ANALYSIS OF DESALINATION PROCESSES FOR TREATMENT OF PRODUCED WATER FOR RE-USE AS IRRIGATION WATER

An Honors Fellow Thesis

by

LAURA ANDREA BRADT

Submitted to Honors and Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

HONORS UNDERGRADUATE RESEARCH FELLOW

May 2012

Major: Chemical Engineering

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Approved by:

Research Advisor:	Mahmoud El-Halwagi
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ABSTRACT

Analysis of Desalination Processes for Treatment of Produced Water for Re-use as Irrigation Water. (May 2012)

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Produced water is a major side product of onshore oil and gas production. This water contains a mixture of organic and inorganic compounds and requires treatment for beneficial reuse. One option for the reuse of this water is irrigation. Treatment options in desalination plants include chemical, physical, and biological methods to create water for consumption and use. This research project defines the contaminants found in produced water and develops two oilfield water hypothetical cases. A literature review describes the definition, model, and cost of the following water treatment technologies: reverse osmosis, ion-exchange, and thermal treatment methods. The analysis evaluates the suitability and performance of each process. For both oilfield cases, the thermal treatment methods performed the best in meeting the requirements for irrigation water.

DEDICATION

Jesus looked up and saw the rich putting their gifts in the offering box, and he saw a poor widow put in two small copper coins. And he said “Truly, I tell you, this poor widow has put in more than all of them. For they all contributed out of their abundance, but she out of her poverty put in all she had to live on.”

-Luke 21:1-4

God, take my faith though it is small.

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My fellow student researcher, Nesreen A., shared my enthusiasm and pushed me to understand the desalination processes. Soil scientists, Cortland Winkle and James Vandyke, offered discussion and insight into the complexity of the soil-irrigation system.

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NOMENCLATURE

TDS	Total Dissolved Solids
SAR	Sodium Adsorption Ratio
gpm	Gallons Per Minute
USGS	United States Geological Survey
Fe	Iron
Mn	Manganese
Cl^-	Chloride Ion
Na^+	Sodium Ion
Mg^{2+}	Magnesium Ion
Ca^{2+}	Calcium Ion
DOC	Dissolved Organic Carbon
RO	Reverse Osmosis
IEX	Ion Exchange
SAC	Strong Acid Cation Exchange
WAC	Weak Acid Cation Exchange
HTC	Hydrotalcite Exchange Resin
RSE	Rapid Spray Evaporation™
FTE	Freeze Thaw Evaporation

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CHAPTER I

INTRODUCTION

An Argonne National Labs study indentifies produced water as underground water brought to the surface by oil or gas production. The United States generates 1.7 to 2.3 billion gallons of produced water every day [1]. This water contains high levels of organic and salt compounds. The Argonne study found that Texas creates the most produced water at over seven million barrels per year. The most used methods of disposal are injection for enhanced recovery, injection or disposal, and surface discharge, respectively [1].

Produced water management either involves reuse or disposal. Disposal can occur by re-injection into the well, discharge into the environment, reuse in oil production, or beneficial consumption. Discharging and reusing for beneficial consumption both involve strict quality regulations. However, current treatments struggle to remove small oil particles and solvated pollutants [2]. Oil producing countries with extreme shortages of water seek to process water for beneficial consumption [3]. Beneficial consumption involves agricultural and consumer use of water.

Produced water requires treatment and processing for beneficial re-use. This usually requires lowering the concentration of salt and organic pollutants in the water [4].

This thesis follows the style of *Desalination.*

Depending on the method, produced water treatment can be cheaper than reinjection. Water poor areas especially value this treated water[5]. The required extent of contaminant removal depends on the end-use for the treated water. Water for agricultural use can contain higher levels of organics, metals and salts than water for potable use. A variety of desalination and water treatment processes exist to reduce contaminant concentrations. Common methods of produced water treatment include adsorption with activated carbon, ozonation, electrochemical oxidation, nanofiltration, reverse osmosis, ion exchange, and coagulation [6]. Each of these processes has unique operating constraints and performance limits. Using a process for a particular water treatment case requires the wastewater to meet the process input requirements as well as the capability of the treatment to meet the output requirements. In addition, several individual processes can work together to achieve the desired water quality.

