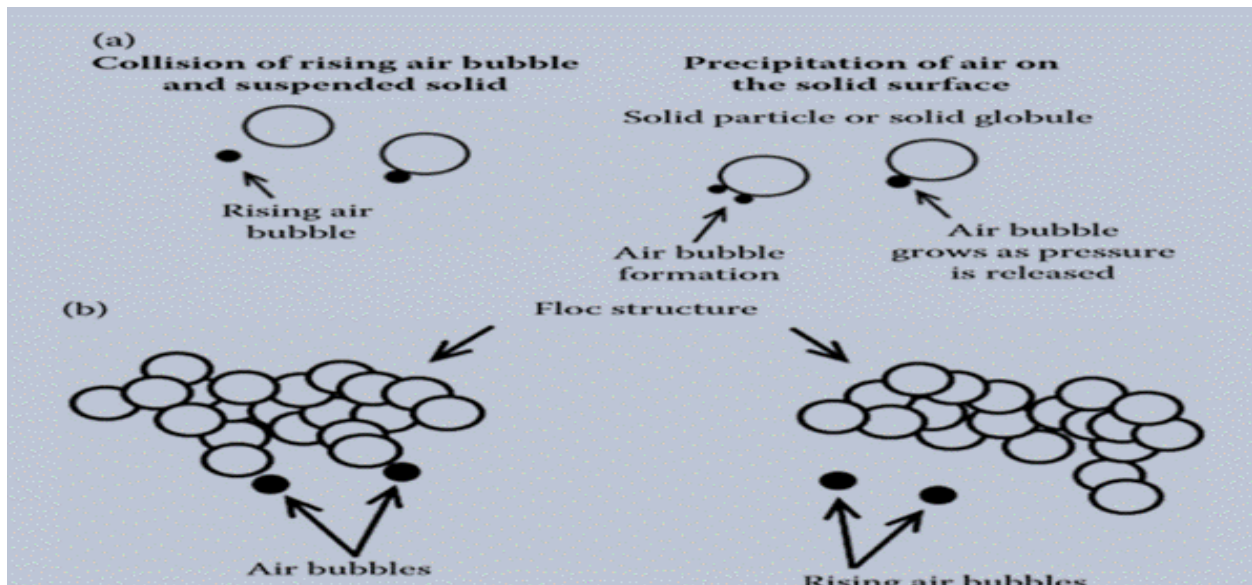


Figure 3.2. Bubble-Particle Attachment Mechanism [63]

Dissolved air flotation is an enticing means of removing solids/liquids in low-turbidity water with low-density solid particles. At the same time, DAF may be more efficient than

conventional gravity settling [64]. Table 3.2 shows the relationship between temperature and volume of air bubbles. Keep in mind that they collide with each other to produce much larger-diameter bubbles.

TABLE 3.2
BUBBLE SIZE AND TEMPERATURE RELATIONSHIP

| Bubble Size (µm) | Rise Velocity (m/h) Based on Stokes' Law | |
|------------------|--|-------|
| | 4°C | 20°C |
| 10 | 0.125 | 0.196 |
| 20 | 0.499 | 0.78 |
| 30 | 1.12 | 1.76 |
| 40 | 2.0 | 3.13 |
| 80 | 3.12 | 4.89 |
| 110 | 7.99 | 12.5 |
| 120 | 15.1 | 23.7 |
| 130 | 18.0 | 28.2 |
| 140 | 21.4 | 33.1 |
| 160 | 24.5 | 38.3 |

Source: A fundamental study of Dissolved Air Flotation [64]

3.4 Adsorption Theory

The sum contaminant adsorbed by the substance (Q_t) at the period (t) was determined from variations in the supernatant between the amounts of contaminants applied to it. The Q_t is determined from the equation of mass balance given by equation (3.15) [65]:

$$Q_t = \frac{V(C_o - C_t)}{m} \quad (3.15)$$

where C_o and C_t are the initial and final adsorbate concentrations in the liquid phase (mg/l), respectively, V (l) is the volume of adsorbate solution, and m (g) is the mass of adsorbent used.

Activated carbon filtration is a widely used procedure based on contaminant adsorption to a filter sheet. This approach is effective in the elimination of wastewater of all organics (such as undesirable flavor and odors, micropollutants), ammonia, and fluorine. It is not an active agent against microbial toxins, metals, nitrates, and other inorganic toxins. The adsorption efficiency depends on the nature of the activated carbon surface area and the water containments.

Isotherms of Langmuir and Freundlich adsorption are widely used to identify the adsorption results. The Langmuir equation is stated as:

$$\log Q_t = \log k + \frac{1}{n} \log C_t \quad (3.16)$$

where k (m mol/g) and $1/n$ are constant characteristics of the treatment system [66].

CHAPTER 4

TECHNICAL ASSESSMENT

This study covered the most widely developed innovations for water treatment and background information relative to conventional methods. It also included existing applications and the latest technologies. This chapter discusses the latest up-to-date techniques, processes, advantages, and disadvantages.

4.1 Emit Water Treatment Technology

The DOW Chemical Corporation (DOWEX G-26) has developed a water treatment method that uses a solid acid cation exchange resin. This resin has a sulfonic acid group (SO_3H^+), alternating Ca^{2+} , Na^+ , Ba^+ , and Mg^{2+} ions with the H^+ ion. The cycle of ion exchange carried out is in a Higgins system. The activity of the Higgins Loop is followed by the addition of calcium to change the pH, sodium adsorption ratio (SAR) balance, and calcium concentration increase. The cycle is based on sodium-ion separation and SAR reduction by the mixture of Higgins Loop and the addition of calcium. During the SAR modification, the rise in calcium, chloride, and sulfate levels is attributed to chemical introduction. The cost of treatment varies from \$0.15 to \$0.25 per barrel of treated water, based on significant composition, SAR, and resource quality. The water generated after this treatment can satisfy environmental requirements [67].

4.2 Electrodialysis

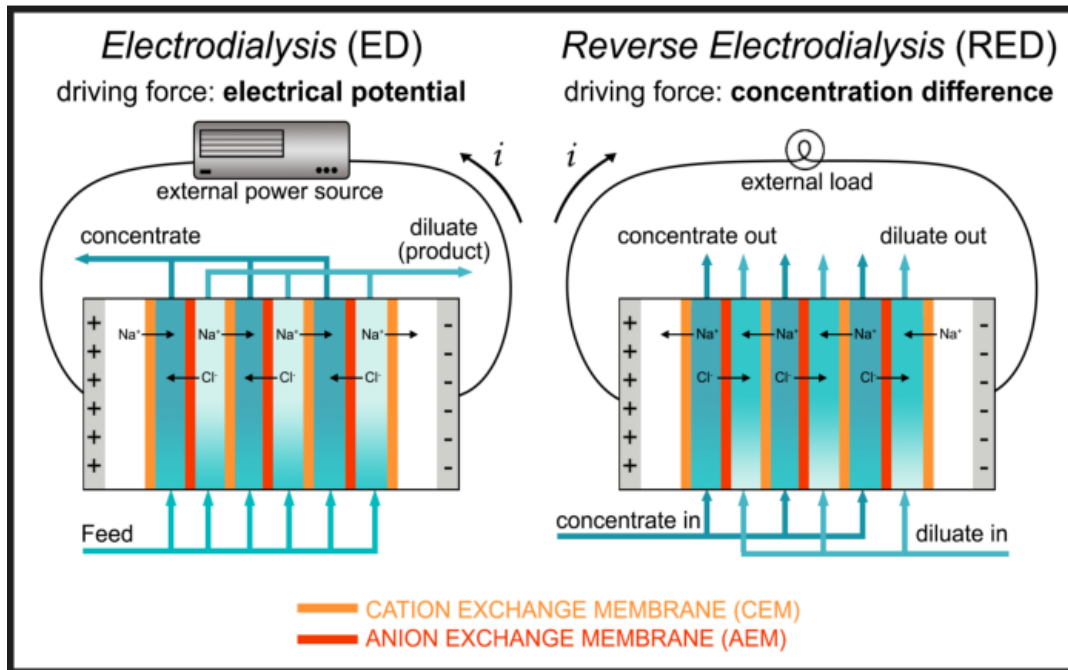
In electrodialysis (ED), a pair of electrodes is placed between membranes, which allow either cations or anions to move. These membranes are arranged in a particular order. A spacer sheet positioned between each pair of membranes allows feed water to flow along the membrane face. The understanding is that up to 95% of salts that dissolve in water are ionic, charged either

positively (catatonic) or negatively (anionic). These ions are drawn to the electrodes of electric charges opposite to them [68].

The charged ions are resisted during migration by likewise charged ion-exchange membranes. Negatively charged ions (Cl^-) move to the cathode, and positively charged ions (Na^+) move to the anode. As a result, water is stored in the alternate container, leaving desalinated water in the next container of the ED unit. The standard electro dialysis unit consisting of several hundred pairs of cells attached to outside electrodes is called a membrane stack. Feed water flows through all the cells concurrently in parallel pathways to provide a steady supply of desalinated water and brine to emerge from the plate. A low-pressure but adequate-strength pump is used to overcome water resistance when it passes through the narrow channels.

The negative side to electro dialysis that raw feed water must be pretreated to eliminate contaminants that may disrupt membranes or obstruct the cells' narrow channels from reaching the membrane stack. In addition, a rectifier must be used to convert the alternating current (AC) into the direct current (DC) supplied to the electrodes beyond the membrane stacks [69]. Figure 4.1 shows the electro dialysis setup with a feed spacer and an ion exchange membrane.

Electro dialysis reversal (EDR) technology works under the same general concept as conventional ED, except that, in design, both the substance and brine channels are similar. As a response, the ions are drawn through the membrane in the opposite direction.



Source: Electrosynthesis Company Inc.[69]

Figure 4.1. Electrodesialysis Technology

4.3 Capacitive Deionization Technology

Capacitive deionization technology (CDT) is a new technology being developed for the purification of brackish groundwater and produced water. Here, soluble salts are collected on the surface of porous carbon electrodes after a constant voltage is applied, thus purifying the water for industrial processes or human consumption. The utilization of CDT involves a brackish water stream that flows between pairs of large-surface-area carbon electrodes that are set at a potential difference of 1.2 V. Due to the opposite charge, the other charged particles (such as microorganisms) and ions are attracted to and held on the electrode. Positively charged ions (cations) such as sodium (Na), calcium (Ca), and magnesium (Mg) are attracted to the negative electrode, while the positively charged electrode attracts negative ions (anions) such as chloride (Cl), and nitrate (NO_3). At some point, the electrode becomes saturated with ions and must be replaced. The electrodes are flushed to release attached ions from the system after the potential is

reduced, producing a more concentrated brine stream [70]. Figure 4.2 provides a schematic of carbon aerogel technology.

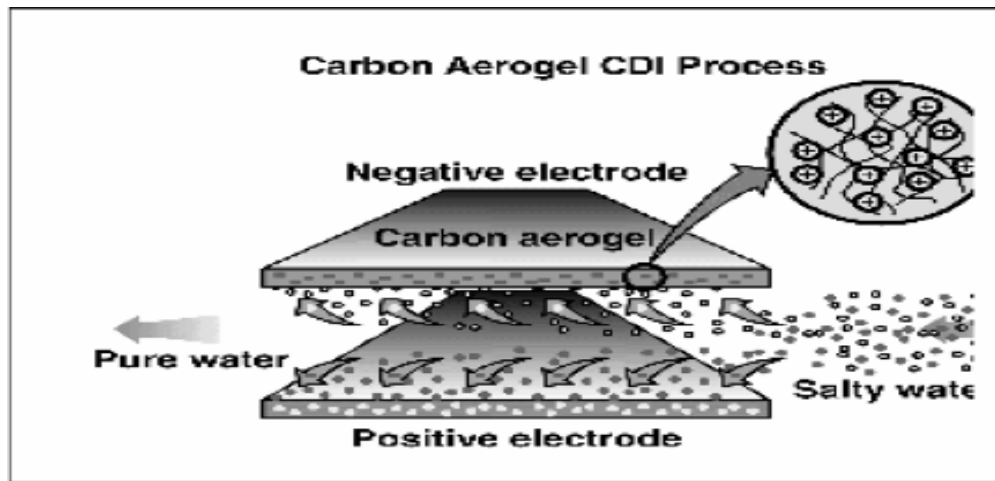


Figure 4.2 Carbon Aerogel Technology [70].

4.4 Rapid Spray Evaporation Technology

AquaSonics International developed a rapid spray evaporation (RSE) system, tested by West Water Resources Inc. This process of injecting wastewater into the disposed heat at high speeds by means of a powerful injector-nozzle was studied in detail. A heat supply, from which air is pumped into an evaporation chamber, is used by the system to heat the vessel. Nebulized water is pumped into the evaporation chamber while the hot air travels into the evaporation vessel. A mechanical filter captures the droplets that travel through the chamber. The filtered water vapor then moves to a condenser. As the water droplets vaporize, the solid particles separate. A vacuum process then collects the condensed water. The downside to this system is that without nozzles, the machine will not operate properly with hydraulic pressure [71]. The RSE system's initial trial by Wastewater Resources Inc., Albuquerque, NM, established that the system could clean water with about 16% salt concentration and a removal rate of 99%. The cost of treatment is between 20 and 35 cents per 1,000 liters. Table 4.1 shows the RSE results obtained during the testing phase [72].

TABLE 4.1
RAPID SPRAY EVAPORATION TEST RESULTS

| Solute | Untreated (ppm) | Treated (ppm) | Concentrate (ppm) |
|----------------|------------------------|----------------------|--------------------------|
| Calcium | 79 | 1.6 | 20 |
| Sodium | 490 | 1.7 | 600 |
| Potassium | 25000 | 160 | 57,000 |
| Magnesium | 610 | 1.9 | 1,100 |
| Chloride | 5000 | 90 | 8,400 |
| Sulfate | 31000 | 150 | 35,000 |
| Bicarbonate | 5700 | 20 | 2,900 |
| Phosphate | 1200 | 0 | – |
| Carbon Dioxide | 3100 | 0 | – |
| TDS | 130,000 | 440 | 180,000 |

Source: Wastewater Resource Inc., NM [72]

4.5 Freeze-Thaw Evaporation Technology

Crystal Solutions, LLC, employed freeze-thaw evaporation (FTE) for produced water treatment at its first reported commercial treatment in a facility near Wamsutta, Wyoming. This process takes advantage of temperature drops below zero during wintertime, depositing the dissolved solids and producing freshwater. Produced water with TDS of 14,000 ppm was reduced to almost 900 ppm and sludge of approximately 64,300 ppm. Water recovery of up to 55% and 15% of concentrated brine, and 30% of the feed water was lost in the process. FTE is a process of storing and holding the produced water until the air temperature drops below freezing (0°C). Then the water is pumped into other freezing containers with a network of elevated pipes and a sprinkler system [73]. The ice melts and drained water is separated by controlled valves, as shown in Figure 4.3.



Source: Hart Energy Publications [73]

Figure 4.3. FTE Water Treatment.

4.6 Membrane Separation Technologies

The most popular technologies for water treatment are based on the principle of high-pressure flow across a membrane and molecular weight cutoff. These technologies are classified based on pore sizes: microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), reverse osmosis (RO), and forward osmosis (FO). The osmotic pressure of TDS must be less than the working demand for the filtered water to cross the membrane in the RO treatment. While the solution flow is from high to low intensity to reach natural equilibrium in the osmosis cycle, the reversal of that is used in RO [74].

Oil and gas companies treat, and reuse produced water for drilling operations. Normally they subcontract mobile treatment units when needed. Osmonics Inc. is one of the better-known companies that manufactures and leases mobile water treatment in the oil and gas industry.

The disadvantages of membranes, in general, are that their performance decreases with a higher temperature of an upper limit of 46°C, with some exceptions of spiral membranes. The

higher the temperature, the higher pressure of the differential is required, and so the energy consumption also increases. Also, the membranes perform well at a higher pH. However, since the produced water normally comes with low pH, pretreatment is required. The other issue with membrane technologies is fouling during the filtration processes due to oil accumulation on the filter surface. An evaluation of produced water treatment methods and limitations are listed in Table 4.2, which covers the latest technologies in the oil and gas industry.

TABLE 4.2

TECHNICAL ASSESSMENT OF PRODUCED WATER TREATMENT METHODS

| Treatment | Method | Limitation |
|--|--|---|
| Media Filtration | Sand, gravel, anthracite coal, silver filters. | Lifetime of filtration media is lower than other methods, frequent replacement, slow flow rate, vessel needed to contain media, chemicals required to increase particle size. |
| Adsorption | Zeolites, organoclays, activated alumina, and activated carbon. | Problem of overloading with contaminants, limited, not ideal for primary treatment, removes up to 80% of heavy metals. |
| Oxidant | Chlorine, chlorine dioxide, permanganate oxygen, and ozone. | Expensive, post-treatment required, chemical metering pumps required. |
| Ceramic Microfiltration (MF)/ Ultrafiltration (UF) | Ceramic membranes oxides, nitrides, carbides of metals such as aluminum, titanium, or zirconium. | More resilient than other types of membranes, mechanically strong, chemically and thermally stable, can achieve high flux rates, more expensive than any other membrane technologies. |
| Electrodialysis (ED)/ Electrodialysis Reversal (EDR) | Electrochemical charge-driven separation processes using ion permeable membranes and electrical field. | Laboratory-scale, limited ability to remove non-charged constituents such as organics molecules, silica, and boron, limited to low turbidity produced water. |
| Capacitive Deionization (CDI) | Ions adsorbed onto the surface of porous electrodes by applying low voltage electric field | Limited to produced water containing less than 3,000 mg/L of TDS, produces deionized water with high cost on lab-scale. |
| Brackish Reverse Osmosis (BRO) | Polyamide layer, polysulfone porous layer (about 50 microns) on top of fabric support sheet. | Limited TDS 500–25,000 mg/l, higher power consumption, 50% recovery, not suitable for highly contaminated produced water, requires hydraulic pressure. |
| Forward Osmosis (FO) | Hydrophilic, cellulose acetate active layer cast onto woven polyester mesh or microporous support structure. | Performs efficiently with feed streams containing high concentrations of soluble salts, large scale not tested not commonly used for produced water. |
| Multi-Stage Flash Distillation (MSF) | Water evaporation by reducing pressure. | Preheating feed water required, high initial cost, required high maintenance. |
| Freeze/Thaw Evaporation (FTE) | Produced water sprayed onto a freezing pad to create an ice pile at 0°C. | New technology just beginning to be used for produced water treatment. |

A combination of the most effective methods of media filtration in the first step of the system and the adsorption method using zeolite and activated carbon in the second stage, together with a microporous ceramic filter in the third stage removes 95% of the limitations and disadvantages of filtration techniques of each stage as the primary treatment. The system displays the characteristics of a complete treatment process through the compatibility of sedimentation, media, adsorption, and ceramic filters. All treatments mentioned above would not increase the quality of treated water, but in this research, the consistency of the treated water increases by injecting oxygen into the treated water through the process of aeration and exposing the water to air via a sprinkler. This system design allowed multiple treatment methods to be integrated into one low-cost unit. This unit will be maintenance-free and have low power consumption [75].

CHAPTER 5

MATERIALS AND METHODS

This chapter covers the materials and methods used in this research. Discussion will include ceramic material properties and applications, system design inspiration, the stages of filtration, preparation of filters and samples, and testing of the water parameters.

5.1 Materials

The research materials for the water treatment system were selected based on each stage's requirements and objectives. The sedimentation tank should be either concrete or aluminum. Research results recommend using concrete for its strength, weather protection, and lower cost than aluminum. Water samples from groundwater, industrial wastewater, local lakes, and the Arkansas River were obtained from January 2018 to February 2020 at different locations.

5.1.1 Ceramic Material Properties and Applications

The materials for the final and most crucial stage of the innovative ceramic filter were purchased from Paul Brown Studio Arts and Supplies, Ohio, USA. They were selected based on their properties, ability to eliminate contamination, and capacity to remove suspended particles in water, as shown in Table 5.1.

TABLE 5.1

CERAMIC MATERIAL SELECTION

| Material | Common Usage |
|---|---|
| Flint/Silica 325 Mesh | Fusing ceramic material to together |
| Grolleg (China Clay) Fine White Kaolin | Low plasticity and low shrinkage for making ceramic filters |
| Dolomite Calcium Magnesium Carbonate | Acid neutralization, conditioner, source of magnesia |
| Petalite | Casting high-temperature resistance |

TABLE 5.1 (continued)

| Material | Common Usage |
|---------------------|---|
| Lithium Carbonite | Helps reduce salt intensity |
| Potassium Silicate | Increases alkalinity and fertilizer |
| Magnesium Carbonate | Source of magnesium |
| Boric Aid | Antibacterial compound |
| Aluminum Hydrate | Acid indigestion and reducing phosphate levels |
| Sawdust | Burns during process, leaving ceramic filter porous and with carbon |
| Calcium Carbonate | A source of calcium and phosphate, and acts as an antacid |
| Activated Carbon | Water filtration, pollution control, and odor removal |
| Zeolite | Unique heavy metal and ammonia adsorption properties, removing a wide range of pollutants |

5.1.2 Produced Water Samples

Produced water samples were obtained from Lario Oil & Gas Co (Kansas Mid-Continent Region). This research employed three different samples:

- Produced water samples from the wellhead (more than 5% oil concentration)
- Produced water samples from the storage tank (up to 2% oil concentration).
- Produced water samples after the three-phase separator (0.1–1.0% oil concentration).

The main target was the water sample produced after the three-phase separator with a less than 0.1–1.0% oil concentration. Figure 5.1 shows a production well at Lario Oil & Gas Co and the surrounding acres of abandoned land. The main goal of this research was to turn this land around the production and injection wells into cotton fields.