Irrigation is a beneficial re-use option for produced water. Forty percent of water demand in the United States is for agricultural irrigation [7]. Any additional source of irrigation water can ease the strain placed on traditional water sources. Title 40 in the Code of Federal Regulations prohibits any discharge of produced waters from onshore facilities unless the following conditions are met: the facility is located west of the 98th meridian in the continental United States, the produced water does not exceed 35 mg/L of oil and grease, the water is used for agricultural purposes, and the water meets the requirements for the specific agricultural purpose [8]. The region to the west of the 98th meridian includes California, Colorado, Idaho, and Montana. These states have the highest levels of water use for agricultural irrigation in the United States [7]. The dry climates in the western United States make irrigation necessary to utilize the very arable land.

Research goals

This research seeks to find the optimal desalination process design for treating a particular source of produced water for beneficial use as irrigation water. As oil wells age, water makes up a greater proportion of the production. Re-injection for enhanced production disposes of the water only as long as the well is running. To add to the challenge, produced water disposal by re-injection will forfeit this valuable water resource. In areas where water is scarce, disposal by re-injection fails to match this water supply with the water demand. Irrigation water sustains crops where rain water alone cannot meet the need for water. Re-using produced water for irrigation makes a resource out of a waste. Optimizing the conversion of produced water to irrigation water ensures the economic feasibility of this beneficial system.

The overall desalination process consists of a series of desalination units working together to remove the contaminants. Process synthesis chooses which process units should be utilized and how these should fit together. Optimization investigates which process unit arrangement best meets production needs and constraints. An objective function quantifies the optimal solution. For desalination, the objective function might be based on energy or monetary resources invested. In this case, minimizing the objective function gives the optimal solution. The number of process units selected reflects both the capital and operating investment for desalination design [9]. For this research, the desalination unit combination that reduces the produced water contaminants to within the defined constraints with the least number of process units is the optimal solution.

The research goals are met through the following tasks:

- Define the parameters in produced water that influence irrigation water quality
- Develop limits for these parameters in irrigation water
- Investigate typical quantities for these parameters in produced water
- Develop oilfield case studies with a given produced water quality
- Research desalination and produced water treatment processes
- Identify operating, performance, economic data for each process
- Develop several process system models based on combining process units
- Compare end water quality and cost of process to find optimal solution
- Describe step by step methodology

Parameters

The process synthesis approach requires parameters for process flow rates, input water contaminant compositions, and desired output water contaminant maximums [9]. This research will adopt water flow rates and input water contaminant compositions from a hypothetical case. The methodology can then be extended to other cases. The desired output water contaminant maximums are given by industry and government regulations and recommendations for irrigation water quality.

The contaminants selected for study are those that can have an impact on soil and agro-ecosystems. Total Dissolved Solids (TDS) quantifies the overall salinity (concentration of elemental ions including sodium, calcium, chloride, boron, sulfates, and nitrates [10]). High TDS values indicate high concentrations of ions in solution. Osmotic stress occurs when plants cannot receive water from the soil due to a high TDS value in the soil water. The extent of this stress depends on the salt tolerance of the plant. In addition, the Safe Drinking Water Act sets a limit for the amount of chloride that will not affect drinking water quality [11]. If the irrigation water mixes with groundwater, the contaminants can enter a drinking water supply.

When irrigation water contains high levels of sodium relative to calcium and magnesium, the soil structure can deteriorate. Clay particles in soil are negatively charged and attract cations. Calcium, magnesium, and potassium cations have a small enough size and large enough charge to cause the soil minerals and organic matter to cluster into aggregates. This builds a soil structure which allows migration of air, water, nutrient, microbes, and other components of the soil ecosystem. However, sodium has a smaller charge for a larger molecule size and tends to disperse the minerals and organic matter of aggregates. Once dispersed, the soil no longer maintains pores for water and nutrient flow. The soil Sodium Adsorption Ration (SAR) divides the sodium concentration (meq/L) by the square root of the average of calcium and magnesium concentrations (meq/L). A lower SAR value indicates more favorable conditions for aggregate formation[11]. One of the goals of treatment is to increase calcium and magnesium ion concentrations while minimizing sodium concentrations in produced water thereby lowering the SAR value. This combination will aid in soil aggregation. However, increasing amounts of calcium and magnesium will also increase the TDS value, and this effect must be taken into account.

The organic components of produced water include benzene, toluene, ethyl benzene, xylene, polyaromatic hydrocarbons, alkylphenols, suspended oil, and grease. These chemicals have complex and often harmful interactions with the environment. Hydrocarbons can have toxic effects on plants and animals. They also have a tendency to accumulate in the environment. Oil and grease will contaminate environments and cause ecosystem health issues.

Boron is also found in small quantities in produced water. Boron is a plant nutrient that supports bud development and plant growth; however it can be toxic to plants in concentrations less than one milligram per liter. Toxic levels of boron affect plant leaves. In irrigation water, boron levels should not exceed 0.5 mg/L [12]. Plants can still satisfy their small need for Boron with the remaining amounts of Boron in the produced water after treatment.

Produced water conditions

A study by Szep and Kohlheb gives a flow rate of 44 gallons per minute (gpm) out of a specific Montana oilfield [13]. Another study gives flow rates as high as 1,500 to 3,000 gpm [14]. Data from the Montana oilfield as well as data from the United States Geological Survey (USGS) offer values for the concentration of produced water contaminants. The USGS data analyzes produced water from eight oil and gas wells in Oklahoma [15]. Table 1 lists the relevant characteristics of the untreated water from both wells.

Table 1
Untreated water characteristics from Oklahoma and Montana oilfields.

Parameter	Montana Oilfield Values[13]	Oklahoma Oilfield Value[15]
pH	8.2	6.4
Total Dissolved Solids (TDS)	3,700 mg/L	148,000 mg/L
Iron (Fe)	0.45 mg/L	48 mg/L
Manganese (Mn)	2 mg/L	4 mg/L
Chloride Ion (Cl^-)	500 mg/L	91,200 mg/L
Sodium Ion (Na^+)	1,570 mg/L	44,500 mg/L
Magnesium Ion (Mg^{2+})	41.9 mg/L	1,880 mg/L
Calcium Ion (Ca^{2+})	57 mg/L	8,440 mg/L

Parameter values vary greatly between the two data sets. Geographic location, geologic formation, type of hydrocarbon produced, and the age of the production well influence the physical and chemical properties of produced water [1]. Wide variations in produced water quality prevent the development of a general treatment solution that works everywhere. Each well’s unique water characteristics require unique treatment solutions.

The Oklahoma and Montana oilfield data in Table 1 focus on the aspects of the produced water that have the greatest impact on soil structure. This neglects many important environmental pollutants commonly found in produced water that affect the agro-ecosystem. Further data from the Oklahoma oilfields provide insight into typical concentrations of additional pollutants in produced water. Table 2 lists the relevant characteristics of the untreated water.

Table 2
Contaminants in Oklahoma oilfield produced water [15].

Parameter	Value
DOC	4 mg/L
Phenols	0.12 mg/L
Benzene	0.57 mg/L
Boron	4.6 mg/L

Desalination process output conditions

Irrigation water needs to meet certain quality requirements in order to avoid environmental damage to the agro-ecosystem as well as to downstream ecosystems that could be impacted by this water. Boron concentrations should be reduced to less than 0.5 mg/L to avoid toxicity to plants [16]. As mentioned before, United States law requires that the oil and grease composition of produced water discharged to land is less than 35 mg/L. The World Bank Group provides a set of parameters for produced water to meet before discharge to land or surface water. Table 3 lists the desired conditions for produced water to meet before reuse as irrigation water [17].

Table 3
Produced water requirements for discharge to land and/or surface water [17].

Parameter	Maximum Concentration
Total hydrocarbons	10 mg/L
pH	6 to 9 (range)
Total heavy metals	5 mg/L
Chloride (Cl^-)	600 mg/L

Finding the ideal concentration of ions in irrigation water involves a balance between protecting soil structure and allowing plant growth. As mentioned above, high TDS values can cause issues for plant growth, and high SAR values can cause soil structure deterioration. To avoid osmotic stress on plants, TDS values of irrigation water should remain below 600 mg/L. TDS should be as low as possible while plants are maturing [11]. However, data shows a relationship exists in which soils with high SAR values need irrigation water with greater overall concentrations of salts in order to avoid structural deterioration. For example, soil with an SAR value in the range of 0-3 should not be irrigated with water with less than 130 mg/L TDS while soil with an SAR value in the range of 6-12 should not be irrigated with water with less than 320 mg/L TDS. Soils with SAR values above 12 should not be irrigated with water with a TDS less than 830 mg/L [5]. However, this value for TDS exceeds the amount that will cause osmotic stress in plants.