Figure 5.1. Production Well and Surrounding Area of Lario Oil & Gas Company (Mid-Continent Region)

5.2 Methods

Most oil and gas companies use three-phase separators to remove oil and gas from produced water, remove high concentrations of dissolved oil, suspend semi-solid oil particle remains, and then dump the rest back into disposal wells. There is a limited number of produced water treatment technologies available at this time.

The filtration framework presented by this research is a one-of-a-kind method that combines water filtration strategies previously applied to wastewater as stand-alone treatment methods. New and advanced microporous ceramics and dissolved air flotation have been added to the sedimentation stage. The setup of the treatment provides an advantage to the system, allowing it to be useful and efficient. The flowchart of this process is shown in Figure 5.2.

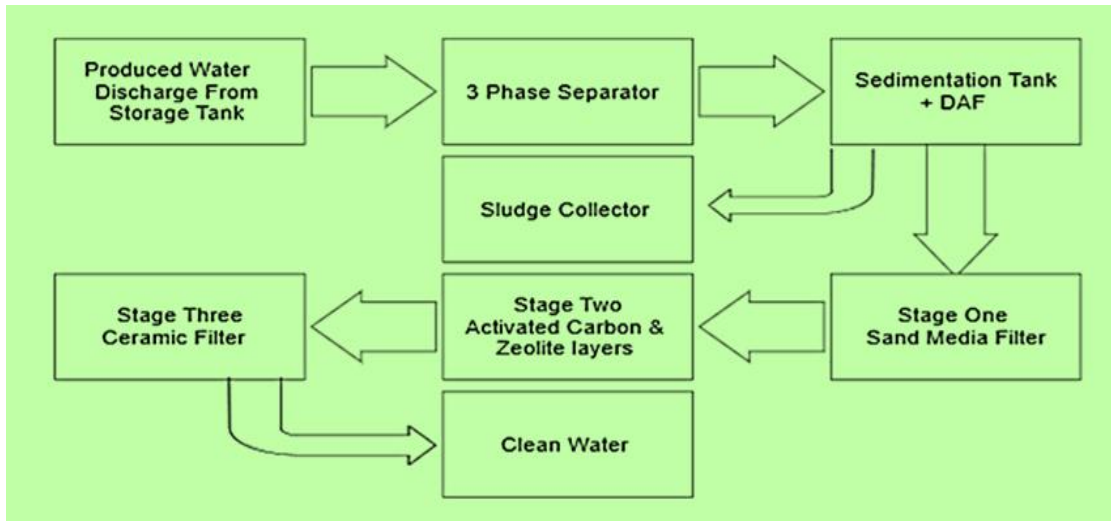


Figure 5.2. Process Flowchart

5.2.1 System Design Inspiration

The system architecture was inspired by the great mosque of Samarra situated on the banks of the Tigris River in Iraq, some 120 km north of Baghdad. This mosque was built in the ninth century and commissioned by the Abbasid caliph Al-Mutawakkil (shown in Figure 5.3), who fled to Samarra to move away from the overpopulated city of Baghdad. He lived there for 56 years [76].



Source: TimesTravel.com[76]

Figure 5.3. Samarra Tower, Iraq

5.2.2 Sedimentation Stage

The framework for the system consisted of a sedimentation tank (principle tower) and three-phase filtration rings joined around the outside of the tank. Produced water was released from sprinkler valves, located within one meter of the first-stage filtration ring, in order to expose the water droplets to more oxygen. The stages were set one meter apart on top of each other.

The tank was used for the purpose of having the sediment sink to the bottom as sludge, whereas oil droplets rose to the surface and were mechanically skimmed off. Settling velocity was based on the gravitational forces on the solid particles and fluid viscosity. Oil droplets flowed upwards to the surface, while the stirring and aeration operation continued for 4–6 hours. The method was implemented to speed up the process of oil/water separation by colliding oil droplets to create a larger size and rise to the surface faster. Sedimentation is a primary stage in wastewater treatment, and sediments collect for further sludge treatment, as shown in Figure 5.4.



Figure 5.4. Sludge Treatment Furnace at Wichita Wastewater Facility

Sedimentation is a physical separation based on gravity, and in this research, it was enhanced with the aid of mechanical stirring and dissolved air flotation. It is comprised of a cylindrical type tank configuration with a cone-shaped bottom to contain the sediment known as sludge. Figure 5.5 illustrates the key elements of the sedimentation and DAF tank. Water enters from the top and accumulates around the sedimentation tank in a reservoir after completing the three levels of filtration.

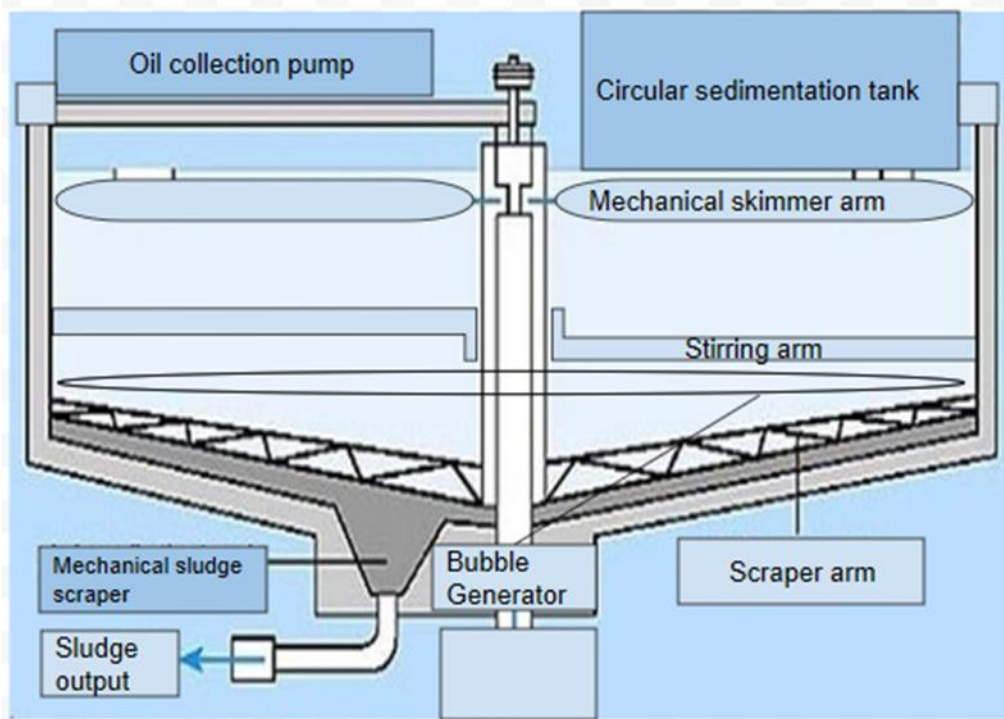


Figure 5.5. Sedimentation and DAF Tank

The tank's cylindrical form features a top inlet zone, which will lower the overflow rate so that the particles with a slower settling velocity can settle faster than the overflow limit. The overflow rate (m/s) is

$$V = Q / A \quad (5.1)$$

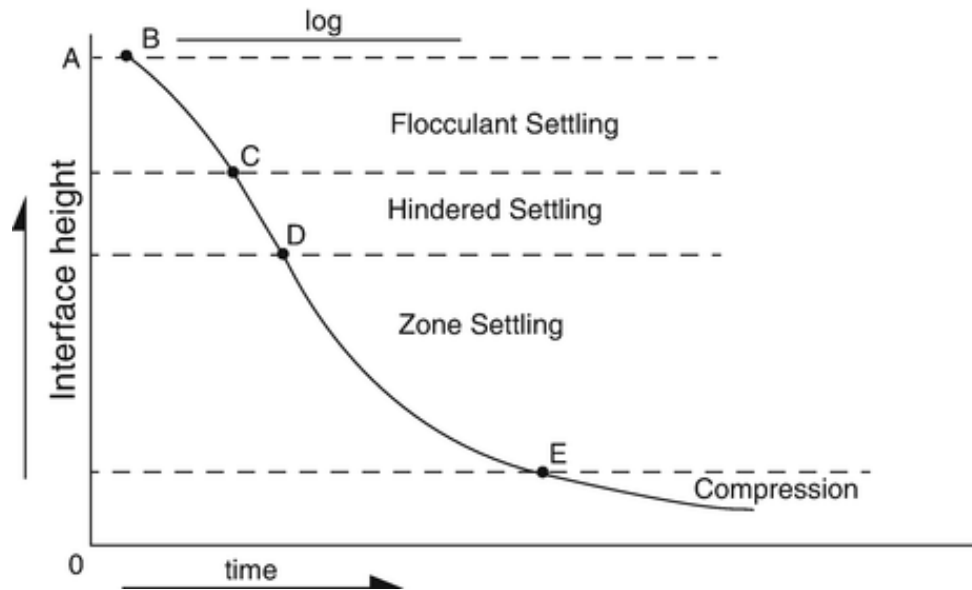
where V is the overflow rate is, Q is the flow of water (m^3/s), and A is the the surface area of the tank (m^2).

The settling time t (s) of solid particles is

$$t = \frac{d}{v} \quad (5.2)$$

where d is the diameter of the circular settling area, and v is the particle velocity.

When particle accumulation in suspension increases, a point is reached when the particles are so close together that they will no longer settle separately from each other. This results in a decreased rate of particle settling, an effect known as impeded settling [77]. Figure 5.6 shows the settling zones and settling velocities at each region of the sedimentation tank [78].



Source: Zone Settling and Compression, Alak De, 2017 [78]

Figure 5.6. Settling Speed

Water samples currently used for irrigation in the state of Kansas were analyzed to compare with the filtered produced water and the state standard parameters. The sedimentation or clarifying stage was accomplished by lowering the velocity of the water to a point at which suspended particles are no longer supported to be in suspension, and gravity removed the solid particles, forcing them to sink to the bottom. Produced water collected in the primary

sedimentation tank after going through a three-phase separator has an oil contamination percentage, on average, of 0.5–1.5 %. The sediments and DAF effects are shown in Figure 5.7.

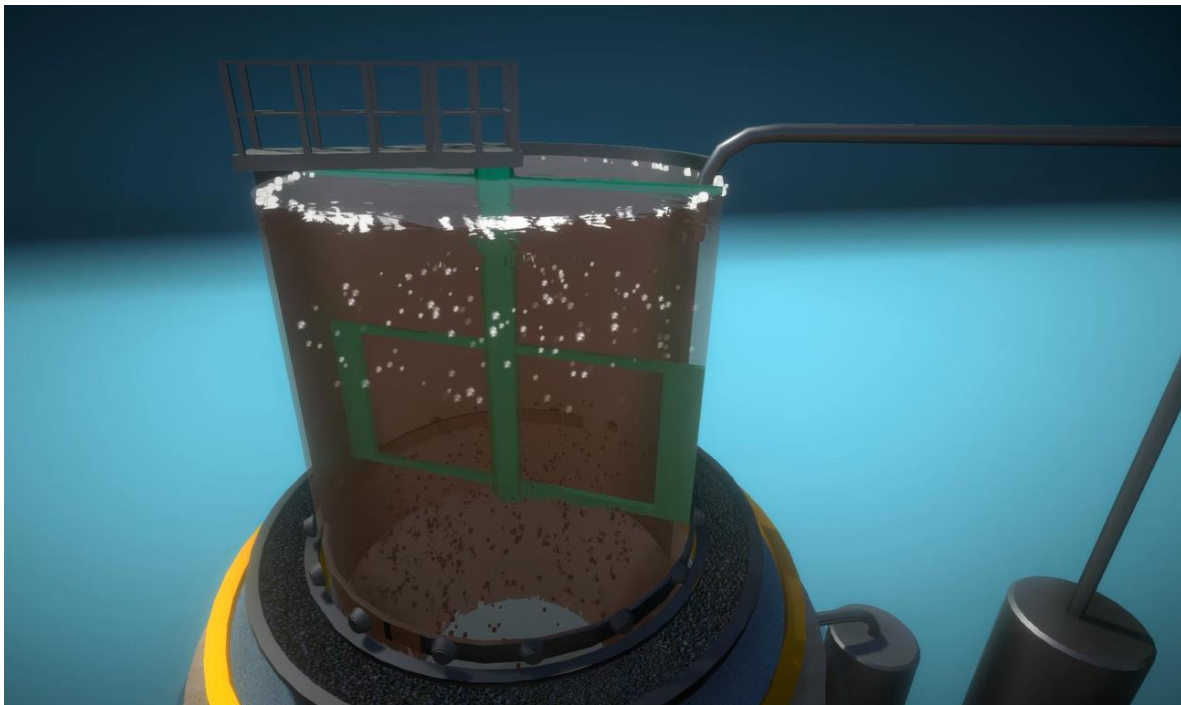


Figure 5.7. Sediments and DAF Effects

5.2.3 Three Stages of Filtration

The three-stage treatment system was designed to filter dissolved gas, suspended solids, bacteria, pollution, and concentrations of salt derived from water. In the first stage, the media filtration mainly uses sand and gravel layers as an efficient method of treating the produced water to eliminate the remaining small droplets of oil, grease, and total organic carbon. Water is released into the sand/gravel filter through the sprinkler valve to remove ferric (hydro) oxide particles with a high flow rate of 3–4 milliliters per centimeter squared per hour.

Some wastewater treatment facilities use this approach as a first step in treating sewage. A spinning sprinkler (shown in Figure 5.8) sprays water on the sand and gravel media surface, then gathers it from the bottom and transfers it for further application, depending on the method.

This research applied the same three-stage filtration process, with the advantages of area management and improved outcome. The water discharge method is shown in Figure 5.9.



Figure 5.8. First Stage of Filtration Process (Wichita Wastewater Facility)

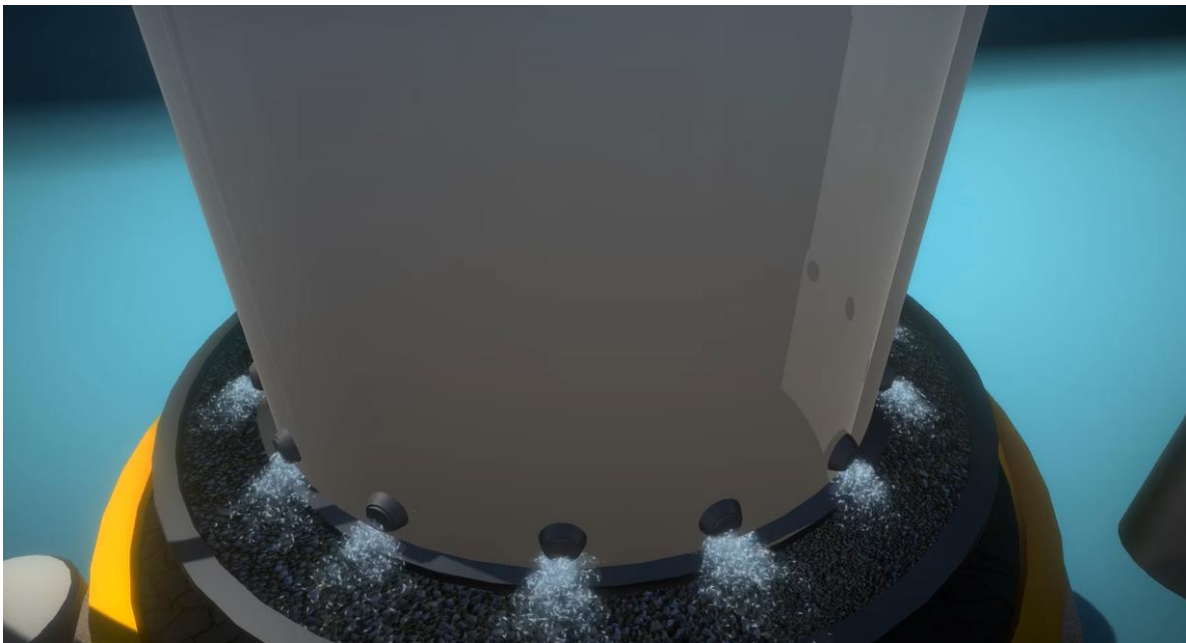


Figure 5.9. Water Discharge Method

The second stage of the filter system consists of activated layers of carbon and zeolite, which remove volatile organic compounds, minerals, salt, and inorganic dissolved substances. Particle sizes between 0.5 and 10 microns escape from the sand media filter and are removed by the zeolite layers. The micro-sized pore ceramic filters in the third stage contain 20% aluminum hydrate that acts as an acid neutralizer as well as reduces phosphate levels, and eliminates bacteria or any particles that passed through the previous filters. As Figure 5.10, reveals, during the water treatment process, the sludge deposited on the bottom of the sedimentation tank is collected in a separate container for further treatment.

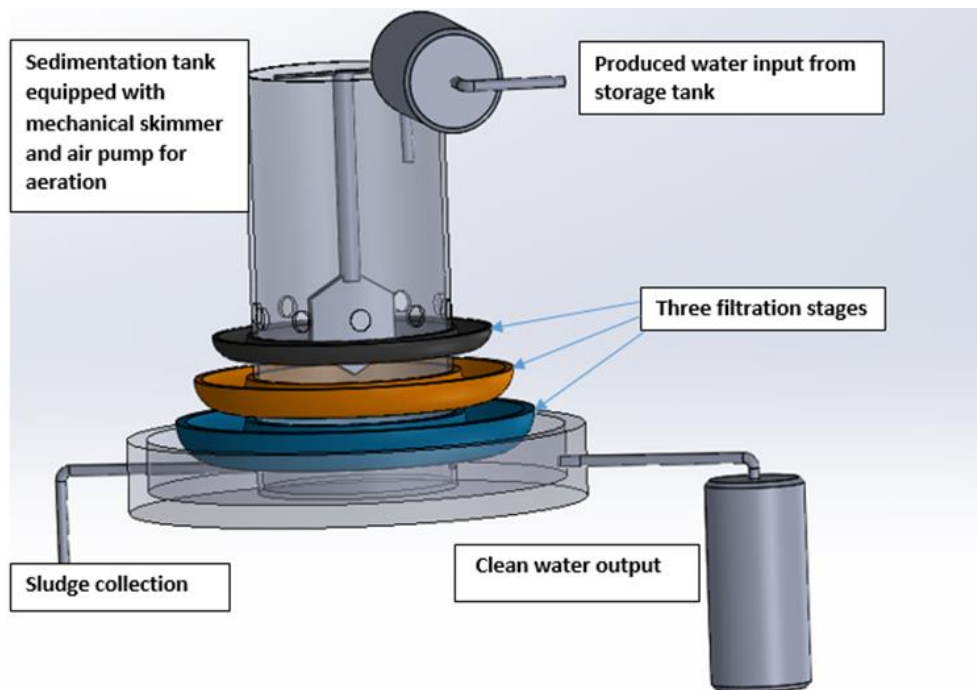


Figure 5.10. S-MAC System Design

5.3 First Stage

In stage one, the media filtration is highly efficient in removing oil; up to 95% of the grease is eliminated during this phase. If coagulants are added to the feed before the filtration, then efficiency can be further enhanced. In addition, there are layers of gradually decreasing sizes of gravel and sand. The filter thickness is 100–150 mm, determined based on Darcy's

equation (3.1). Droplets of water discharge from the 0.5-meter-high sprinklers and then pass through the media at an average flow rate of 0.5 liters per minute.

The Centers for Disease Control and Prevention (CDC) has published recommendations for safe water systems, in which the water level is stipulated to be at a height of 5–6 cm above the sand filter by placing a diffuser plate over the sand. This shallow layer of water gives way to the formation of another layer called the bioactive layer that grows on top of the filter, which contributes to the reduction of organisms that cause disease. Often, the diffuser plate is used to eliminate biolayer disturbance when applying water.

Studies of the effectiveness of the low-speed sand filter with a mature biolayer found 99.98% protozoan, 90–99% bacterial, and variable viral elimination. Studies on the productivity of fields have recorded elimination in the range of 80–98% [79]. The national standard related to water treatment, NSF/ANSI Standard 61, and American Water Works Association (AWWA) Standard B100-01 recommend the following: effective particle sizes of 2.0–2.5 mm, Moh's hardness of 7, uniform coefficient of 1.3–1.7, specific gravity of 2.67, and density of 1680–1850 kg/m³. Figure 5.11 shows the sand gravel media filter in stage one.



Figure 5.11. Stage One Setup

5.4 Second Stage

Adsorption is typically used as a polishing step in the treatment process rather than as a stand-alone method because organics can quickly dominate adsorbents. Adsorption is widely used in processed water to remove manganese, copper, TOC, oil, and more than 80% of heavy metals. Adsorbents, made of two layers of activated carbon and another two layers of zeolite, interact and are held by retaining fabric in stage two of the system. The method of adsorption is applicable to water treatment, regardless of salinity. The retaining material is designed to contain media for extracting particles captured in media voids. Media replacement or regeneration may be needed, depending on the nature of the supply water and the media lifespan. The media usage rate is one of the critical operating costs of adsorption technology, as blocked layers often lead to liquid waste disposal and material restoration outcomes in waste disposal management.

The adsorption method is based on the idea of excess current surface forces, whereby a rigid surface in contact with a liquid appears to produce a surface layer of solute molecules. It is closely related to the surface tension of solutions, and its strength depends on temperature, type, and concentration of the adsorbed material and the physical state of the adsorbent.

Zeolite was selected due to its unique properties relative to cation exchange capacity, surface adsorption, and structural water storage [80]. Table 5.2 shows the properties and chemical composition of zeolite.

Activated carbon is an efficient adsorbent because it is a highly porous substance that has a significant surface area for adsorption by chemicals. Granular activated carbon (GAC) and powdered activated carbon (PAC) are the two primary forms of activated carbon used in water treatment applications.