Irrigation with saline water will cause a change in the SAR value for the soil. The complexity of soil system prohibits the analysis of the extent of this SAR change for the soil. The full understanding of this phenomenon requires development of a soil model based on empirical data. This research assumes that the water is applied to soil with a SAR of less than 12 which will change negligibly with the addition of irrigation water. This means that the TDS concentration leaving the desalination process should range from 320 – 600 mg/L TDS.

Case studies

This research develops two hypothetical oilfields located in the United States west of the 98th meridian; the location qualifies the produced water for agricultural purposes such as irrigation. The Oklahoma and Montana oilfield data form the basis for the hypothetical produced water characteristics. These characteristics give the input water composition for the desalination process. The requirements for irrigation water quality constrain the desired output water contaminant maximums for the desalination process. The input characteristics and output requirements influence and constrain the treatment process design. Each type of process has its own constraints as well. The input stream must fit within the process constraints, and the final product should meet the irrigation water quality. The parameter values are summarized in Table 4 for each of the oilfield cases as well as for irrigation water.

Table 4
Desalination process parameters.

Parameter	Case I Input Value	Case II Input Value	Output Concentration Constraint
Total hydrocarbons	4.69 mg/L	200 mg/L	10 mg/L maximum
TDS	148,000 mg/L	3,700 mg/L	320-600 mg/L
Boron	4.6 mg/L	1.8 mg/L	0.5 mg/L maximum
pH	6.4	8.2	6 to 9
Chloride (Cl^-)	91,200 mg/L	500 mg/L	150 mg/L maximum
Flow rate	2,000 gpm	44 gpm	-

CHAPTER II

METHODS

The research involves two phases: a literature review to compile process data and a process analysis to determine performance of treatment methods for each hypothetical case. This results in a high-level understanding of desalination process technology as well as wastewater treatment process synthesis.

Literature review

Desalination and wastewater treatment technology are the focus of significant engineering research work especially in the disciplines of mass transport and environmental engineering. The literature review involves searching for resources covering the specific processes and technology involved in wastewater treatment. These resources come from scholarly journals including Desalination, Journal of Hazardous Materials, Journal of Membrane Science, as well as Water Science and Technology. The Elsevier website as well as the Texas A&M University library catalog website, libcat, allowed the search for relevant journal articles. In addition, publications by the USGS, Argonne National Laboratory, and Society of Petroleum engineers provided relevant information. Finally, books and reference materials from the library at Texas A&M University as well as Elsevier added to the literature. The search focused on finding descriptions of the processes, potential process performance models, and process costs.

Process description

The process description provides a foundational understanding of each process. This involves finding information on the contaminant removal mechanism as well as any constraints on the amount and type of contaminants in the water. Any advantages or disadvantages for the process will also form part of the description. Understanding the separation mechanism contributes to the development of a process performance model.

Process performance models

The process performance model allows for an output composition to be found based on the input concentration for a given process. There are several different approaches for developing a model. The simplest model involves setting a linear reduction of contaminate concentration based on a single set of input/output data. If additional data points are added, the model will become more complicated; however, the model will also have greater accuracy and applicability. Mass transfer models give a different view from simple reduction models.

Process cost

A process is useless if it is not economically feasible. Several factors aid in understanding the total cost of the process: initial capital investment, maintenance cost, labor cost, energy cost [18]. Process economics balance the value of the product with the total cost to find an optimal solution. The value of the treated water depends on many factors including local demand for water, local water abundance, and water quality. The process cost aids in understanding the potential for produced water reuse as irrigation water.

Conducting the literature review for each water treatment process gives significant amounts of information and data for review and synthesis into a comprehensive process summary. This summary has the process definition as a foundation, a process model for performance evaluation, and process cost for feasibility evaluation. The high-level summary allows for analysis of each process.

Process analysis

The analysis evaluates how each process meets the needs of the produced water cases introduced in chapter one. The description determines whether the process can even accommodate the water within its constraints and capabilities. For instance, reverse osmosis has an upper limit on the TDS levels. Any water exceeding this level does not meet the process constraints and cannot use this treatment method. If a produced water case meets all of the process constraints, the process model gives values for post-treatment contaminant concentrations. Economic data assigns a cost for treating the water. This analysis repeats for each produced water case with each process. Several combinations of any number of the processes provide additional analysis.