TABLE 5.2

ZEOLITE PROPERTIES AND CHEMICAL COMPOSITION

| Indices of properties ^a | | Chemical composition (%) | |
|------------------------------------|--------|--------------------------------|-------|
| pH | 7.8 | SiO ₂ | 66.05 |
| CEC (meq/100 g) | 136.35 | Al ₂ O ₃ | 12.11 |
| Exchangeable K (meq/100 g) | 7.12 | Na ₂ O | 2.12 |
| Exchangeable Na (meq/100 g) | 47.55 | CaO | 3.86 |
| Exchangeable Ca (meq/100 g) | 46.89 | K ₂ O | 1.10 |
| Exchangeable Mg (meq/100 g) | 0.54 | H ₂ O | 13.29 |
| Soluble Si (ppm) | 474.53 | MgO | 0.89 |
| Saturation water content (%) | 121.32 | MnO | 0.32 |
| Capillary water content (%) | 87.11 | P ₂ O ₅ | 0.17 |
| | | Fe ₂ O ₃ | 0.11 |

Source: CDC [80]

In this research, GAC was made from date seeds, an organic material with a high carbon content. Particle size diameter ranges between 1.0 and 1.7 mm and has an apparent density range between 320 and 400 kg/m³. The bed density is about 10% less than the apparent density and is used to determine the amount of GAC required to fill a given size filter. The GAC has a high uniformity coefficient, usually roughly 19, to facilitate post-backwashing stratification and mitigate desorption and premature breakthrough that may occur from combining activated carbon particles with zeolite particles with smaller quantities of adsorbed compounds. Iodine numbers and molasses usually describe the GAC. These numbers define the sum of small to large amounts of pores in a GAC sample. The AWWA guidelines require a minimum iodine amount of 500 for the activated carbon [81]. The setup of stage 2 is shown in Figure 5.12.

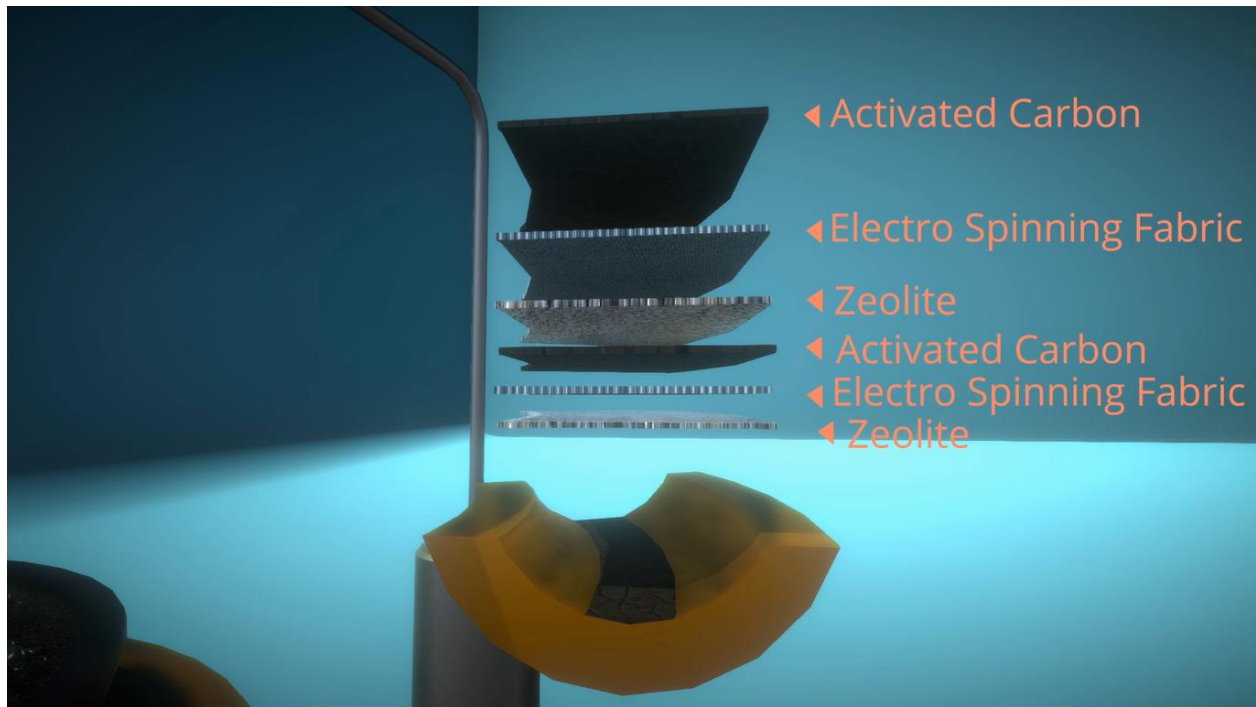


Figure 5.12. Stage Two of System

5.5 Third Stage

Microporous ceramic filters are used in the third stage because of their ability to extract suspended solids and almost all non-dissolved organic material. Ceramic filters have an estimated lifetime of ten years, with low maintenance costs. Regarding the thickness of the ceramic filter and the amount of sawdust, the flow rate was a key issue on the experiment scale. The depth of 10–12 mm and 55% sawdust was found to produce the best results, based on efficiency and a flow rate of 1.78 ml/cm² h.

5.6 Preparation of Filters

The dry clay mixed with sawdust and other materials was developed using an average percentage and average particle size to test their effects on the filtration of water quality and flow rate. More than 20 additives and formulations were tested during months of preparation to

determine the most appropriate class of ceramic filters for the treatment process. This study investigated the influence of firing temperature on the ceramic output, as shown in Figure 5.13.



Figure 5.13. Ceramic Samples (Wichita State University Ceramics Laboratory)

The ceramic mixing ratio was as follows:

- Sawdust, essential for the formation of ceramic pores, with an ideal configuration of 55% (55% of #30). The two main factors related to sawdust percentage in the ceramic process are the plasticity of the filter, and the material strength during firing and the solidification process. Changes in the filtration rate were based on the amount of sawdust, which showed a large effect on the quality of the filtered water.
- Aluminum hydrate, 5%, added as an acid neutralizer and to reduce phosphate levels in the filtered water.
- Flint/silica 325 mesh, 2% to help the ceramic material to fuse.
- Dolomite (calcium magnesium carbonate), 2% added as an acid neutralizer and source of magnesia.
- Petalite, 1%, to help making this a high-temperature resistance filter.
- Dry clay, 35%.

Wedging the clay after mixing removes the air bubbles, which may reduce the water filtration efficiency to a minimum. Thickness started at 20 mm and went down to an average of 10 mm. Air drying occurred for 24–48 hours, and then the clay was placed in an electric kiln/furnace programmed to increase the temperature slowly by about 100°C per hour (to allow the remaining moisture to evaporate) until reaching about 1200°C, start to finish in about 8–9 hours. Figure 5.14 shows samples that were subjected to a temperature range of 850–1200°C. The ceramic filter must be soaked in water after 2–3 hours of air cooling before use.



Figure 5.14. Ceramic Samples Subjected to Temperature Range of 850–1200°C

The firing process affects the porous ceramics, because water evaporates and no longer keeps the clay molecules together. The process of sintering at 700–890°C starts to form the ceramic substance that produces hard ceramics as the crystals start bonding. At this stage, the ceramic becomes highly porous, leaving burnt carbon particles stuck in the pores between the ceramic molecule, as shown previously in Figure 5.14.

5.7 Activated Carbon Preparation

Activated carbon is currently used in many applications, including filtration of drinking water, food processing, the prevention of emissions, and the elimination of odor. Activated carbon comes from charcoal, wood, date nuts, coconuts, and nutshells.

Date seeds and olive seeds were the products used in this research for preparing activated carbon, and zinc chloride (ZnCl_2) as activation reagents. At room temperature, the seeds were washed and dried for 24 hours, then crushed and sieved to particles 3–4 mm in diameter. ZnCl_2 impregnated with chemical agents was used for activation. The 25% ZnCl_2 solution was prepared using 15 g of deionized (DI) water and 5 g of ZnCl_2 . Once the mixture was packed, 20 g of date/olive seeds were impregnated with 20 g of the ZnCl_2 solution and stirred on a magnetic hotplate stirrer at 85°C for 2 hours. Then, the saturated solution was dehydrated in an oven for 24 hours at 110°C , followed by 60 minutes at 800°C after activation. After refrigerating the activated carbon, the seeds were washed and filtered at 90°C for 30 minutes with a 3M HCl solution. Then the carbon was rinsed with DI water until the solution's pH was nearly 7. A rinsing cycle with 1M NaOH was used to neutralize the influence of the concentrated HCl, taking the solution of carbon to a pH of 6.7–7. The activated carbon was then filtered out and dried in an oven at 120°C for 12 hours. Multiple types of activated carbon are shown in Figure 5.15.



Figure 5.15. Multiple Types of Activated Carbon Prepared at WSU Laboratory

5.8 Samples Preparation for ICP-OES Testing

Produced water samples were prepared for testing using the Varian 710-ES optical emission spectrometer, as shown in Figure 5.16. A standard surface water solution was used as reference. Samples were acidified with HNO_3 and HCl , and cooked in an oven for 8 hours, in compliance with ASTM Standards D1976 and D3919. After digestion they were filtered to avoid degradation of the particulate or colloidal content that may be present in the sample. Upon filtration, the samples were ready for evaluation by flammable atomic absorption spectroscopy, graphite furnace atomic absorption spectroscopy, plasma emission spectroscopy, or plasma mass spectrometry (ASTM Standards 1970-16).



Figure 5.16. Varian 710-ES Optical Emission Spectrometer Testing System

The process to prepare the samples is as follows:

1. Add 4 mL of HNO_3 per liter of sample.
2. Add 1.0 mL of concentrated HCl for each 50 mL of sample.
3. Shake the samples to mix the contents, and then put them into the oven at 65°C for 8 hours.

4. Allow the samples to cool to room temperature before filtration.
5. Collect the samples using paper funnels.

5.9 Water Parameters Testing

Testing for standard parameters (pH, conductivity, hardness, turbidity, and TDS) was conducted with an Apera instrument, model PC60-Z from Zen testing, as shown in Figure 5.17.



Figure 5.17. Apera Testing Instrument

5.10 System Technical Specifications

If a 10-meter-diameter and 10-meter-high cylindrical type sedimentation tank was selected, then the capacity would be 785.4 m^3 , would hold 207,480 gallons of water (4,149 barrels), and have an inlet pipe 8 inches in diameter. The flowrate was estimated to be in the range of 313–350 gal/min, with a water rotating speed of 1.5–2 ft/sec. The Hazen-Williams equation for flow rate and pipe diameter is

$$v = 0.408 q/d^2 \quad (5.1)$$

where v is the water velocity, q is the flow rate, and d is the pipe diameter.

Based on the calculation, the tank would fill in 10–11 hours, and it would take 8 hours of sedimentation and 16 hours of filtration stages to filtrate. Based on these specifications mentioned, the S-MAC system can treat 130,000 gallons (2,738 barrels) of water in 36 hours. The laboratory model of the system, shown in Figure 5.18, reported that the $1.7 \text{ mL/cm}^2 \cdot \text{s}$ flow rate and water parameters match Kansas standards.

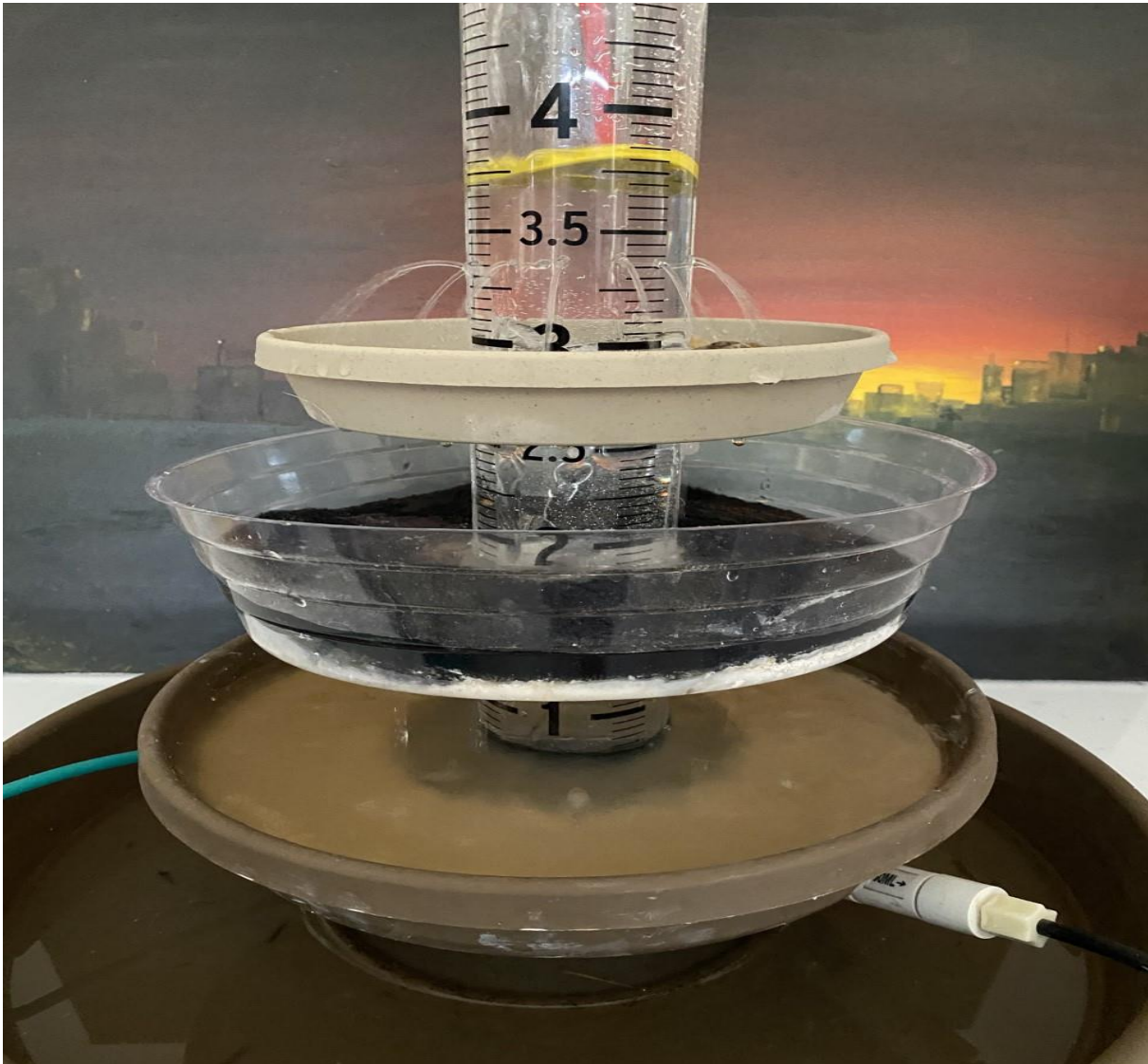


Figure 5.18. S-MAC System Laboratory Model

CHAPTER 6

RESULTS AND DISCUSSION

6.1 Inductively Coupled Plasma Optical Emissions Spectroscopy Test

Produced water samples obtained from the Lario Oil & Gas Company, Kansas, were tested using ICP-OES. The results are valid to the specific area mentioned since produced water is a complex blend of organic and inorganic materials [82]. Produced water's physical as well as chemical characteristics vary from one region to another, depending upon the geographical location of the oil and gas field, the characteristics of the reservoir, and the type of oil production [83]. Other varying factors include the season, well temperature, and depth in the same region. As a result, the produced water's configuration and element percentage highly fluctuate.

Testing of the Arkansas River samples, and groundwater samples obtained from a variety of different locations over the period of time between July 2018 and February 2020 was performed with ICP-OES. The provided produced water samples before and after treatment were also tested. The latest results of ICP-OES testing on water samples were carried out on February 24, 2020.

The mean concentrations of the elements in groundwater, surface water, and water produced before and after treatment were used to assess the efficacy of the system as opposed to the state requirements, taking the standard deviation (SD) to confirm outcome. Table 6.1 displays 23 elements and their typical wavelengths and concentrations (in ppb) recorded over the span of the last two years, relative to the average groundwater and surface water parameters (S/G) and Kansas state standards (limits).

TABLE 6.1

SELECTED KANSAS WATER ELEMENTS AND PRODUCED WATER
BEFORE AND AFTER TREATMENT

| Element | PW (ppb) | Kansas S/G (ppb) | Treated PW (ppb) | PW SD | Limits |
|----------------|---------------------|-----------------------------|-----------------------------|--------------|---------------|
| Ca 396.847 | 5,346,676 | 1,891,316 | 1,001,137 | 54,400 | <1,000,000 |
| Mg 279.553 | 324,526 | 149,669 | 153,126 | 13,450 | <150,000 |
| Na 589.592 | 310,610 | 239,464 | 186,010 | 24,765 | <200,000 |
| K 766.491 | 36,920 | 32,204 | 17,678 | 1,874 | <25,000 |
| B 249.772 | 801 | 222.3 | 195.4 | 12.33 | 100-200 |
| Fe 238.204 | 130.25 | 121.41 | 86.03 | 8.27 | 10-100 |
| Mo 202.032 | 23.32 | 19.73 | 4.43 | 1.54 | 10-100 |
| Sr 407.771 | 40,872 | 28,676 | 36,726 | 3,036 | <200,000 |
| As 188.980 | 2.49 | 2.26 | 1.16 | 0.45 | <5 |
| Ba 455.403 | 9,552 | 3,849 | 5,146 | 528 | <6,000 |
| Ni 231.604 | 7.22 | 4.57 | 4.12 | 0.90 | <2 |
| V 292.401 | 37.15 | 15.74 | 10.12 | 1.54 | <100 |
| Zn 213.857 | 17.31 | 11.95 | 9.02 | 1.04 | <10 |
| Mn 257.610 | 398 | 185.8 | 209 | 12.7 | 1-200 |
| Co 238.892 | 19.37 | 7.68 | 6.95 | 1.26 | <5 |
| Pb 220.353 | 15.38 | 4.70 | 4.49 | 0.55 | <15 |
| Be 313.042 | 239.69 | 1296 | 257.1 | 13.41 | 100-300 |
| Cd 214.439 | 3.07 | 1.69 | 2.80 | 0.67 | <10 |
| Cu 327.395 | 108.78 | 72.58 | 78.8 | 4.28 | 20-75 |
| Cr 267.716 | 15.54 | 6.79 | 6.28 | 0.86 | 100-200 |
| Bi 223.061 | 1.29 | 0.05 | 0.12 | 0.67 | <1 |
| Se 196.026 | 2.04 | 0.47 | 1.75 | 0.30 | <10 |
| Tl 190.794 | 33.83 | 22.23 | 21.76 | 2.39 | 20-24 |

The elements of treated produced water were found to be equal to or to have surpassed the consistency of an average standard element concentration found in water currently used for agriculture, and they surpassed the surface and groundwater consistency of Kansas. The error bar shown in Figure 6.1 indicates that, based on the results of the ICP-OES relative to element intensity, the averages are consistent. The standard deviations of the samples are close to the mean values.

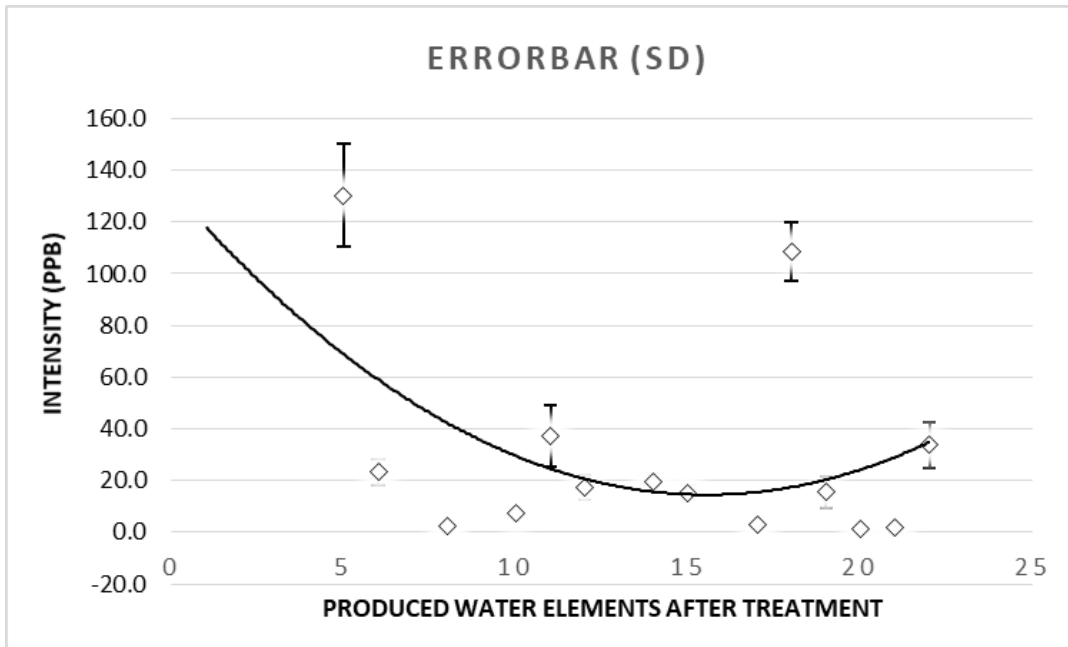


Figure 6.1. Error Bar of Treated PW Elements

6.2 Toxic Substances

Concentrations of elements such as aluminum, sulfur, cadmium, chromium, mercury, cobalt, copper, iron, lead, manganese, nickel, and zinc are normally found in produced water. One study suggested that the toxicity of these elements increases over time, after discharging the produced water. Experiments conducted by a group of researchers using the Microtox test showed a sustained toxic response for more than a week after the oxidation of the newly discharged produced water, which initially showed little or no toxic response [84].