CHAPTER III

RESULTS

Literature review

This literature review involves finding characteristic process information in order to achieve an overall perspective for each process. Although many resources offer information on desalination processes, finding a comprehensive source is difficult. Process literature tends to focus on a single aspect or use of a process instead of the definitive information which allows for high-level process analysis.

The literature review has a subsection dedicated to each process. These subsections are further divided into sections dedicated to performance models and economic data. The analysis will follow the description of literature review results.

Reverse osmosis

Extensive research and industry efforts focus on the use of reverse osmosis (RO) for wastewater treatment. RO is a type of membrane treatment process.

Process

Osmosis involves the movement of water between a solution of high contaminant concentration and a solution of low contaminant concentration. In the absence of other driving forces, osmotic pressure drives the flow of water from low concentration to high concentration. This forms two impure solutions. RO involves application of a pressure greater than and opposite to the osmotic pressure; this causes water to flow from high concentration to low concentration forming a relatively pure water solution as well as a waste brine with concentrated contaminants [19]. RO primarily removes dissolved inorganic and ionic contaminants; however, small organic molecules (less than 200 g/mol molecular weight) and dissolved gases remain in the treated water [19, 20]. Alleman gives the upper level of TDS that RO can treat to acceptable levels as 40,000 mg/L TDS[21]. Due to its inability to remove small organic molecules and high TDS levels, RO alone is not sufficient for treatment of produced water. A significant body of research involves the combination of RO with other water treatment processes.

Venkatesan gives polyamide resin as a common material for the membrane. Potential issues with this type of membrane involve the interaction of chloride ions with the polyamide resin. The chloride can remove the hydrogen from the amide group on the membrane molecules[22]. The removal of hydrogen would create a charged membrane. A charged membrane would not maintain its impermeability to ions. Another issue with the RO membrane involves the phenomenon of scaling also referred to as fouling. Scaling occurs when the concentration of brine increases as water passes into the treated solution. Certain salts (especially calcium and magnesium salts) will reach saturated levels in the brine and begin to precipitate out of the solution [22]. These solids could settle on the membrane and cause damage. The removal of compounds harmful to the membrane gives another reason for the combination of RO with other processes.

Performance models and cost

One method of modeling process performance involves creating a linear relationship based on input and output concentration values. A study presented at the 12th Aachener Membrane Kolloquium gives input and output concentration values for the following reverse osmosis process set-up: 2.5 m^3/ h (11 gpm) of water pretreated by oil/water separation, softeners, and filtration with an applied pressure of 15 bar and a pH of 7. The membrane used is a polyamide spiral round cross-flow membrane [5]. The values are given in Table 5.

Table 5
Low TDS RO process inputs and outputs[5].

Parameter	Input Value	Output Value	Percent Reduction
Total hydrocarbons	1.5 mg/L	1 mg/L	33.3%
TDS	816 mg/L	33 mg/L	96.0%
Sodium	245 mg/L	1.93 mg/L	99.2%
Calcium	0.7 mg/L	0.1 mg/L	85.7%
Magnesium	135 mg/L	100 mg/L	25.9%
Chlorine	753 mg/L	18 mg/L	97.6%
Boron	0.252 mg/L	0.125 mg/L	50.4%

An additional study gives input and output concentration values for the following reverse osmosis process set-up: 0.25 L/s (4 gpm) of water pretreated by colloidal separation, softeners, and filtration with an applied pressure of 19 bar and a pH of 4 to 11. The membrane is a thin-film spiral round cross-flow membrane[23]. The permeate flow was 0.028 L/s (0.4 gpm). These conditions give a RO recovery (ratio of permeate flow to feed flow) of around 10%. The values are given in Table 6.

Table 6
High TDS RO process inputs and outputs[23].

Parameter	Input Value	Output Value	Percent Reduction
Total hydrocarbons	77.4 mg/L	18.4 mg/L	76.2%
TDS	6,554 mg/L	295 mg/L	95.5%
Sodium	2,252 mg/L	69 mg/L	96.9%
Calcium	56 mg/L	0.1 mg/L	98.9%
Magnesium	9.1 mg/L	0.1 mg/L	98.9%
Chloride	3,361 mg/L	106 mg/L	96.8%
Boron	28 mg/L	17 mg/L	39.3%
pH	7.7	6.7	13.0%