Results of the ICP-OES test show that the concentration of toxic elements in the provided treated water is within acceptable limits, and that after the treatment process, no further oxidation was observed, and the parameter of the filtered water was stable even after one week of filtration. Figure 6.2 shows zinc concentrations decreasing after treatment. The concentration of zinc was 15.5–18.65 ppb prior to treatment and 8.97–9.15 ppb after treatment, which is below the average groundwater level of Kansas and within the state limits. Lead averages were 4.5 ppb, and the

appropriate state limit is up to 15 ppb. Sulfur was not found in a detectable level in the water samples.

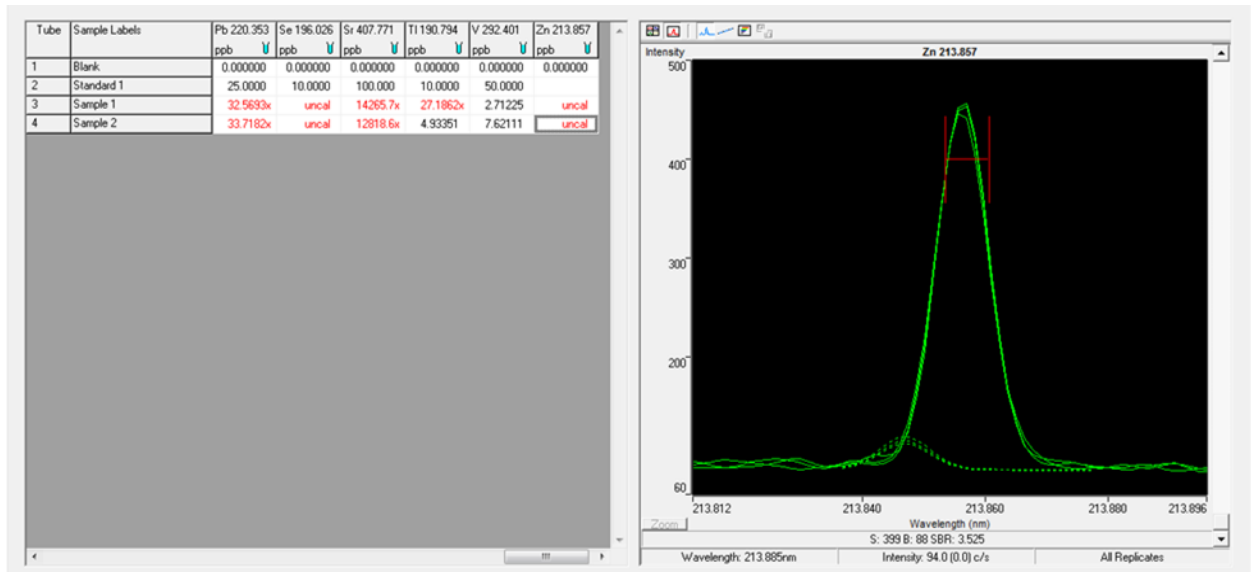


Figure 6.2. Zinc Concentrations (ICP-OES)

6.3 Organic Elements

In general, the amounts of organic compounds in produced water are significantly higher than in other natural waters, exceeding the acetate content of ~10,000 mg/l. The maximum concentrations are present at temperatures of 80–120° C in produced water. At lower temperatures, concentrations usually decrease predominantly due to bacterial degradation and at higher temperatures decrease due to thermal decarboxylation[85]. However, even if all oil droplets are eliminated in the oilfield-produced water, a significant amount of organic compounds, such as acetic acid, propionic acid, and valeric acid, are dissolved in the oilfield-produced water. These organic compounds produce bad smells and environmental harm, so step two of the current filtration method is allocated for extracting organic compounds. Direct contact of the solid adsorbent with the produced water will adsorb and extract the dissolved organic

content in this treatment system, thus eliminating dissolved organic compounds from the produced water.

6.4 Sedimentation Process Analysis

Physical, biological, and chemical water quality parameters can be divided into three classes. The first class is physical properties such as turbidity, color, taste, odor, total dissolved solids, total suspended solids, and electrical conductivity. The second class is chemical properties, such as pH, acidity, alkalinity, residual chlorine, DO for chemical oxygen demand, and radioactive and organic/inorganic toxic substances. The third class is biological properties like bacteria, algae, viruses, protozoa, etc. [86].

Throughout this study, the aim was to optimize certain properties that can boost the quality of water at each treatment stage. Aeration and stirring accelerate the process throughout the sedimentation and DAF, which introduces oxygen into water that has been stored for thousands of years underground. Aeration increases the amount of oxygen in the water and speeds up the process of separating the oil, by allowing oil droplets to rise at a faster rate to the surface of the tank. On the other hand, it is important to stir while the air bubbles rise, so that smaller oil droplets can collide with each other or with smaller diameter particles, and then float to the top to be skimmed.

After eight hours in the sedimentation tank, as shown in Figure 6.3, water parameters such as turbidity improved up to 70%, from nearly 100 NTU to 28–35 NTU, and oil percentages decreased by 70–80%, The electrical conductivity dropped by 10–15%, and total solids were suspended by 25–30%.



Figure 6.3. Gravity Sedimentation (4–10 hours)

The settling velocity observed was 5–8 hours relying on the model, but the settling period was shortened by up to 40% with the DAF and stirring system. Figure 6.4 displays variations in the oil content at the time of water being discharged from the wellhead to the separation tank and after eight hours of sedimentation.

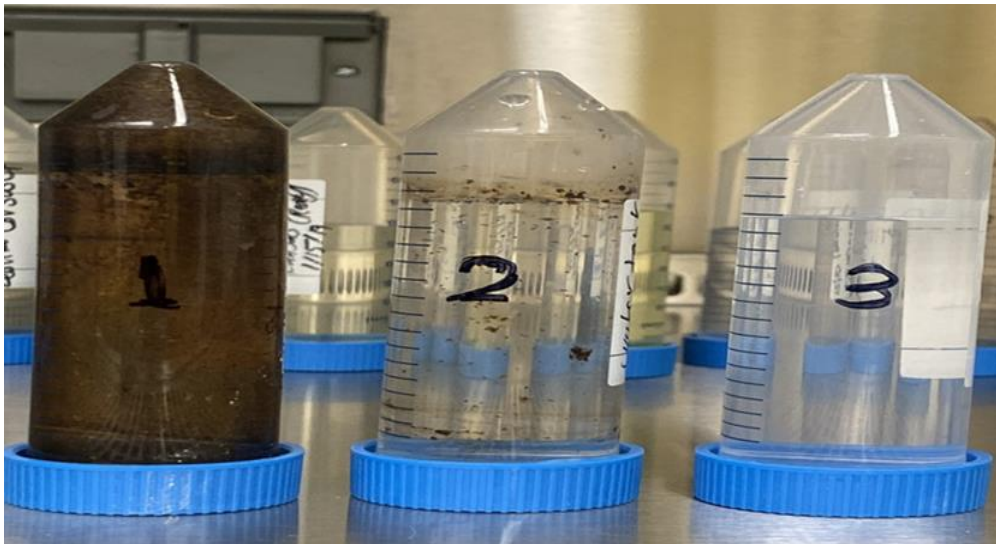


Figure 6.4. Variations in Oil Content: (1) Produced Water Samples, (2) Wellhead Separation Tank, and (3) Sedimentation Tank

6.5 Activated Carbon Surface Analysis

Following a study of the physical and chemical adsorption of the activated carbon surface, it was discovered that the particle accumulation was due to chemical forces (van der Waals forces) as the result of electron exchange. For each gram of date seed-based carbon activated with zinc chloride (ZnCl_2), the pore volume per cm^3 was greater than the dateseed-based carbon activated with calcium chloride (CaCl_2), as shown in Figure 6.5.

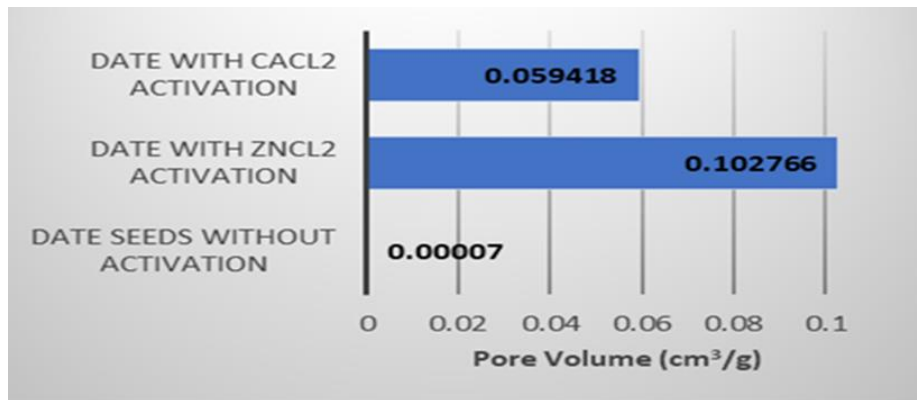


Figure 6.5. Pore Volume of Activated Carbon ZnCl_2 vs. CaCl_2

The surface area decreased as the number of pores decreased. Zinc chloride-activated carbon has the largest pore depth, measuring $0.1 \text{ cm}^3/\text{g}$, and diameter of $30\text{--}60 \mu\text{M}$. Scanning electron microscopy (SEM) images of the activated carbon surface area are shown in Figure 6.6. Zinc chloride activation produced 32 times the surface area of a char without activation and nearly 7.5 times the surface area of calcium chloride with activation.

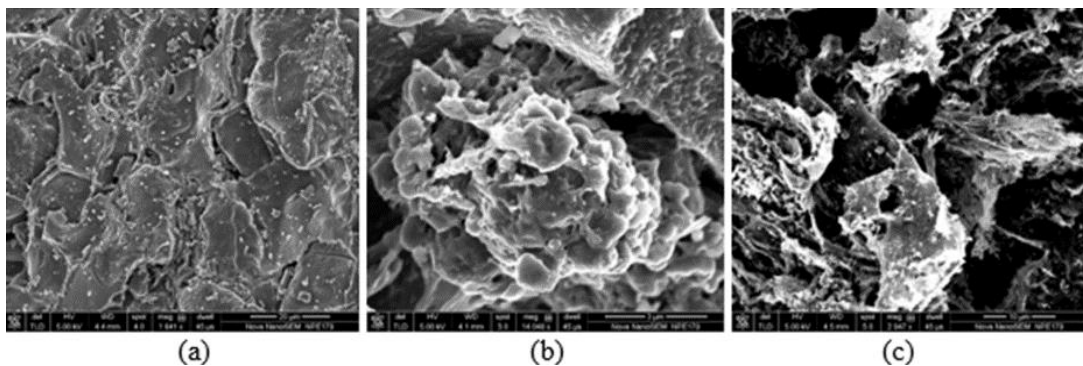


Figure 6.6. SEM Images: (a) No Activation, (b) ZnCl_2 Activated, and (c) CaCl_2 Activated

6.6 Ceramic Filter Analysis

Ceramic filter analysis was used to analyze the surface property and porosity, using scanning electron microscopy, as shown in Figure 6.7. The sum of pores per unit of surface was obtained, as shown in the illustration of each side. Previous studies have analyzed the perimeters and shape of the pore together along with its diameter. Pore size and density tests were used to measure the water flow rate of the ceramic filter according to the thickness and carbon percentage.

The percentage of sawdust was studied to determine its effect on the properties of the filter such as pressure, porosity, permeability, and plasticity. Key factors related to the percentage of sawdust during this process are the plasticity of the clay and the strength of the filter after firing during the solidification process. Changes in the filtration rate are based on the percentage of sawdust. Figure 6.7 shows three samples with thicknesses of 10, 15, and 20 mm and 55% sawdust [87].



Figure 6.7. Ceramic Filter Surface with 55% Sawdust

Aluminum hydrate in the amount of 5% was applied to neutralize the acid and to reduce the levels of phosphate in the filtered water. Two percent of dolomite (calcium magnesium carbonate) was used for acid neutralization and as a magnesium source.

The ceramic's physical properties were analyzed at 50%, 55%, and 60% of sawdust composite material. After being fired in a kiln, the sawdust transforms into the pores and deposits carbon at 25%, 30%, and 35 %, respectively, in the ceramic filter. The carbon content of this filter was determined based on permeability and consistency of the water. The 50% sawdust ceramic composite contained porosities $> 25\%$ with a small number of pores filled with carbon deposits. Figure 6.8 shows the relation between the percentage of sawdust in the ceramic filter and its impact on the rate of flow. Research found that 55–60% sawdust provided an average of 0.85–0.95 liters per hour, a stable ceramic structure, and a total coliform reduction of 98%.

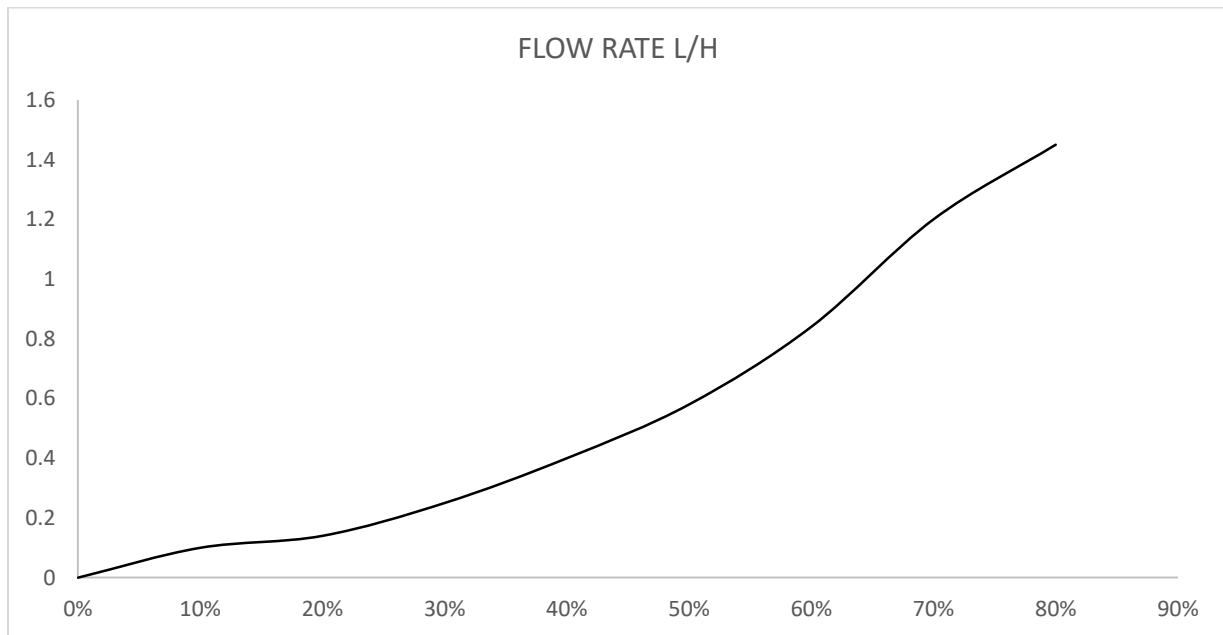


Figure 6.8. Flow Rate vs. Percent of Sawdust

Given the carbon deposition, composite material porosities were much lower than that of the 55% sawdust content. This experiment showed that the best outcome is with a 55% presence

of sawdust, indicating a high percentage of pores filled with carbon deposits of a 50-micrometer diameter, high specific surface area, and high flow rate [88], as shown in Figure 6.9.

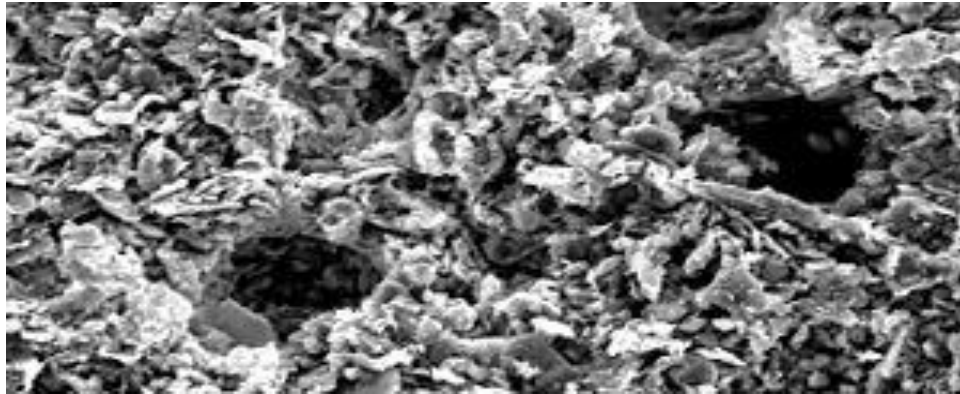


Figure 6.9. SEM Image of Ceramic with 55% Sawdust

6.7 Water Standard Parameters

This research began by evaluating the initial produced water quality generated and the elements after it was discharged from a three-phase separator. This was done to determine the feasibility of introducing a treatment system and to improve the quality to suit other Kansas water supplies. Based on the results of the ICP-OES study, the research found a small percentage of toxic elements at a manageable level, as shown in Figure 6.10.

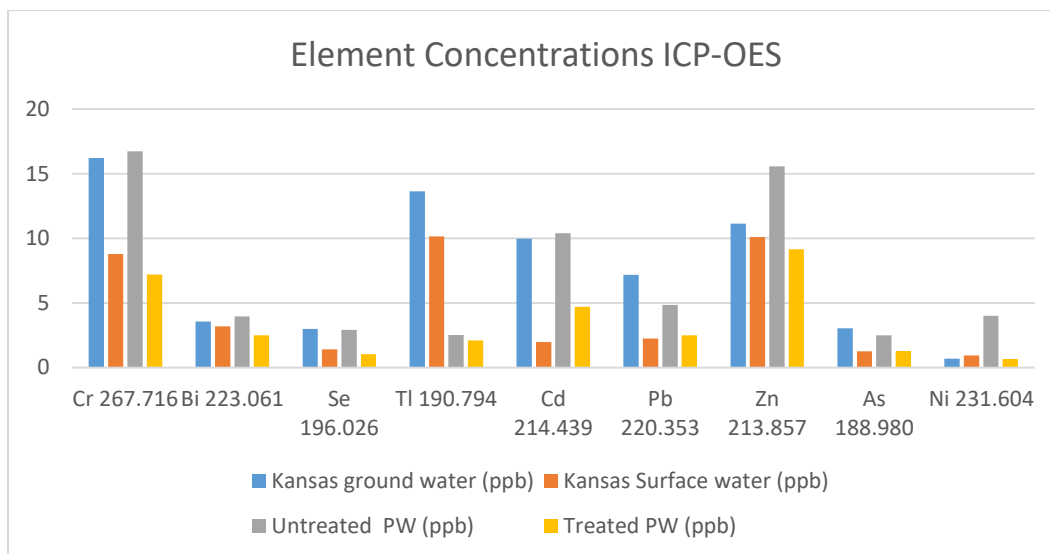


Figure 6.10. Kansas Water Resources vs. Produced Water Before and After Treatment

Surface water samples collected from different locations around Sedgwick County (2018–2020) showed high concentrations of salt elements and iron. The intensities of Na, Mg, K, Ca, and Fe in parts per billion (ppb), in comparison to standard solutions of six different concentrations, were selected for finding the mean of all samples, as shown in Table 6.2.

TABLE 6.2

ELEMENTS OF WATER SALINITY INTENSITIES IN PARTS PER BILLION

| Element | Blank | Standard 1 | Standard 2 | Standard 3 | Standard 4 | Standard 5 |
|----------------|------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Na | 2,398 | 32,977 | 128,360 | 303,930 | 411,057 | 584,053 |
| Mg | 47 | 54,388 | 146,082 | 241,312 | 306,645 | 216,741 |
| K | 247 | 9,059 | 35,086 | 57,887 | 92,545 | 129,756 |
| Ca | 1,891,316 | 1,133,914 | 1,201,680 | 120,0475 | 1,276,006 | 1,909,775 |
| Fe | 3.42 | 85.53 | 256.96 | 570.37 | 878.55 | 1201.9 |
| Element | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
| Na | 239,464 | 133,467 | 207,246 | 292,855 | 134,547 | 125,034 |
| Mg | 149,669 | 155,596 | 165,747 | 127,530 | 150,453 | 164,240 |
| K | 32,204 | 45,741 | 10,404 | 18,004 | 40,095 | 49,550 |
| Ca | 2840413 | 3,133,914 | 3,201,680 | 3,200,475 | 3,276,006 | 2,909,775 |
| Fe | 121.41 | 115.22 | 93.92 | 64.77 | 202.33 | 124.15 |
| Element | Sample 7 | Sample 8 | Sample 9 | Sample 10 | Sample 11 | Sample 12 |
| Na | 124,224 | 180,185 | 139,412 | 145,915 | 141,346 | 149,048 |
| Mg | 120,103 | 146,601 | 162,398 | 166,738 | 161,984 | 157,096 |
| K | 32,082 | 38,445 | 31,478 | 30,355 | 36,661 | 33,814 |
| Ca | 2,058,302 | 3,440,390 | 2,984,428 | 3,178,786 | 3,126,725 | 3,811,776 |
| Fe | 94.71 | 135.76 | 93.28 | 104.63 | 146.73 | 148.33 |
| Element | Sample 13 | Sample 14 | Sample 15 | Sample 16 | Sample 17 | Sample 18 |
| Na | 204,173 | 165,917 | 211,015 | 352,783 | 154,468 | 153,919 |
| Mg | 900,690 | 187,350 | 102,540 | 937,324 | 988,499 | 116,967 |
| K | 31,303 | 30,801 | 18,589 | 10,154 | 11,499 | 17,922 |
| Ca | 1,841,066 | 1,842,569 | 1,955,244 | 1,746,459 | 1,935,969 | 1,837,408 |
| Fe | 112.00 | 138.00 | 127.36 | 111.40 | 124.80 | 97.86 |
| Element | Sample 19 | Sample 20 | Sample 21 | Sample 22 | Sample 23 | Sample 24 |
| Na | 164,563 | 193,037 | 178,854 | 174,212 | 176364 | 161,015 |
| Mg | 147,223 | 153,081 | 141,905 | 114,463 | 951037 | 132,541 |
| K | 36,323 | 35,413 | 40,628 | 51,005 | 35161 | 32,110 |
| Ca | 2,128,952 | 2,129,730 | 1,498,159 | 1,527,839 | 250297 | 1,550,480 |
| Fe | 105.10 | 127.50 | 115.90 | 125.90 | 127.20 | 107.34 |

This study examined the standard elements that exist in the irrigation sources used in the state of Kansas for cotton farming. Concentration variability is due to the time of year, temperature difference, and areas where the samples were collected. Figure 6.11 shows the concentrations of Na, Mg, K, Ca, and Fe in surface water samples.

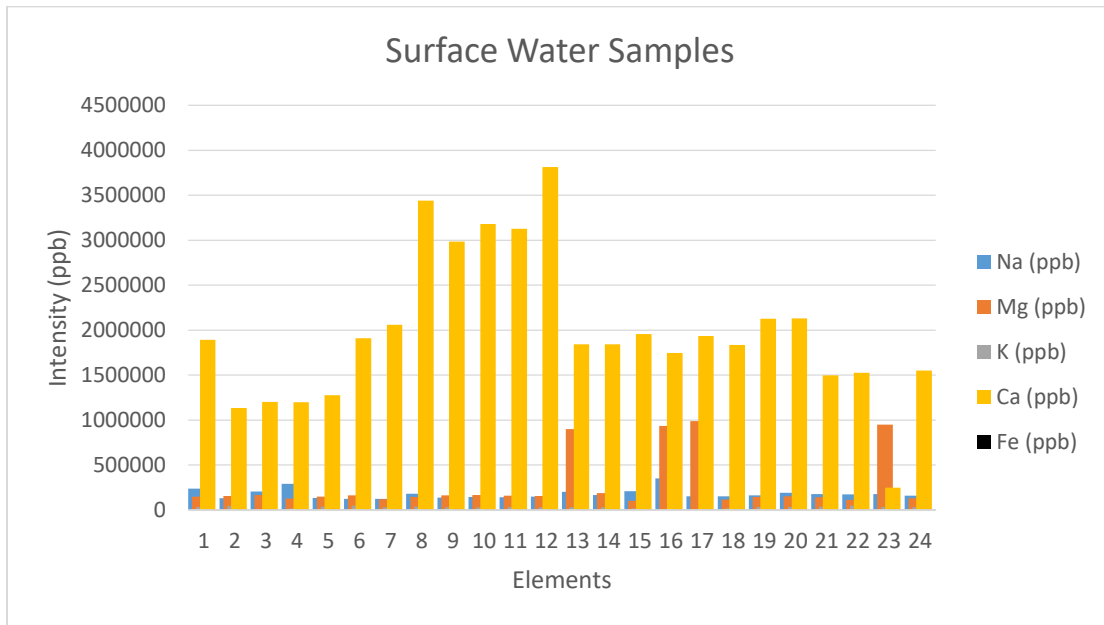


Figure 6.11. Surface Water Samples

Testing for standard water parameters (pH, conductivity, TDS, hardness, and turbidity) pre- and post-treatment was carried out at the Meridian Water Testing Laboratory, a reputable test facility in the state of Kansas that is used by the Wichita Water Department. Results are shown in Table 6.3.

TABLE 6.3

PRODUCED WATER PARAMETERS BEFORE AND AFTER TREATMENT

| Parameter | Treated PW | Untreated PW |
|----------------------|------------|--------------|
| pH (S.U) | 6.67 | 6.02 |
| Conductivity (µS/cm) | 2,090 | 2,140 |
| TDS (mg/l) | 1,350 | 1,370 |
| Hardness (mg/l) | 31,500 | 47,500 |
| Turbidity (NTU) | 20 | 90 |

Water samples were obtained in downtown Wichita from the Arkansas River. Well water used for cotton irrigation in Derby and Hutchinson fields in January 2019, August 2019, and January 2020 was also used for testing. Appendix A shows testing data. The averages of the testing parameters are shown in Table 6.4 and are compared to produced water before and after treatment. Table 6.5 shows the results of testing done for standard water parameters (pH, TDS, turbidity, conductivity, hardness, and DO) over a range of two years from the Arkansas River, Derby groundwater (GW), Hutchinson surface water (SW), and Wichita lakes (SW).

TABLE 6.4

KANSAS SURFACE AND GROUNDWATER PARAMETERS

| Parameter | Treated PW | Untreated PW | Kansas Irrigation Water | Recommended Level for Irrigation |
|----------------------|-------------------|---------------------|--------------------------------|---|
| pH | 6.5–6.7 | 4.4–6.02 | 6.5 –8.72 | 5–7 |
| Conductivity (µS/cm) | 2,050–2,100 | 2,100–2,400 | 1,540–6,010 | 1,500– 3,000 |
| TDS (ppm) | 1,340– 1,380 | 1,370–1,460 | 1,160–4,460 | 500–2,000 |
| Hardness (ppm) | 31.5–39.5 | 47.5–80 | 26–76 | 30–60 |
| Turbidity (NTU) | 15–25 | 80–90 | 1.21–18.96 | 2–20 |

TABLE 6.5

PARAMETERS OF WATER SAMPLES COLLECTED FROM 2018 TO 2020

| Date | Arkansas River | pH | TDS (ppm) | Turbidity (NTU) | Conductivity (µS/cm) | Hardness (ppm) | DO (mg/L) |
|-------------|-----------------------|-----------|------------------|------------------------|-----------------------------|-----------------------|------------------|
| 11/18/18 | | 8.7 | 1,860 | 12 | 2,500 | 34 | 6.3 |
| 1/7/19 | | 8.7 | 2,200 | 18 | 3,090 | 42 | 6.4 |
| 8/18/19 | | 8.6 | 3,890 | 19 | 4,000 | 59 | 6.2 |
| 10/2/19 | | 8.5 | 2,700 | 16 | 3,100 | 40 | 6.5 |
| 1/18/20 | | 8.1 | 1,950 | 10 | 3,050 | 36 | 6.5 |
| Date | Derby, KS (GW) | pH | TDS (ppm) | Turbidity (NTU) | Conductivity (µS/cm) | Hardness (ppm) | DO (mg/L) |
| 12/5/19 | | 4.6 | 3,950 | 10 | 1850 | 72 | 5.3 |
| 3/24/19 | | 5.3 | 3,100 | 9.4 | 1860 | 64 | 4.8 |
| 7/26/19 | | 4.5 | 4,400 | 10 | 2200 | 70 | 5.3 |
| 10/23/19 | | 5.9 | 3,800 | 9.8 | 2150 | 58 | 6.4 |
| 1/11/20 | | 5.5 | 3,200 | 9.6 | 1970 | 60 | 6.3 |

TABLE 6.5 (continued)

| Date | Hutchinson (SW) | pH | TDS (ppm) | Turbidity (NTU) | Conductivity (μS/cm) | Hardness (ppm) | DO (mg/L) |
|----------|--------------------|-----|-----------|-----------------|----------------------|----------------|-----------|
| 12/26/18 | | 7 | 2,500 | 8.7 | 1,340 | 27 | 6.5 |
| 2/3/19 | | 7.2 | 2,200 | 8.9 | 1,420 | 28 | 6.5 |
| 6/15/19 | | 6.8 | 2,600 | 8 | 1,390 | 27 | 6.4 |
| 9/22/19 | | 7.5 | 2,100 | 8.7 | 1,400 | 23 | 6.5 |
| 1/4/20 | | 7 | 2,200 | 8.7 | 1,410 | 26 | 6.4 |
| Date | Wichita Lakes (SW) | pH | TDS (ppm) | Turbidity (NTU) | Conductivity (μS/cm) | Hardness (ppm) | DO (mg/L) |
| 11/18/18 | | 7.4 | 2,350 | 11 | 1,290 | 24 | 5.9 |
| 1/7/19 | | 7.9 | 2,340 | 11 | 1,288 | 24 | 5.7 |
| 8/18/19 | | 6.8 | 2,780 | 12 | 1,367 | 25 | 5.5 |
| 10/2/19 | | 7.2 | 2,430 | 11 | 1,255 | 23 | 5.6 |
| 2/20/20 | | 7.9 | 2,170 | 10 | 1195 | 22 | 5.7 |

6.7.1 pH Level

The pH is a measure of the acidic nature of a solution. The amount of hydrogen ions [H⁺], i.e., percentage in a solution, determines the pH level in water. Mathematically this is expressed as [89]

$$\text{pH} = -\log [\text{H}^+] \quad (6.1)$$

The pH of surface water in Kansas is typically within the range 6.0–9.0. The potassium concentration of surface water is typically within the range 5–12 mg/L in southwest Kansas. The linear regression of potassium and precise conductance is important (at the 99% level) and thus indicates a relationship between potassium content and salinity. The determination coefficient is small; however, it suggests that other elements have a more powerful impact in the manipulation of variation in potassium concentration than those regulating the salinity of the river water.

The concentrations of nitrates in low Arkansas River flows in southwestern Kansas are typically in the range of 1–3 mg/L as nitrate-nitrogen. High flows consist of lower concentrations. The content of nitrate-nitrogen is usually 2 mg/L and frequently 1 mg/L. For

example, all samples collected during the height flow period along the river at Wichita yielded 0.5 mg/L of nitrate-nitrogen. The content of nitrate is indeed linked with the salinity of river water, as demonstrated with the aid of the special conductance relationship. The concentration of nitrates would usually be measured accurately to around ± 0.6 mg/L based on the linear regression equation:

$$\text{NO}_3 = 0.000926 \text{ Sp.C.} - 1.35 \quad (6.2)$$

where NO_3 is nitrate, and Sp.C, is the specific conductivity.

Certain contaminants have increased concentrations in the Arkansas River water in southwestern Kansas; however, they still meet the Kansas Department of Health and Environment's high surface-water levels for specified uses. These include fluoride, boron and selenium. Of these components, in irrigation water, both fluoride and boron in low-flow saline water may surpass the required maximum degree of 1.0 mg/L and 0.75 mg/L, respectively. All materials are correlated with the river water's salinity as demonstrated by using the full-size correlations of specific conductivity. While the river water's boron concentration is usually much lower than the fluoride content, it differs from that of fluoride. The boron concentration is also expressed in the significantly greater association between boron content material and specific conductivity, rather than for the concentration and conductivity of fluorides. Fluoride (F) and boron (B) concentrations can be estimated from these linear regression equations:

$$F = 0.0000589 \text{ Sp.C} + 0.81 \quad (6.3)$$

$$B = 0.000216 \text{ Sp.C.} - 0.121 \quad (6.4)$$

The river water flowing into Kansas carries a concentration of selenium that is almost constantly greater than the requirement for aquatic life and the considered maximum for irrigation water. Pesticide concentrations are almost continually below detection[90]. The

sensitivity to sulfate exceeds around 2,600 mg/L when the discharge is small. The concentration of chloride, on the other hand, no longer meets the maximum restriction, as sulfate and dissolved solid content tends to increase with reduced discharge.

6.7.2 Electrical Conductivity

Water’s electrical conductivity is a chemical element that is proportional to the concentration of TDS. Conductivity is the most important consideration for crop irrigation water and also one of the easiest field measurements. Consequently, water’s electrical conductivity is often calculated and used as an indicator of salinity. In Kansas waters, the electrical conductance has been reported as 1,540–6,010 $\mu\text{S}/\text{cm}$, and the variance in dissolved solids has been reported as 1,160–4,460 mg/L (sum-of-constituent’s values), as shown in Figure 6.12.

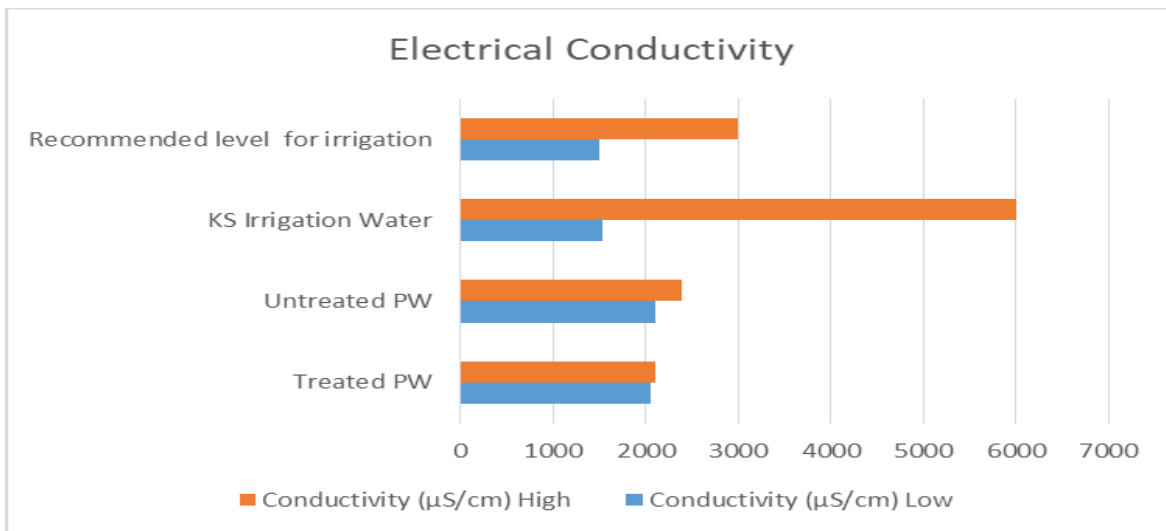


Figure 6.12. Electrical Conductivity Levels in Kansas Surface Water vs. Produced Water.

6.7.3 Total Dissolved Solids

The proportion of TDS is dependent on the water salinity. Much of the TDS content material is made up of the principal dissolved constituents. TDS concentrations can be determined by evaporating a specified volume of water sample to dryness, using an increased

drying temperature, then boiling (usually 190° C, while other methods use temperatures of 105–115°C), and residual weighing.

The residue left to dry following the evaporation of Arkansas River water consists of sodium, calcium, magnesium sulfates, and carbonates, in particular. Gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) precipitates during the drying process and then partly dehydrates at higher drying temperatures by the termination of the process. However, Hem has indicated that “even though dehydration of gypsum is supposed to be complete at 180°C, it is now not possible for water high in calcium and sulfate concentrations to yield a residue after drying for an hour at 180°C that exceeds the computed dissolved solids via various hundred milligrams per liter”[91].

Retention of crystallized water may provide a clarification as to why higher values for dissolved solids in the Arkansas River waters have been pronounced in the residue evaluation, rather than in the measurement of constituent amount. At temperatures greater than 100°C, bicarbonate is unstable. Half of the bicarbonate decomposes to shape carbonate, which combines with cations in the residue, and the other half is misplaced as carbon dioxide and water. The Kansas Geological Survey follows the sum-of-constituents manner of the U.S. Geological Survey that is responsible for this decomposition. The bicarbonate is expanded with the aid of a gravimetric components.

The comparison of TDS concentration against specific conductance for Arkansas River water in southwest Kansas can be used for estimating dissolved solids content given a unique conductance measurement. Figure 6.13 shows TDS concentration levels of produced water before and after treatment, and the averages of Kansas surface water based on the samples collected.

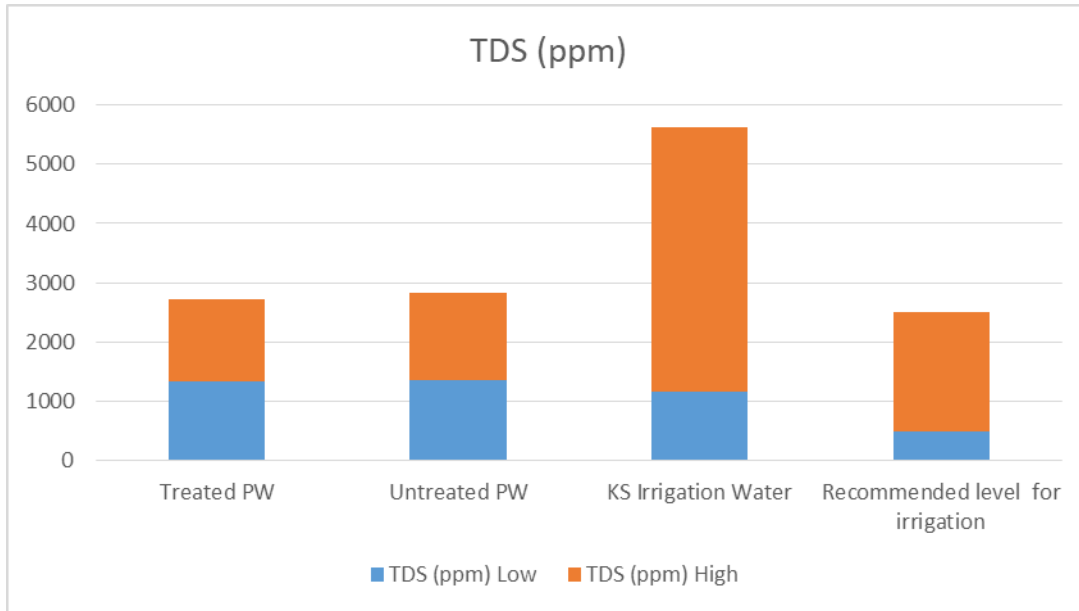


Figure 6.13. TDS Concentrations Recorded 2019–2020

6.7.4 Hardness

Hardness is generally a problem in the state of Kansas, primarily due to its geology. The water retrieved from oil-produced limestone, for all intents and purposes, is even harder, due to the higher concentrations of calcium and magnesium. Hardness can result in developing some very toxic metals when calcium ions (Ca_2^+) interact with other water elements, and is the main source of water alkalinity and scale formation in a subtle way [92].

Calcium concentration in Kansas water samples ranges from 456,598 to 896,878 ppb, and the produced water was found to be almost double the amount of concentration at 1,891,928 ppb. Magnesium concentration was in the range of 104,915 to 139,791 ppb, while the concentration in produced water was 149,422 ppb. After filtration, it can be concluded that the levels of calcium and magnesium significantly decrease to the acceptable level at 76,351 ppb and 87,362 ppb, respectively. For example, Figure 6.14 shows the intensity of calcium as detected in the ICP-OES, based on its wavelength and other factors related to hardness and water alkalinity.

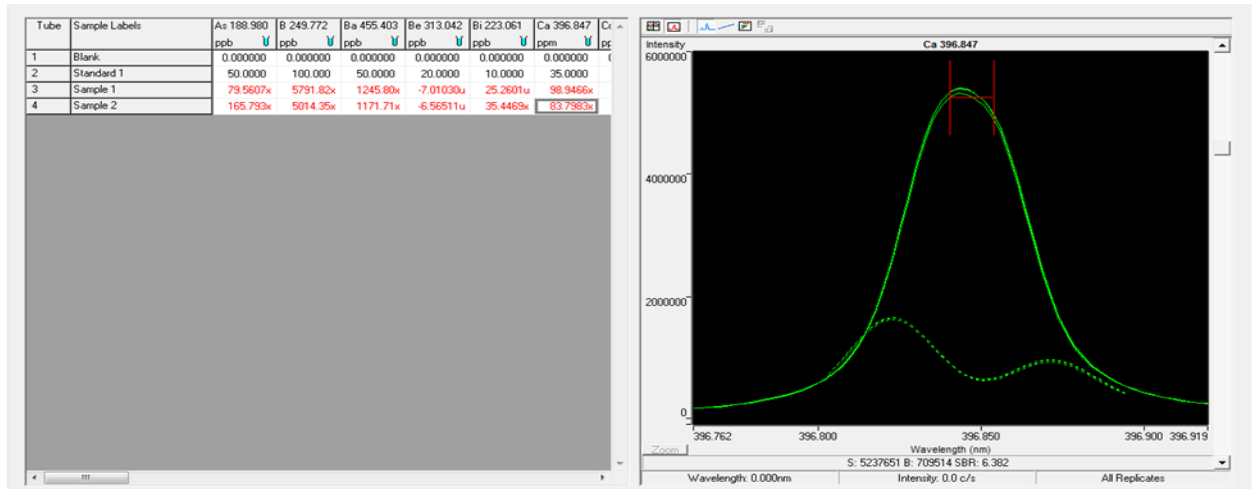


Figure 6.14. Calcium Concentration in Kansas Produced Water (ICP-OES Test)

In produced water, both calcium and magnesium normally exist bonded either to bicarbonate, to sulfate, or to chloride. When produced water is subjected to heat above 61°C/141°F, bicarbonate converts to carbonate to form calcium carbonate (CaCO_3) scale [93].

6.7.5 Turbidity

Turbidity is a measure of light distribution due to total suspended solid particles in water. Relationships between turbidity and TSS are site-specific and are not generally applied. The water turbidity used for irrigation is essential for the quality and quantity of crops, soil productivity, and environmental safety [94].

The U.S. Department of Agriculture recommends a level lower than 2 NTU for directly consumed crops and unrestricted irrigation, lower than 10 NTU for vegetables, and under 5 NTU for processed food crops. The Kansas Department of Health and Environment adopted the standards for fruits and vegetables, with no restrictions on cotton and other inconsumable crops [95].

Turbidity may have a positive or negative effect depending on the type of crop. The suspended particles that create turbidity may have a positive effect on many agricultural uses

such as improving the water-holding capacity on irrigated fields. On the other hand, high turbidity will accelerate wear on irrigation equipment, thereby increasing maintenance expenses [96].

6.7.6 Medium- and High-Range Hydrocarbons

The Kansas Department of Health and Environment requires other specific testing to be conducted on water discharged onto the surface and into the ground. Testing of water with reference to the percentage of hydrocarbons and other organic materials is also required. The Kansas testing method is designated to measure the total concentration of petroleum hydrocarbons in water and soil/sediment.

The quantitative measurements of extractable hydrocarbons are based on two ranges: C9–C18, medium-range hydrocarbons (MRH); and C19–C35, high-range hydrocarbons (HRH), which correspond to a range of boiling points between the values of approximately 150°C and 265°C. The testing of MRH and HRH levels in water and soil is important for the determination of total petroleum hydrocarbon.

The reporting limit of this test for each of the ranges is about 20 mg/kg in soil/sediment and roughly 100 µg/L in water. The C9–C18 MRHs are well-defined as all hydrocarbon compounds, which have between 9 and 18 carbon atoms and are regulated by release of the oil product to the environment. The C19–C35 HRHs are defined as all hydrocarbon combinations that contain between 19 and 35 carbon atoms of a petroleum product to be released into the environment [97]. The result of produced water after treatment matches the standard parameters set by the Kansas Department of Agriculture.

CHAPTER 7

CONCLUSIONS

This study was initiated in 2018 and was driven by the analysis of inductively coupled plasma optical emission spectroscopy test findings. This testing was carried out to examine and study the produced water elements and also to understand the requirements for new water sources in Kansas. The biggest environmental challenge faced by the Kansas oil and gas industry is produced water as a by-product of oil and gas production. Apart from this, there are numerous financial benefits for the state of Kansas in utilizing the treated water for farming. This option is particularly useful because the state knows about the depleting underground water sources every passing year. This depletion is primarily due to the fact that eight states take their share from the Ogallala aquifer. The management of water produced by the oil and gas industries involves merely drilling and directing the produced water back into the ground. Samples of produced water were gathered and studied to rule out the existence of any harmful components that may leave the water unsuitable for treatment. The literature that is available regarding this topic was sufficient to cover the majority of the latest work regarding treatment technologies. This information is useful in determining the best way to treat water. On the basis of the literature review, it was discovered that produced water from the state of Kansas has a degree of hydrocarbon elements, other organic materials, bacteria, low dissolved oxygen, and a high percentage of salt.

The system that has been developed as the result of this study and research is capable of saving natural resources and also of generating profits by reutilizing the produced water. This water can prove to be a new and additional source of irrigation water in Kansas for the sake of inconsumable crops.

Many different characteristics were investigated, studied, and modeled for the development of the proposed compact system design. Characteristics such as system design, low maintenance cost, low power consumption, low initial cost, high financial rewards, and environmentally friendly methods were studied. After study and research, the treatment methods found to be the most effective and beneficial were dissolved air flotation sedimentation, adsorption, media, and microporous ceramic filtration. This research has been conducted over two years, and during this time, multiple samples were collected from locations such as the Arkansas River and other water bodies in Kansas. The samples of produced water that were undertaken for the purpose of this study were gathered from the Lario Oil & Gas Company, which produces an average of 3,618 barrels of oil, 4,278 MCF (MCF-1000 cubic feet) of gas, and 1,151 barrels of produced water per day from 249 wells in the state of Kansas [98]. Treatment of produced water is a far better option than disposing of it (at a cost in the range of \$2,300–\$2,800) because it will only cost 10% of the current expenditure. The saved money can be used to obtain a minimum of \$1,000 per acre of newly sourced revenue from cotton crops.

The treatment process and filtration systems were closely studied and analyzed, and it was concluded that this new system provides promising results with reference to the adjustment of the water parameter. This was done to match and beat palatable water parameters that were discovered in the ground and surface water of Kansas state. This was concluded after taking into consideration the fact that the chemicals present in the water do not pose a threat to human life and wildlife. Additionally, other components of the produced water can prove to be just as harmful to the soil, like high salt content. These components can be heavy metals, oil, dissolved and suspended solids, organic compounds, and other toxins. The turbidity of treated produced water was recorded to have lowered from an average value of 80 NTU to the range of 10–15

NTU. The main components of water hardness are calcium and magnesium, which significantly decrease to an acceptable level at 76,351 ppb and 87,362 ppb, respectively. TDS in the range of 1,300–1,400 ppm and pH at 6.5–7 are considered appropriate for mildly acceptable and highly acceptable crops that are recommended for irrigation water. Harmful salts such as sodium and potassium in high concentrations were removed, along with a recovery percentage of 70%, and total oil removal was > 95%. The water quality for sodium and potassium levels was maintained below the irrigation standards of 1.7 ppm and 160 ppm, respectfully. Sulfate was reduced by more than 95%, from 310,00ppm to 150 ppm. Zinc was reduced to below 0.1 mg/L, copper at 0.04 mg/L, and mercury at a mean +/- SD (0.5+/- 0.4 µg/L).

Another important factor is that the treated water passes the requirements and test methods of Kansas, which are designated to measure the total concentration of petroleum hydrocarbons in water and soil/sediment based on medium- and high-range hydrocarbon. This test’s reporting limit for each range is approximately 20 mg/kg in soil/sediment and approximately 100 mg/L in water. Table 7.1 provides a comparison of the major water parameters.

TABLE 7.1
TREATED PRODUCED WATER VS. KANSAS STANDARDS

| Parameter | Untreated PW | Treated PW | Recommended Level for Irrigation |
|----------------------|---------------------|-------------------|---|
| pH | 4.4–6.02 | 6.5–6.7 | 5–7 |
| Conductivity (µS/cm) | 2,100–2,400 | 2,050–2,100 | 1,500–3,000 |
| TDS (ppm) | 1,370–1,460 | 1,340–1,380 | 500–2000 |
| Hardness (ppm) | 47.5–80 | 31.5–39.5 | 30–60 |
| Turbidity (NTU) | 80–90 | 15–25 | 2–20 |

Research indicates that this new system might be an influential development for the future of produced water and its effective treatment. Given the use of potential treatment techniques to conduct desalination, de-oiling, and elimination of suspended solids from produced

water, it is important to consider several drawbacks that accompany these techniques. High disposal costs, secondary waste output and release, high energy costs, and in some situations the use of chemicals are growing problems that these technologies are facing.

Compared to the model proposed in this study, modern technologies show that the S-MAC treatment is superior over others, as outlined in Table 7.2. The main and widely used five filtration technologies are media, membrane (polymer or ceramic), biological, adsorption (activated carbon and zeolite), and microporous polymer extraction (MPPE) treatments. The criteria selected are energy consumption, pre- and post-treatment, water recovery, oil-removal percentage, standard parameters, and feasibility.

TABLE 7.2

COMPARISON CHART OF PRODUCED WATER TECHNOLOGIES

| Criteria | Technology | | | | | |
|--------------------|---|--|---|---|--|--|
| | Media Filtration | Membrane Filtration | Biological Treatment | Adsorption Filtration | MPPE Treatment | S-MAC Treatment |
| Energy Consumption | Minimal | 0.07 KWh/bbl | 1-4 KWh/bbl | Minimal | 0.1 KWh/bbl | Minimal |
| Pre/Post-Treatment | None | Required | Required | None | Required | None |
| Water Recovery | >95% | <75% | <80% | >95% | >95% | <80% |
| Total Oil | <85% | <70% | <80% | <80% | <90% | >95% |
| TDO | None | None | None | None | None | >95% |
| Hardness | <65% | >90% | >80% | <80% | <90% | <80% |
| TDS | <70% | <80% | <90% | <80% | <90% | <95% |
| Feasibility | Widely utilized for treatment of PW; applies to all TDS and is independent of salt concentration. | Used by industry but also applicable to all forms of PW provided, regardless of turbidity and TDS. | Mainly effective for feeding water with levels below 6,600 mg /l of chloride. | Usually used as polishing stage rather than major method of treatment to prevent rapid consumption of adsorbent material. | Easy to run, efficient, fully automated, and suitable for integrated process applications. | Substantial reduction in energy consumption and high quality water outcome; low cost and no release of contaminants. |

CHAPTER 8

FUTURE RESEARCH

Due to the coronavirus situation, further research on this new treatment has been delayed. However, more experiments in this area will be conducted in the future. The second phase of this research can be recommended for future work, which opens avenues for investigation regarding the treatment of sludge collected after the filtration of produced water, and the process of harvesting rare earth metals and other elements found in Kansas produced water. This researcher was alarmed at the percentage of silver (Ag) (range of 60–65 mg/L) in the produced water samples, as shown in Table 8.1. Also, the percentage of yttrium (average of 20 mg/L) was alarming. Yttrium is rarely found in the Earth’s crust as a stable isotope of Y-89, or yttrium oxide (Y₂O₃). Hafnium (Hf), used in nuclear reactors as the best absorber of neutrons, was found at an interesting average of 13 mg/L. The adsorption process using solid adsorbents has been the most preferred option for heavy metal removal. While constantly looking to find low-cost adsorbents to remove heavy metals, researchers more commonly use activated carbon [101].

TABLE 8.1

RARE EARTH METALS FOUND IN KANSAS PRODUCUED WATER

| Element | Mean (Int.) (mg/L) | Percent Relative SD (Int.) |
|----------------|---------------------------|-----------------------------------|
| Zr 343 | 23.2 | 9.87 |
| Mo 202 | 43.3 | 2.85 |
| Ag 328 | 60.2 | 9.01 |
| Hf 264 | 13.1 | 2.1 |
| Au 242 | 8.2 | 2.85 |
| V 292 | 12.2 | 3.81 |
| In 230 | 18.0 | 4.30 |
| Pb 220 | 15.4 | 2.64 |
| Rh 343 | 17.7 | 6.70 |
| Ta 268 | 13.0 | 4.31 |
| Ti 336 | 22.8 | 1.34 |
| Y 371 | 21.6 | 5.96 |

REFERENCES

REFERENCES

- [1] P. J. C., Tibbetts, I. T. Buchanan, L. J. Gawel, and R. Large, "A Comprehensive Determination of Produced Water Composition," in *Produced Water*, edited by J. P. Ray and F. R. Englehart, Plenum Press, New York, 1992, pp. 97–112.
- [2] J. D. Arthur, P. E. Bruce, G. Langhe's, and C. Patel, "Technical Summary of Oil & Gas Produced Water Treatment Technologies," All Consulting LLC, Tulsa, OK, March 2005, pp. 19–31.
- [3] E. K. Nixon, "The Petroleum Industry in Kansas," *Transactions of the Kansas Academy of Science*, vol. 51, no. 4, December 1948, pp. 369–424.
- [4] Kansas Office of Revisor of Statutes, "Chapter 55—Oil and Gas," *Kansas Office of Revisor of Statutes*, Chapter 55, Article 10, Section 55-1001–55-1007, July 1, 1989, URL: https://www.ksrevisor.org/statutes/ksa_ch55.html [cited November 11, 2018].
- [5] H. L. Stone and A. O. Garder, "Analysis of Gas-Cap or Dissolved-Gas Drive Reservoirs," *Society of Petroleum Engineers Journal*, vol. 1, no. 2, January 1961, pp. 92–104.
- [6] Chevron Corporation, "Enhanced Oil Recovery (EOR)," *Chevron Corporation*, March 25, 2019, URL: <https://www.chevron.com/technology/enhanced-oil-recovery> [cited November 12, 2018].
- [7] F. D. Martin, "Enhanced Oil Recovery for Independent Producers," Society of Petroleum Engineers/Department of Energy Enhanced Oil Recovery Symposium, Tulsa, OK, April 22–24, 1992.
- [8] T. R. Carr, and W. J. Guy, "Enhanced Carbonate Reservoir Model for an Old Reservoir Utilizing New Techniques: The Schaben Field (Mississippian), Ness County, Kansas," *Semantic Scholar*, vol. 80, no. 1, 1996, pp. 75–90.
- [9] C. S. Evans and K. D. Newell, "The Mississippian Limestone Play in Kansas: Oil and Gas in a Complex Geologic Setting," Kansas University, Kansas Geological Survey, Public Information Circular 33, March 2013, URL: <http://www.kgs.ku.edu/Publications/PIC/pic33.html> [cited November 20, 2018].
- [10] J. M. Deines, M. Schipanski, B. Golden, S. Zipper, and C. Rottler, "Transitions from Irrigated to Dryland Agriculture in the Ogallala Aquifer: Land Use Suitability and Regional Economic Impacts," *Agricultural Water Management*, vol. 233, 2020, p. 106061.
- [11] Arkansas Natural Resources Commission, "The 2018-2023 Nonpoint Source Pollution Management Plan," Arkansas Natural Resources Commission, April 2018, pp. 102–181.

REFERENCES (continued)

- [12] T. Huang, Z. Pang, and W. M. Edmunds, “Soil Profile Evolution Following Land-Use Change: Implications for Groundwater Quantity and Quality,” Wiley Online Library, *Hydrological Processes*, vol. 27, no. 8, March 8, 2012, pp. 1238–1252.
- [13] B. Oram, “Drinking Water Testing Private Well Owners Well Water Testing City Drinking Water,” Water Research Center, May 2018, URL: <https://www.water-research.net/> [cited January 16, 2019].
- [14] Central Public Relations Office, University of Kansas, “Groundwater Levels Steady in Western Kansas, Decrease around Wichita,” February 14, 2018, URL: <http://news.ku.edu/2018/02/13/groundwater-levels-steady-western-kansas-decrease-around-wichita> [cited January 16, 2019].
- [15] M. A. Townsend, and G. L. Macpherson, “Water Chemistry and Sustainable Yield,” Chapter 5, Bulletin 239, *University of Kansas*, 1998, pp. 117–154.
- [16] The National Academies, “Report Sets Dietary Intake Levels for Water, Salt, and Potassium to Maintain Health and Reduce Chronic Disease Risk,” February 11, 2004, URL: www.nationalacademies.org/news/2004/02/report-sets-dietary-intake-levels-for-water-salt-and-potassium-to-maintain-health-and-reduce-chronic-disease-risk [cited January 18, 2019].
- [17] D. L. Barbie, “Water Resources Data, Texas, Water Year 2002,” U.S. Department of the Interior and U.S. Geological Survey, vol. 6, Groundwater, Water-Data Report TX-02-6, 2003, pp. 16–58.
- [18] K. E. Hendrickson and J. E. Sherow, “Watering the Valley: Development along the High Plains Arkansas River, 1870–1950,” *The Journal of American History*, vol. 78, no. 4, 1992, p. 1459.
- [19] R. McNary, “Growing Cotton in Kansas,” *Kansas Living*, November 21, 2016, URL: <https://kansaslivingmagazine.com/articles/2016/11/21/growing-cotton-in-kansas> [cited February 2, 2019].
- [20] National Agricultural Statistics Service, “Cotton,” Kansas Department of Agriculture, January 2018, URL: https://agriculture.ks.gov/docs/default-source/ag-growth-summit/january-2018-documents/cotton-sector.pdf?sfvrsn=f03d80c1_16 [cited February 04, 2019].
- [21] K. Gregory, R. D. Vidic, and D. A. Dzombak, “Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing,” *Elements*, vol. 7, no. 3, January 2011, pp. 181–186.

REFERENCES (continued)

- [22] D. N. Simkus, J. C. Aponte, J. E. Elsila, E. T. Parker, D. P. Glavin, and J. P. Dworkin, “Methodologies for Analyzing Soluble Organic Compounds in Extraterrestrial Samples: Amino Acids, Amines, Monocarboxylic Acids, Aldehydes, and Ketones,” U.S. National Library of Medicine, National Institutes of Health, *Life*, vol. 9, no. 2, June 6, 2019, p. 47.
- [23] J. Rosenblum, K. Sitterley, E. Thurman, I. Ferrer, and K. Linden, “Hydraulic Fracturing Wastewater Treatment by Coagulation-Adsorption for Removal of Organic Compounds and Turbidity,” *Journal of Environmental Chemical Engineering*, vol. 4, no. 2, 2016, pp. 1978–1984.
- [24] A. Malekizadeh and P. M. Schenk, “High Flux Water Purification Using Aluminum Hydroxide Hydrate Gels,” *Scientific Reports*, vol. 7, no. 1, document id 17437, December 12, 2017.
- [25] S. Maphutha, K. Moothi, M. Meyyappa, and S. Lyuke, “A Carbon Nanotube-Infused Polysulfone Membrane with Polyvinyl Alcohol Layer for Treating Oil-Containing Wastewater,” *Scientific Reports*, vol. 3, no. 1, document id 1509, March 22, 2013.
- [26] C. Murray-Gulde, J. Heatley, T. Karanfil, J. Rogers, and J. Myers, “Performance of a Hybrid Reverse Osmosis-Constructed Wetland Treatment System for Brackish Oil Field Produced Water,” *Water Research*, vol. 37, no. 3, 2003, pp. 705–713.
- [27] P. Dong, M. Puerto, K. Ma, K. Mateen, G. Ren, G. Bourdarot, D. Morel, M. Bourrel, S. Biswal, and G. Hirasaki, “Low-Interfacial-Tension Foaming System for Enhanced Oil Recovery in Highly Heterogeneous/Fractured Carbonate Reservoirs,” Society of Petroleum Engineers International Conference on Oilfield Chemistry, Montgomery TX, April 3–5, 2017, document id, pp. 253–259.
- [28] T. Sirivedhin and L. Dallbauman, “Organic Matrix in Produced Water from the Osage-Skiatook Petroleum Environmental Research Site, Osage County, Oklahoma,” *Chemosphere*, vol. 57, no. 6, 2004, pp. 463–469.
- [29] A. Pendashteh, A. Fakhru’l-Razi, A. Chuah, and D. Radiah, “Review of Technologies for Oil and Gas Produced Water Treatment,” *Journal of Hazardous Materials*, vol. 170, no. 2–3, October 30, 2009, pp. 530–551.
- [30] M. Lu, Z. Zhang, W. Yu, and W. Zhu, “Biological Treatment of Oilfield-Produced Water: A Field Pilot Study,” *International Biodeterioration and Biodegradation*, vol. 63, no. 3, April 2009, pp. 316–321.
- [31] H. Salehizadeh and S. Shojaosadati, “Removal of Metal Ions from Aqueous Solution by Polysaccharide Produced from *Bacillus Firmus*,” *Water Research*, vol. 37, no. 17, 2003, pp. 4231–4235.

REFERENCES (continued)

- [32] S. Tsuneda, “Characterization of Nitrifying Granules Produced in an Aerobic Upflow Fluidized Bed Reactor,” *Water Research*, vol. 37, no. 20, 2013, pp. 4965–4973.
- [33] R. Shpiner, D. Stucky, and S. Vathi, “Treatment of Oil Well ‘Produced Water’ by Waste Stabilization Ponds: Removal of Heavy Metals,” *Water Research*, vol. 43, no. 17, 2009, pp. 4258–4268.
- [34] R. Asmatulu, Z. Veisi, W. Khan, A. Asaduzzaman, N. Nuraje, and H. Muppalla, “Study of Hydrophilic Electrospun Nanofiber Membranes for Filtration of Micro and Nanosize Suspended Particles,” *Membranes*, vol. 3, no. 4, 2013, pp. 375–388.
- [35] D. Bromley, “Potable Water Treatment with RSL Membranes,” David Bromley Engineering Ltd., 2017, URL: www.dbe2000.com/wp-content/uploads/2018/06/Small-Community-RSL-membrane-Brochure-Jun18-18.pdf [cited October 26, 2019].
- [36] M. Stewart and K. E. Arnold, *Produced Water Treatment Field Manual*, 1st ed., Chapters 1 and 2, Gulf Professional Publishing, Houston, TX, August 2011, pp. 8–43.
- [37] P. McEachern, “Lithium Recovery from Oilfield Produced Water Brine & Wastewater Treatment,” Report Prepared for MGX Minerals, April 24, 2017, pp. 9–21.
- [38] J. Brant, C. Manson, and J. Hoberg, “Resource Extraction and Exploitation, The Center of Excellence in Produced Water Management (CEPWM), University of Wyoming, 2018, URL: www.cepwm.com/research/resource-extraction-and-exploitation/ [cited August 1, 2019].
- [39] N. Nirmalakhandan, G. Tellez, and J. L. Gardea-Torresdey, “Evaluation of Biokinetic Coefficients in Degradation of Oilfield Produced Water under Varying Salt Concentrations,” *Water Research*, vol. 29, no. 7, 1995, pp. 1711–1718.
- [40] M. H. Al-Malack and A. A. Basaleh, “Adsorption of Heavy Metals Using Activated Carbon Produced from Municipal Organic Solid Waste,” *Desalination and Water Treatment*, vol. 57, no. 51, June 2014, pp. 24519–24531.
- [41] W. Basma, “Produced Water Treatment for Beneficial Use: Emulsified Oil Removal,” Ph.D. Dissertation, Department of Science and Technology, Chapter 3, University of Connecticut, September 2016, pp. 43–67.
- [42] P. Xu, D. Heil, G. Wang, and J. E. Drewes, “Treatment of Brackish Produced Water Using Carbon Aerogel-Based Capacitive Deionization Technology,” *Water Research*, vol. 42, no. 10-11, 2008, pp. 2605–2617.

REFERENCES (continued)

- [43] N. F. Gray, “Chlorine Dioxide,” in *Microbiology of Waterborne Diseases*, 2nd ed., Chapter 32, edited by S. L. Percival, M. V. Yates, D. D. Williams, R. Chalmers, and N. F. Gray, 2014, pp. 591–598.
- [44] Laura Martin, “10 Produced Water Treatment Technologies: Evaluating the Pros and Cons,” *Water Online*, April 14, 2014,
URL: www.wateronline.com/doc/produced-water-treatment-technologies-evaluating-the-pros-and-cons-0001 [cited November 28, 2019].
- [45] Vilcaez Lab, “*Geofluids/Hydrogeology: Water-Energy-CO2 Nexus*,” October 2018,
URL: vilcaez.wordpress.com/research/ [cited January 8, 2020].
- [46] G. T. Tellez, N. Nirmalakh, and J. L. Gardea-Torresdey, “Performance Evaluation of an Activated Sludge System for Removing Petroleum Hydrocarbons from Oilfield Produced Water,” *Advances in Environmental Research*, vol. 6, no. 4, 2002, pp. 455–470.
- [47] H. Tesfaalem Haile, L. Sopkow, and Tamer Crosby, “Assessing the Corrosivity of Field Produced Water Obtained from In-Situ Oil Sands Water Treatment Systems,” *NACE International Corrosion Conference & Expo*, New Orleans, LA, March 26–30, 2017, document id 2017-9389.
- [48] A. Ali, C. J. Quist-Jensen, E. Drioli, and F. Macedonio, “Evaluation of Integrated Microfiltration and Membrane Distillation/Crystallization Processes for Produced Water Treatment,” *Desalination*, vol. 434, 2018, pp. 161–168.
- [49] O. R. Lokare, S. Tavakkoli, G. Rodriguez, V. Khanna, and R. D. Vidic, “Integrating Membrane Distillation with Waste Heat from Natural Gas Compressor Stations for Produced Water Treatment in Pennsylvania,” *Desalination*, vol. 413, 2017, pp. 144–153.
- [50] D. Silva, C. Lucas, H. Juviniiano, M. Moura, A. Neto, and T. Dantas, “Novel Produced Water Treatment Using Microemulsion Systems to Remove Oil Contents,” *Journal of Water Process Engineering*, vol. 33, 2020, pp. 1016–1057.
- [51] J. Kim, J. Kim, J. Kim, and S. Hong, “Osmotically Enhanced Dewatering-Reverse Osmosis (OED-RO) Hybrid System: Implications for Shale Gas Produced Water Treatment,” *Journal of Membrane Science*, vol. 554, 2018, pp. 282–290.
- [52] A. Atangana, *Fractional Operators with Constant and Variable Order with Application to Geo-Hydrology*, Academic Press, 2018, pp. 15–47.
- [53] R. Asmatulu, “Advanced Chemical-Mechanical Dewatering of Fine Particles,” Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA, April 3, 2001, pp. 25–56.

REFERENCES (continued)

- [54] S. Wang and M. Xu, “Axial Couette Flow of Two Kinds of Fractional Viscoelastic Fluids in an Annulus,” *Nonlinear Analysis: Real World Applications*, vol. 10, no. 02, November 2009, pp. 1087–1096.
- [55] K. Arnold and M. Stewart, *Surface Production Operations: Vol. 1: Design of Oil-Handling Systems and Facilities*, 2nd ed., Gulf Professional Publishing, Houston, TX, 1998, Chapters 3 and 4, pp. 58–134.
- [56] M. Stewart, *Surface Production Operations: Vol 2: Design of Gas-Handling Systems and Facilities*, 3rd ed., Gulf Professional Publishing, Houston, TX, Chapter 2, 1999, pp. 12–39.
- [57] N. Kumar, *Comprehensive Physics for Class XI*. Laxmi Publications, New Delhi, vol. 1, 1992, pp. 801–887.
- [58] W. H. Finlay, *The Mechanics of Inhaled Pharmaceutical Aerosols: An Introduction*, 2nd ed., Academic Press, 2019, pp. 21–72.
- [59] J. K. Edzwald, “Principles and Applications of Dissolved Air Flotation,” *Water Science and Technology*, vol. 31, iss. 3-4, 1995, pp. 1–23.
- [60] J. Rubio, Carissimi, E., and J. J. Rosa, “Flotation in Water and Wastewater Treatment and Reuse: Recent Trends in Brazil,” *International Journal of Environment and Pollution*, vol. 30, no. 2, 2007, pp. 197–212.
- [61] J. Haarhoff and J. K. Edzwald, “Dissolved Air Flotation Modelling: Insights and Shortcomings,” *Aqua: Journal of Water Supply: Research and Technology*, vol. 53, no. 3, 2004, pp. 127–150.
- [62] M. J. Bauer, R. Bayley, A. Eades, and R. Scriven, “Enhanced Rapid Gravity Filtration and Dissolved Air Flotation for Pre-Treatment of River Thames Reservoir Water,” *Elsevier Ltd*, vol. 37, no. 2, 1998, pp. 35–42.
- [63] Y.-T. Hung, L. K. Wang, M.-H. Wang, N. K. Shamma, and J. P. Chin, *Waste Treatment in the Service and Utility Industries*, CRC Press, Chapter 5, 2017, pp 78–93.
- [64] B. Lakghomi, Y. Lawryshyn, and R. Hofmann, “Importance of Flow Stratification and Bubble Aggregation in the Separation Zone of a Dissolved Air Flotation Tank,” *Water Research*, vol. 46, no. 14, 2012, pp. 4468–4476.

REFERENCES (continued)

- [65] J. Zhu, J. Zou, C. Pan, and J. Ma, “Comparative Study of Dissolved Air Flotation and Sedimentation Process for Treating Reservoir Water with Low Temperature, Low Turbidity and High Natural Organic Matter,” *Applied Mechanics and Materials*, vol. 71–78, 2011, pp. 2767–2771.
- [66] G. Crini, E. Lichtfouse, L. Wilson, and N. Morin-Crini, “Adsorption-Oriented Processes Using Conventional and Non-Conventional Adsorbents for Wastewater Treatment,” in *Green Adsorbents for Pollutant Removal*, edited by G. Crini, E. Lichtfouse, Environmental Chemistry for a Sustainable World 18, Springer Nature, 2018, pp. 23–71
- [67] M. N. Rashed, ed., *Organic Pollutants: Monitoring, Risk and Treatment*, InTech Open, Chapter 7, 2013, pp. 167–191.
- [68] D. Kyung, D. Kim, N. Park, and W. Lee “Estimation of CO₂ Emission from Water Treatment Plant—Model Development and Application,” *Journal of Environmental Management*, vol. 131, 2013, pp. 74–81.
- [69] R. Kwak, and J. Han. “REMOVED: Microscale Electrodialysis: Concentration Profiling and Vortex Visualization,” *Procedia Engineering*, vol. 44, 2012, pp. 409–414.
- [70] H. Hamelers, M. Tedesco, and P. Biesheuvel “Nernst-Planck Transport Theory for (Reverse) Electrodialysis: II. Effect of Water Transport through Ion-Exchange Membranes,” *Journal of Membrane Science*, vol. 531, 2017, pp. 172–182.
- [71] T. Welgemoed and C. F. Schutte, “Capacitive Deionization Technology: An Alternative Desalination Solution,” *Desalination*, vol. 183, no. 1-3, 2005, pp. 327–340.
- [72] W. Y. Teoh, R. Amal, and L. Mädler “Flame Spray Pyrolysis: An Enabling Technology for Nanoparticles Design and Fabrication,” *Nanoscale*, vol. 2, no. 8, 2010, pp. 1324–1327.
- [73] C. G. Whitney, “Petrology of Clay Minerals in the Subsurface Morrison Formation Near Crown Point, Southern San Juan Basin, New Mexico: An Interim Report,” in *A Basin Analysis Case Study: The Morrison Formation, Grants Uranium Region, New Mexico*, edited by C. E. Turner-Peterson, E. S. Santos, and N. S. Fishman, AAPG Studies in Geology, American Association of Petroleum Geologists, 1986, pp. 315–329.
- [74] E. T. Igunnu and G. Z. Chen, “Produced Water Treatment Technologies,” *International Journal of Low-Carbon Technologies*, vol. 9, no. 3, September 2014, pp. 157–177.
- [75] V. K. Gupta, I. Ali, T. A. Saleh, A. Nayak, and S. Agarwal, “Chemical Treatment Technologies for Waste-Water Recycling,” *Royal Society of Chemistry Advances*, vol. 2, iss. 16, April 4, 2012, pp. 6380–6388.

REFERENCES (continued)

- [76] A. Carpenter, C. De Lannoy, and M. R. Wiesner, “Cellulose Nanomaterials in Water Treatment Technologies,” *Environmental Science & Technology*, vol. 49, no. 9, 2015, pp. 5277–5287.
- [77] Amusing Planet, “The Historic Great Mosque of Samarra,” *Times of India Travel*, 25 August 25, 2014, URL: timesofindia.indiatimes.com/travel/destinations/the-historic-great-mosque-of-samarra/as40188702.cms [cited January 3, 2020].
- [78] M. S. Hussain, *Mechanism of Sedimentation and Design of Sedimentation Process*, PowerPoint Presentation, November 6, 2019.
- [79] A. De, *Sedimentation Process and Design of Settling Systems*, Springer India, April 2017, pp. 49–52.
- [80] Centers for Disease Control and Prevention, “Slow Sand Filtration,” March 21, 2012, URL: <https://www.cdc.gov/safewater/sand-filtration.html> [cited February 4, 2020].
- [81] H. Xiubin He and Z. Huang, “Zeolite Application for Enhancing Water Infiltration and Retention in Loess Soil,” *Resources Conservation and Recycling*, vol. 34, no. 1, 2001, pp. 45–52.
- [82] T. Speth, “US EPA’s Research on PFAS,” U.S. Environmental Protection Agency Environmental and Health Leadership Meeting, Cincinnati, OH, August 7, 2019, document id. 346153.
- [83] M. Nasiri, I. Jafari, and B. Parniankhoy, “Oil and Gas Produced Water Management: A Review of Treatment Technologies, Challenges, and Opportunities” *Chemical Engineering Communications*, vol. 204, no. 8, 2017, pp. 990–1005.
- [84] R. A. Neff, C. L. Parker, F. L. Kirschenmann, J. Tinch, and R. S. Lawrence. “Peak Oil, Food Systems, and Public Health,” *American Journal of Public Health*, vol. 101, no. 9, 2011, pp. 1587–1597.
- [85] K. Azetsu-Scott, P. Yeats, G. Wohlgeschaffen, J. Dalziel, S. Niven, and K. Lee. “Precipitation of Heavy Metals in Produced Water: Influence on Contaminant Transport and Toxicity,” *Marine Environmental Research*, vol. 63, no. 2, 2007, pp. 146–167.
- [86] Y. I. Kharaka, G. Ambats, T. S. Presser, R. A. Davis, “Removal of Selenium from Contaminated Agricultural Drainage Water by Nanofiltration Membranes,” *Applied Geochemistry*, vol. 11, no. 6, November 1996, pp. 797–802

REFERENCES (continued)

- [87] N. H. Omer, “Water Quality Parameters,” Intech Open, October 16, 2019, URL: <https://www.intechopen.com/online-first/water-quality-parameters> [cited January 3, 2020].
- [88] M. Klarman, “Investigation of Ceramic Pot Filter Design Variables,” Master’s Thesis, Rollins School of Public Health, Emory University, May 2009, pp. 29–45.
- [89] Rakib Mustafa, “Investigation of Wastewater Treatment Using Waste Materials and Algae through Carbonization and Activation Processes,” Master’s Thesis, Department of Mechanical Engineering, Wichita State University, December 2018, pp. 54–83.
- [90] M. Kumar and A. Puri, “A Review of Permissible Limits of Drinking Water,” *Indian Journal of Occupational and Environmental Medicine*, vol. 16, no. 1, 2012, pp. 40–44.
- [91] M. Stone, A. Zeigler, and Brian Klager, “Water-Quality and Geochemical Variability in the Little Arkansas River and Equus Beds Aquifer, South-Central Kansas, 2001–16,” *Scientific Investigations Report*, vol. 11, no. 2019–5026, 2019.
- [92] J. D. Hem, “Study and Interpretation of the Chemical Characteristics of Natural Water,” 3rd ed., U.S Geological Survey Water-Supply Paper 2254, 1985, pp. 59–98.
- [93] L. Ribeiro, T. Dantas, A. Neto, K. Melo, M. Moura, and P. Aum, “The Use of Produced Water in Water-Based Drilling Fluids: Influence of Calcium and Magnesium Concentrations,” *Brazilian Journal of Petroleum and Gas*, vol. 10, no. 4, 2016, pp. 233–245.
- [94] H. E. Diggs and J. M. Parker, “Aquatic Facilities,” in *Planning and Designing Research Animal Facilities*, edited by R. Hessler and Noel D.M. Lehner, Academic Press, 2009, Chapter 23, pp. 323-331.
- [95] M. J. Hammer, “Water Recycling for Agricultural Irrigation” *Lenntech*, URL: <https://www.lenntech.com/water-reuse-agricultural-irrigation.htm> [cited January 28, 2020].
- [96] H. Jeong, H. Kim, and T. Jang, “Irrigation Water Quality Standards for Indirect Wastewater Reuse in Agriculture: A Contribution toward Sustainable Wastewater Reuse in South Korea,” *Water*, vol. 8, no. 4, 2016, pp. 169–187.
- [97] T. Pick, “Assessing Water Quality for Human Consumption, Agriculture, and Aquatic Life Uses,” United States Department of Agriculture, Environment Technical Note No. MT-1, rev. 2, June 2011.

REFERENCES (continued)

- [98] Bureau of Environmental Remediation, “Total Petroleum Hydrocarbons (TPH) and Light Non-Aqueous Phase Liquid (LNAPL) Characterization, Remediation and Management,” Policy # BER-041, *Kansas Department of Health and Science*, May 24, 2017.

- [99] Lario Oil & Gas Company, “Properties & Operations,” 2015, URL: <https://www.lariooil.com/> [cited February 3, 2020].

- [100] C. Carpenter, “Advanced Technologies for Produced-Water Treatment and Reuse,” *Journal of Petroleum Technology*, vol. 66, no. 12, January 2014, pp. 131–134.

- [101] A. Ghorpade and M. M. Ahammed, “Water Treatment Sludge for Removal of Heavy Metals from Electroplating Wastewater” *Environmental Engineering Research*, vol. 23, no. 1, June 2017, pp. 92–98.

APPENDIX

APPENDIX

ICP-EOS TESTING DATA

Date: 3/14/2019

| Label | Sol'n Conc. | Units | SD(Int) | %RSD(Int) | Int. (c/s) |
|--------------|--------------------|--------------|----------------|------------------|-------------------|
| As 188.980 | 0.000000 | ppb | 0.484 | 25.9 | 1.87135 |
| B 249.772 | 0.000000 | ppb | 0.698 | 1.9 | 36.4703 |
| Ba 455.403 | 0.000000 | ppb | 6.748 | 43.4 | 15.5651 |
| Be 313.042 | 0.000000 | ppb | 10.586 | 2.1 | 513.881 |
| Bi 223.061 | 0.000000 | ppb | 1.152 | 35.5 | 3.24193 |
| Ca 396.847 | 0.000000 | ppm | 7.900 | 9.1 | 86.8687 |
| Cd 214.439 | 0.000000 | ppb | 2.019 | 101.8 | 1.98249 |
| Co 238.892 | 0.000000 | ppb | 2.212 | 55.8 | 3.96361 |
| Cr 267.716 | 0.000000 | ppb | 1.695 | 72.3 | 2.34342 |
| Cu 327.395 | 0.000000 | ppb | 1.669 | 52.3 | 3.19300 |
| Fe 238.204 | 0.000000 | ppb | 0.304 | 9.4 | 3.24765 |
| K 766.491 | 0.000000 | ppb | 0.907 | 11.3 | 7.99945 |
| Mg 279.553 | 0.000000 | ppm | 1.705 | 40.0 | 4.26778 |
| Mn 257.610 | 0.000000 | ppb | 2.913 | 74.3 | 3.92162 |
| Mo 202.032 | 0.000000 | ppb | 1.870 | 69.2 | 2.70125 |
| Na 589.592 | 0.000000 | ppm | 6.698 | 8.7 | 77.0561 |
| Ni 231.604 | 0.000000 | ppb | 1.207 | 35.7 | 3.38384 |
| Pb 220.353 | 0.000000 | ppb | 0.634 | 25.9 | 2.44546 |
| Se 196.026 | 0.000000 | ppb | 1.225 | 48.1 | 2.54815 |
| Sr 407.771 | 0.000000 | ppb | 2.783 | 10.8 | 25.7092 |
| Tl 190.794 | 0.000000 | ppb | 0.214 | 16.4 | 1.30912 |
| V 292.401 | 0.000000 | ppb | 1.464 | 26.6 | 5.51033 |
| Zn 213.857 | 0.000000 | ppb | 1.435 | 77.5 | 1.85079 |

APPENDIX (continued)

Date: 6/07/2019

| Label | Replicates | Intensity | (c/s) |
|--------------|-------------------|------------------|--------------|
| Bi 223.061 | 4.13189 | 1.94054 | 3.65338 |
| Ca 396.847 | 92.6838 | 90.0478 | 77.8744 |
| Cd 214.439 | 4.29281 | 0.560265 | 1.09439 |
| Co 238.892 | 2.96868 | 6.49796 | 2.42421 |
| Cr 267.716 | 3.81540 | 2.72528 | 0.489601 |
| Cu 327.395 | 3.72635 | 4.52973 | 1.32292 |
| Fe 238.204 | 2.89665 | 3.44030 | 3.40599 |
| K 766.491 | 7.65582 | 9.02765 | 7.31488 |
| Mg 279.553 | 5.29344 | 5.21064 | 2.29925 |
| Mn 257.610 | 1.48976 | 3.12478 | 7.15032 |
| Mo 202.032 | 1.45196 | 1.80052 | 4.85127 |
| Na 589.592 | 84.7612 | 73.7809 | 72.6262 |
| Ni 231.604 | 2.12084 | 3.50606 | 4.52461 |
| Pb 220.353 | 2.50604 | 1.78326 | 3.04710 |
| Se 196.026 | 2.85839 | 1.19828 | 3.58778 |
| Sr 407.771 | 22.8660 | 25.8346 | 28.4270 |
| Tl 190.794 | 1.54585 | 1.12910 | 1.25241 |
| V 292.401 | 5.28053 | 4.17468 | 7.07579 |
| Zn 213.857 | 3.50736 | 1.03482 | 1.01019 |

APPENDIX (continued)

Date: 08/12/2019

| Label | Sol'n Conc. | Units | SD(Int) | %RSD(Int) | Int. (c/s) |
|--------------|--------------------|--------------|----------------|------------------|-------------------|
| As 188.980 | 50.0000 | ppb | 0.908 | 40.1 | 2.26165 |
| B 249.772 | 100.000 | ppb | 4.737 | 2.1 | 222.337 |
| Ba 455.403 | 50.0000 | ppb | 28.026 | 0.7 | 3848.89 |
| Be 313.042 | 20.0000 | ppb | 19.436 | 1.5 | 1296.14 |
| Bi 223.061 | 10.0000 | ppb | 0.709 | 17.5 | 4.05306 |
| Ca 396.847 | 35.0000 | ppm | 42877.898 | 2.3 | 1891316 |
| Cd 214.439 | 20.0000 | ppb | 0.916 | 8.6 | 10.6940 |
| Co 238.892 | 25.0000 | ppb | 1.504 | 8.5 | 17.6822 |
| Cr 267.716 | 20.0000 | ppb | 3.394 | 20.2 | 16.7869 |
| Cu 327.395 | 20.0000 | ppb | 0.338 | 0.4 | 82.5803 |
| Fe 238.204 | 100.000 | ppb | 5.049 | 4.2 | 121.407 |
| K 766.491 | 3000.00 | ppb | 283.616 | 0.9 | 32204.5 |
| Mg 279.553 | 15.0000 | ppm | 2187.233 | 1.5 | 149669 |
| Mn 257.610 | 30.0000 | ppb | 8.255 | 4.4 | 185.760 |
| Mo 202.032 | 100.000 | ppb | 0.886 | 4.5 | 19.7262 |
| Na 589.592 | 8.00000 | ppm | 3897.974 | 1.6 | 239464 |
| Ni 231.604 | 50.0000 | ppb | 1.272 | 8.7 | 14.5723 |
| Pb 220.353 | 25.0000 | ppb | 2.536 | 53.9 | 4.70445 |
| Se 196.026 | 10.0000 | ppb | 1.762 | 71.1 | 2.47668 |
| Sr 407.771 | 100.000 | ppb | 166.574 | 0.6 | 28676.2 |
| Tl 190.794 | 10.0000 | ppb | 1.215 | 54.3 | 2.23805 |
| V 292.401 | 50.0000 | ppb | 4.364 | 12.2 | 35.7410 |

APPENDIX (continued)

As 188.980 Calibration **12/20/2019, 2:03:24 PM** **Correlation Coefficient: 1.000000**
 (ppb)

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|---------|---------|------------|-----------|------------|------------|---------|
| Blank | 1.87135 | 0.000000 | 0.000000 | - | Standard 1 | 2.26165 |
| 50.0000 | 50.0000 | -0.000027 | 0.0 | | | |

Curve Type: Linear Equation: $y = 0.0 x + 1.9$

B 249.772 Calibration **12/20/2019, 2:03:24 PM** **Correlation Coefficient: 1.000000**

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|-------|------------|-----------|------------|----------|--------|
| Blank | | 36.4703 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 222.337 | 100.000 | 100.000 | 0.000000 | 0.0 |

Curve Type: Linear Equation: $y = 1.9 x + 36.5$

Ba 455.403 Calibration **12/20/2019, 2:03:24 PM** **Correlation Coefficient: 1.000000**
 (ppb)

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|-------|------------|-----------|------------|----------|--------|
| Blank | | 15.5651 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 3848.89 | 50.0000 | 50.0000 | 0.000000 | 0.0 |

Curve Type: Linear Equation: $y = 76.7 x + 15.6$

Be 313.042 Calibration **12/20/2019, 2:03:24 PM** **Correlation Coefficient: 1.000000**
 (ppb)

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|-------|------------|-----------|------------|----------|--------|
| Blank | | 513.881 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 1296.14 | 20.0000 | 20.0000 | 0.000000 | 0.0 |

Curve Type: Linear Equation: $y = 39.1 x + 513.9$

Bi 223.061 Calibration **12/20/2019, 2:03:24 PM** **Correlation Coefficient: 1.000000**
 (ppb)

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|-------|------------|-----------|------------|-----------|--------|
| Blank | | 3.24193 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 4.05306 | 10.0000 | 10.0000 | -0.000001 | 0.0 |

Curve Type: Linear Equation: $y = 0.1 x + 3.2$

Ca 396.847 Calibration **12/20/2019, 2:03:24 PM** **Correlation Coefficient: 1.000000**
 (ppm)

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|-------|------------|-----------|------------|----------|--------|
| Blank | | 86.8687 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 1891316 | 35.0000 | 35.0000 | 0.000000 | 0.0 |

Curve Type: Linear Equation: $y = 54035.1 x + 86.9$

APPENDIX (continued)

Cd 214.439 Calibration

| (ppb) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|--------------------|--------------|-------------------------------|------------------|--|--------------|---------------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 1.98249 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 10.6940 | 20.0000 | 20.0000 | 0.000000 | 0.0 |
| Curve Type: Linear | | Equation: $y = 0.4 x + 2.0$ | | | | |

Co 238.892 Calibration

| (ppb) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|-----------------------------|--------------|-------------------------------|------------------|--|--------------|--------------------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 3.96361 | 0.000000 | 0.000000 | - | - |
| Standard 1 | 17.6822 | 25.0000 | 25.0000 | 0.000002 | 0.0 | Curve Type: Linear |
| Equation: $y = 0.5 x + 4.0$ | | | | | | |

Cr 267.716 Calibration

| (ppb) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|--------------------|--------------|-------------------------------|------------------|--|--------------|---------------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 2.34342 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 16.7869 | 20.0000 | 20.0000 | 0.000000 | 0.0 |
| Curve Type: Linear | | Equation: $y = 0.7 x + 2.3$ | | | | |

Cu 327.395 Calibration

| (ppb) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|--------------------|--------------|-------------------------------|------------------|--|--------------|---------------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 3.19300 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 82.5803 | 20.0000 | 20.0000 | 0.000000 | 0.0 |
| Curve Type: Linear | | Equation: $y = 4.0 x + 3.2$ | | | | |

Fe 238.204 Calibration

| (ppb) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|--------------------|--------------|-------------------------------|------------------|--|--------------|---------------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 3.24765 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 121.407 | 100.000 | 100.0000 | -0.000008 | 0.0 |
| Curve Type: Linear | | Equation: $y = 1.2 x + 3.2$ | | | | |

K 766.491 Calibration

| (ppb) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|--------------------|--------------|-------------------------------|------------------|--|--------------|---------------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 7.99945 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 32204.5 | 3000.00 | 3000.00 | 0.000000 | 0.0 |
| Curve Type: Linear | | Equation: $y = 10.7 x + 8.0$ | | | | |

APPENDIX (continued)

Mg 279.553 Calibration

| (ppm) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|------------|-------|------------------------|-----------|-----------------------------------|----------|--------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 4.26778 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 149669 | 15.0000 | 15.0000 | 0.000000 | 0.0 |

Curve Type: Linear Equation: $y = 9977.6 x + 4.3$

Mn 257.610 Calibration

| (ppb) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|---------|---------|------------------------|-----------|-----------------------------------|------------|---------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | 3.92162 | 0.000000 | 0.000000 | - | Standard 1 | 185.760 |
| 30.0000 | 30.0000 | 0.000000 | 0.0 | | | |

Curve Type: Linear Equation: $y = 6.1 x + 3.9$

Mo 202.032 Calibration 12/20/2019, 2:03:24 PM Correlation Coefficient: 1.000000

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|-------|------------|-----------|------------|----------|--------|
| Blank | | 2.70125 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 19.7262 | 100.000 | 100.000 | 0.000000 | 0.0 |

Curve Type: Linear Equation: $y = 0.2 x + 2.7$

Na 589.592 Calibration

| (ppm) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|------------|-------|------------------------|-----------|-----------------------------------|----------|--------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 77.0561 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 239464 | 8.00000 | 8.00000 | 0.000000 | 0.0 |

Curve Type: Linear Equation: $y = 29923.4 x + 77.1$

Ni 231.604 Calibration

| (ppb) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|------------|-------|------------------------|-----------|-----------------------------------|----------|--------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 3.38384 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 14.5723 | 50.0000 | 50.0000 | 0.000000 | 0.0 |

Curve Type: Linear Equation: $y = 0.2 x + 3.4$

Pb 220.353 Calibration

| (ppb) | | 12/20/2019, 2:03:24 PM | | Correlation Coefficient: 1.000000 | | |
|------------|-------|------------------------|-----------|-----------------------------------|----------|--------|
| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
| Blank | | 2.44546 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 4.70445 | 25.0000 | 25.0000 | 0.000000 | 0.0 |

Curve Type: Linear Equation: $y = 0.1 x + 2.4$

APPENDIX (continued)

Se 196.026 Calibration

(ppb) **12/20/2019, 2:03:24 PM**

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|-------|------------|-----------|------------|-------|--------|
| Blank | | 2.54815 | 0.000000 | -0.000000 | - | - |
| Standard 1 | | 2.47668 | 10.0000 | 10.0000 | - | - |

Negative slope.

Curve Type: Linear

Sr 407.771 Calibration

(ppb) **12/20/2019, 2:03:24 PM** **Correlation Coefficient : 1.000000**

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|-------|------------|-----------|------------|----------|--------|
| Blank | | 25.7092 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 28676.2 | 100.000 | 100.000 | 0.000000 | 0.0 |

Curve Type: Linear

Equation: $y = 286.5 x + 25.7$

Tl 190.794 Calibration

(ppb) **12/20/2019, 2:03:24 PM** **Correlation Coefficient: 1.000000**

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|---------|------------|-----------|------------|-------|--------|
| Blank | | 1.30912 | 0.000000 | 0.000000 | - | - |
| Standard 1 | 2.23805 | 10.0000 | 10.0000 | 0.000001 | 0.0 | |

Curve Type: Linear

Equation: $y = 0.1 x + 1.3$

V 292.401 Calibration

(ppb) **12/20/2019, 2:03:24 PM** **Correlation Coefficient: 1.000000**

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|------------|-------|------------|-----------|------------|-----------|--------|
| Blank | | 5.51033 | 0.000000 | 0.000000 | - | - |
| Standard 1 | | 35.7410 | 50.0000 | 50.0000 | -0.000004 | 0.0 |

Curve Type: Linear

Equation: $y = 0.6 x + 5.5$

Zn 213.857 Calibration

(ppb) **12/20/2019, 2:00:58 PM**

| Label | Flags | Int. (c/s) | Std Conc. | Calc Conc. | Error | %Error |
|-------|-------|------------|-----------|------------|-------|--------|
| Blank | | 1.85079 | 0.000000 | 0.000000 | - | - |

Insufficient data. Curve Type: Linear

APPENDIX (continued)

Date: 12/20/2019

| Label | Sol'n Conc. | Units | SD(Int) | %RSD(Int) | Int. (c/s) | Calc Conc. |
|------------|-------------|-------|----------|-----------|------------|------------|
| Cd 214.439 | 2.49742uv | ppb | 3.31409 | 132.7 | 3.07030 | 2.49742 |
| Co 238.892 | 9.86708 | ppb | 1.38994 | 14.1 | 9.37813 | 9.86708 |
| Cr 267.716 | 18.2793x | ppb | 8.46089 | 46.3 | 15.5443 | 18.2793 |
| Cu 327.395 | 202.952x | ppb | 6.34965 | 3.1 | 808.784 | 202.952 |
| Fe 238.204 | 107.487x | ppb | 15.1379 | 14.1 | 130.254 | 107.487 |
| K 766.491 | 157732x | ppb | 3739.82 | 2.4 | 1692814 | 157732 |
| Mg 279.553 | 32.5249x | ppm | 1.83982 | 5.7 | 324526 | 32.5249 |
| Mn 257.610 | 657.115x | ppb | 68.5080 | 10.4 | 3986.88 | 657.115 |
| Mo 202.032 | 3.66399 | ppb | 1.52435 | 41.6 | 3.32504 | 3.66399 |
| Na 589.592 | 103.799x | ppm | 13.8124 | 13.3 | 3106100 | 103.799 |
| Ni 231.604 | 17.1440 | ppb | 7.85497 | 45.8 | 7.22014 | 17.1440 |
| Pb 220.353 | 32.5693x | ppb | 20.6475 | 63.4 | 5.38840 | 32.5693 |
| Se 196.026 | uncal. | ppb | 200.756 | 282.8 | 2.04090 | uncal. |
| Sr 407.771 | 14265.7x | ppb | 317.105 | 2.2 | 4087226 | 14265.7 |
| Tl 190.794 | 27.1862x | ppb | 9.92705 | 36.5 | 3.83452 | 27.1862 |
| V 292.401 | 2.71225 | ppb | 1.86884 | 68.9 | 7.15020 | 2.71225 |
| Zn 213.857 | uncal. | ppb | 0.000000 | NA | 397.314 | uncal. |

APPENDIX (continued)

Date: 8/12/2019

| Label | Sol'n Conc. | Units | SD(Int) | %RSD(Int) | Int. (c/s) |
|------------|-------------|-------|-----------|-----------|------------|
| As 188.980 | 50.0000 | ppb | 0.908 | 40.1 | 2.26165 |
| B 249.772 | 100.000 | ppb | 4.737 | 2.1 | 222.337 |
| Ba 455.403 | 50.0000 | ppb | 28.026 | 0.7 | 3848.89 |
| Be 313.042 | 20.0000 | ppb | 19.436 | 1.5 | 1296.14 |
| Bi 223.061 | 10.0000 | ppb | 0.709 | 17.5 | 4.05306 |
| Ca 396.847 | 35.0000 | ppm | 42877.898 | 2.3 | 1891316 |
| Cd 214.439 | 20.0000 | ppb | 0.916 | 8.6 | 10.6940 |
| Co 238.892 | 25.0000 | ppb | 1.504 | 8.5 | 17.6822 |
| Cr 267.716 | 20.0000 | ppb | 3.394 | 20.2 | 16.7869 |
| Cu 327.395 | 20.0000 | ppb | 0.338 | 0.4 | 82.5803 |
| Fe 238.204 | 100.000 | ppb | 5.049 | 4.2 | 121.407 |
| K 766.491 | 3000.00 | ppb | 283.616 | 0.9 | 32204.5 |
| Mg 279.553 | 15.0000 | ppm | 2187.233 | 1.5 | 149669 |
| Mn 257.610 | 30.0000 | ppb | 8.255 | 4.4 | 185.760 |
| Mo 202.032 | 100.000 | ppb | 0.886 | 4.5 | 19.7262 |
| Na 589.592 | 8.00000 | ppm | 3897.974 | 1.6 | 239464 |
| Ni 231.604 | 50.0000 | ppb | 1.272 | 8.7 | 14.5723 |
| Pb 220.353 | 25.0000 | ppb | 2.536 | 53.9 | 4.70445 |
| Se 196.026 | 10.0000 | ppb | 1.762 | 71.1 | 2.47668 |
| Sr 407.771 | 100.000 | ppb | 166.574 | 0.6 | 28676.2 |
| Tl 190.794 | 10.0000 | ppb | 1.215 | 54.3 | 2.23805 |
| V 292.401 | 50.0000 | ppb | 4.364 | 12.2 | 35.7410 |

APPENDIX (continued)

sattar.wmq All Data Report 2/24/2020, 2:09:53 PM

Method Parameters

Analysis Lines

| Label | El | Wavelen. | Type | I/S | Bkg Mode | PPP | OBCL | OBCR |
|------------|----|----------|---------|-----|----------|-----|------|------|
| As 188.980 | As | 188.980 | Analyte | - | Fitted | 2 | | |
| B 249.772 | B | 249.772 | Analyte | - | Fitted | 2 | | |
| Ba 455.403 | Ba | 455.403 | Analyte | - | Fitted | 2 | | |
| Be 313.042 | Be | 313.042 | Analyte | - | Fitted | 2 | | |
| Bi 223.061 | Bi | 223.061 | Analyte | - | Fitted | 2 | | |
| Ca 396.847 | Ca | 396.847 | Analyte | - | Fitted | 2 | | |
| Cd 214.439 | Cd | 214.439 | Analyte | - | Fitted | 2 | | |
| Co 238.892 | Co | 238.892 | Analyte | - | Fitted | 2 | | |
| Cr 267.716 | Cr | 267.716 | Analyte | - | Fitted | 2 | | |
| Cu 327.395 | Cu | 327.395 | Analyte | - | Fitted | 2 | | |
| Fe 238.204 | Fe | 238.204 | Analyte | - | Fitted | 2 | | |
| K 766.491 | K | 766.491 | Analyte | - | Fitted | 2 | | |
| Mg 279.553 | Mg | 279.553 | Analyte | - | Fitted | 2 | | |
| Mn 257.610 | Mn | 257.610 | Analyte | - | Fitted | 2 | | |
| Mo 202.032 | Mo | 202.032 | Analyte | - | Fitted | 2 | | |
| Na 589.592 | Na | 589.592 | Analyte | - | Fitted | 2 | | |
| Ni 231.604 | Ni | 231.604 | Analyte | - | Fitted | 2 | | |
| Pb 220.353 | Pb | 220.353 | Analyte | - | Fitted | 2 | | |
| Se 196.026 | Se | 196.026 | Analyte | - | Fitted | 2 | | |
| Sr 407.771 | Sr | 407.771 | Analyte | - | Fitted | 2 | | |
| Tl 190.794 | Tl | 190.794 | Analyte | - | Fitted | 2 | | |
| V 292.401 | V | 292.401 | Analyte | - | Fitted | 2 | | |
| Zn 213.857 | Zn | 213.857 | Analyte | - | Fitted | 2 | | |

Conditions Sets (All lines share a single condition set)

| Pwr(kW) | PlasFlow(L/min) | AuxFlow(L/min) | NebPres(kPa) | Replicate Time(s) | Stab Time(s) | Multi Frame |
|---------|-----------------|----------------|--------------|-------------------|--------------|-------------|
| 1.20 | 15.0 | 1.50 | 200 | 5.000 | 15 | On |

Sample Introduction

| Sample Uptake(s) | Rinse Time(s) | Pump Rate(rpm) | Fast Pump |
|------------------|---------------|----------------|-----------|
| 20 | 10 | 15 | On |

General Settings

| Replicates |
|------------|
| 3 |

APPENDIX (continued)

saltar.wmq, All Data Report 2/24/2020, 2:09:53 PM

| Label | Replicates Intensity (c/s) | | |
|------------|----------------------------|----------|----------|
| Bi 223.061 | 4.13189 | 1.94054 | 3.65338 |
| Ca 396.847 | 92.6838 | 90.0478 | 77.8744 |
| Cd 214.439 | 4.29281 | 0.560265 | 1.09439 |
| Co 238.892 | 2.96868 | 6.49796 | 2.42421 |
| Cr 267.716 | 3.81540 | 2.72528 | 0.489601 |
| Cu 327.395 | 3.72635 | 4.52973 | 1.32292 |
| Fe 238.204 | 2.89665 | 3.44030 | 3.40599 |
| K 766.491 | 7.65582 | 9.02765 | 7.31488 |
| Mg 279.553 | 5.29344 | 5.21064 | 2.29925 |
| Mn 257.610 | 1.48976 | 3.12478 | 7.15032 |
| Mo 202.032 | 1.45196 | 1.80052 | 4.85127 |
| Na 589.592 | 84.7612 | 73.7809 | 72.6262 |
| Ni 231.604 | 2.12084 | 3.50606 | 4.52461 |
| Pb 220.353 | 2.50604 | 1.78326 | 3.04710 |
| Se 196.026 | 2.85839 | 1.19828 | 3.58778 |
| Sr 407.771 | 22.8660 | 25.8346 | 28.4270 |
| Tl 190.794 | 1.54585 | 1.12910 | 1.25241 |
| V 292.401 | 5.28053 | 4.17468 | 7.07579 |
| Zn 213.857 | 3.50736 | 1.03482 | 1.01019 |

| Label | Sol'n Conc. | Units | SD(Int) | %RSD(Int) | Int. (c/s) |
|------------|-------------|-------|---------|-----------|------------|
| As 188.980 | 0.000000 | ppb | 0.484 | 25.9 | 1.87135 |
| B 249.772 | 0.000000 | ppb | 0.698 | 1.9 | 36.4703 |
| Ba 455.403 | 0.000000 | ppb | 6.748 | 43.4 | 15.5651 |
| Be 313.042 | 0.000000 | ppb | 10.586 | 2.1 | 513.881 |
| Bi 223.061 | 0.000000 | ppb | 1.152 | 35.5 | 3.24193 |
| Ca 396.847 | 0.000000 | ppm | 7.900 | 9.1 | 86.8687 |
| Cd 214.439 | 0.000000 | ppb | 2.019 | 101.8 | 1.98249 |
| Co 238.892 | 0.000000 | ppb | 2.212 | 55.8 | 3.96361 |
| Cr 267.716 | 0.000000 | ppb | 1.695 | 72.3 | 2.34342 |
| Cu 327.395 | 0.000000 | ppb | 1.669 | 52.3 | 3.19300 |
| Fe 238.204 | 0.000000 | ppb | 0.304 | 9.4 | 3.24765 |
| K 766.491 | 0.000000 | ppb | 0.907 | 11.3 | 7.99945 |
| Mg 279.553 | 0.000000 | ppm | 1.705 | 40.0 | 4.26778 |
| Mn 257.610 | 0.000000 | ppb | 2.913 | 74.3 | 3.92162 |
| Mo 202.032 | 0.000000 | ppb | 1.870 | 69.2 | 2.70125 |
| Na 589.592 | 0.000000 | ppm | 6.698 | 8.7 | 77.0561 |
| Ni 231.604 | 0.000000 | ppb | 1.207 | 35.7 | 3.38384 |
| Pb 220.353 | 0.000000 | ppb | 0.634 | 25.9 | 2.44546 |
| Se 196.026 | 0.000000 | ppb | 1.225 | 48.1 | 2.54815 |
| Sr 407.771 | 0.000000 | ppb | 2.783 | 10.8 | 25.7092 |
| Tl 190.794 | 0.000000 | ppb | 0.214 | 16.4 | 1.30912 |

APPENDIX (continued)

Insufficient data.
Curve Type: Linear

| Sample 1 (Samp) | 2/24/2020, 2:06:13 PM | | | Tube 3 |
|-----------------|----------------------------|----------|----------|-------------|
| Weight: 1 | Volume: 1 | | | Dilution: 1 |
| Label | Replicates Intensity (c/s) | | | |
| As 188.980 | 2.16710 | 2.26601 | 3.04408x | |
| B 249.772 | 11236.1x | 10794.7x | 10373.8x | |
| Ba 455.403 | 97470.0x | 94026.1x | 95084.3x | |
| Be 313.042 | 229.563u | 234.778u | 254.724u | |
| Bi 223.061 | 2.19550u | 9.49919x | 4.17786x | |
| Ca 396.847 | 5507081x | 5276351x | 5256599x | |
| Cd 214.439 | 2.53982 | 4.70403 | 1.96706u | |
| Co 238.892 | 8.51279 | 9.66890 | 9.95270 | |
| Cr 267.716 | 20.6649x | 17.1873 | 8.78049 | |
| Cu 327.395 | 779.749x | 825.029x | 821.573x | |
| Fe 238.204 | 148.376x | 129.774 | 112.612 | |
| K 766.491 | 1648134x | 1704490x | 1725817x | |
| Mg 279.553 | 341299x | 327363x | 304916x | |
| Mn 257.610 | 4446.64x | 3874.88x | 3639.13x | |
| Mo 202.032 | 3.42401 | 3.52051 | 3.03060 | |
| Na 589.592 | 3582818x | 2848158x | 2887324x | |
| Ni 231.604 | 6.88152 | 5.65639 | 9.12251 | |
| Pb 220.353 | 5.42760x | 3.50342 | 7.23418x | |
| Se 196.026 | 3.68248 | 1.02678 | 1.41344 | |
| Sr 407.771 | 4189856x | 4054738x | 4017084x | |
| Tl 190.794 | 4.56576x | 2.79858x | 4.13921x | |
| V 292.401 | 5.95514 | 8.20117 | 7.29428 | |
| Zn 213.857 | 429.701 | 399.155 | 363.085 | |

| Label | Sol'n Conc. | Units | SD | %RSD | Int. (c/s) | Calc Conc. |
|------------|-------------|-------|----------|-------|------------|--------------|
| As 188.980 | 79.5607x | ppb | 61.5329 | 77.3 | 2.49240 | 79.5607 ppb |
| B 249.772 | 5791.82x | ppb | 231.995 | 4.0 | 10801.5 | 5791.82 ppb |
| Ba 455.403 | 1245.80x | ppb | 23.0095 | 1.8 | 95526.8 | 1245.80 ppb |
| Be 313.042 | -7.01030uv | ppb | 0.339530 | 4.8 | 239.688 | -7.01030 ppb |
| Bi 223.061 | 25.2601uvx | ppb | 46.5637 | 184.3 | 5.29085 | 25.2601 ppb |
| Ca 396.847 | 98.9466x | ppm | 2.57730 | 2.6 | 5346677 | 98.9466 ppm |