Venkatesan and Wankat use a model to prove that RO recovery versus input TDS has a linear relationship. Their results show that an initial TDS value of 5000 mg/L gives a maximum RO recovery of 95% while an initial TDS value of 12000 mg/L gives a maximum RO recovery of 87% [24]. The line with these values has the equation

$$\text{RO recovery (\%)} = -0.00115\ (\text{L/mg}) * (\text{input TDS mg/L}) + 100 \tag{1}$$

Another way to view the system is by a mass balance where the amount of contaminant in the input must equal the amount leaving in the output and waste streams. The amount of contaminant is the product of flow rate times the concentration for a particular stream. This is expressed as

$$Q_F*C_F = (1- Q_O)* C_W + Q_O*C_O \tag{2}$$

where Q_F is the feed flow rate, Q_O is the output flow rate, C_F is the feed concentration, C_W is the waste concentration, C_O is the output concentration[22]. High recovery gives higher contaminant concentrations in the output stream. The data in Table 6 has a low RO recovery value and thus has lower values of contaminants in the output stream.

Operating with a low RO recovery removes a greater percentage of contaminants yielding lower amounts of very pure water. However, a large amount of technology and resources are invested in producing more product. Higher RO recovery has a lower cost, while lower RO recovery has a higher cost. Venkatesan gives the cost of product water at a 26.2% RO recovery as ranging from \$4.11/m^3 to \$21.08/m^3 depending on the cost of brine disposal; at 35% RO recovery the cost ranges from \$3.06/m^3 to \$14.07/m^3 [22]. Large RO facilities with capacities exceeding 50,000 gpm can achieve costs as low as \$0.53/m^3 [25]. RO will be most economically favorable at lower initial values of TDS giving a higher maximum RO recovery. Also, running the process at high flow rates will increase economic feasibility.

Ion exchange

Ion exchange (IEX) involves the transfer of ions between a resin and the solution needing treatment. Though exchanging ions for ions may seem counterproductive, IEX can provide advantages in produced water treatment by replacing less desirable ions.

Process

The IEX process targets the removal of ionized atoms especially calcium ions and magnesium ions [26]. The treatment occurs in an IEX column which is packed with the exchange resin. Wastewater passes through this column with the exchange happening further and further along the length of the column as the resin progressively exchanges its ions for the contaminant ions. The wastewater has continuous contact with unexchanged resin improving the contaminant removability [22]. Eventually the exchange resin will have exchanged all of its available ions and will require regeneration. Ion exchange is a reversible process allowing for regeneration [27]. Resin regeneration is achieved with through the use of a solution that will replace the waste ions saturating the resin with the original exchange ions.

The technical summary prepared by J.D. Arthur, B.G. Langhus, and C. Patel discusses several points regarding IEX. This source indicates that IEX favors the removal of divalent ions (i.e. Ca^{2+} and Mg^{2+}) over the removal of monovalent ions (i.e. Na^{+}).This is due to the thermodynamics of the process. The resin ion is usually monovalent and releases two ions for every divalent ion adsorbed to maintain charge neutrality. Two ions in solution have a higher entropy value than one ion in solution. Systems will favor changes that increase entropy. IEX can also remove arsenic, heavy metals, nitrates, radium, salts, and uranium. Typical resins are either composed of naturally occuring zeolites or synthetic organic resins.

J.D. Arthur, B.G. Langhus, and C. Patel introduce the different kinds of ion exchange. Strong acid cation (SAC) exchange has a sulfonic acid (SO_3H) group on the exchange resin which gives up the hydrogen as H^{+} to exchange for sodium, calcium, magnesium, and barium ions in solution. SAC resins require the use of a strong acid for regeneration. Weak acid cation (WAC) exchange has a carboxylic acid (COOH) group on the exchange resin to primarily remove divalent salts as well as bicarbonate ions. WAC resins require the use of a strong acid and base for regeneration. The performance of WAC resins depends on the solution’s pH. Base resins are used for anion removal. Strong base resins have an ammonia hydroxide (NH_3OH) group to exchange with anions. These resins are regenerated with sodium hydroxide. Weak base resins can also be used for anion removal Acid resins are the most common resins for water treatment and as the names indicate selectively remove cations and not necessarily anions [27].

One advantage of IEX is its use as a water softening process. Water hardness indicates the concentration of calcium and magnesium ions in solution. Hard water has higher amounts of calcium and magnesium. As discussed before, these ions can cause scaling damage to an RO membrane. SAC and WAC resins can remove calcium and magnesium, softening the water and decreasing the risk of RO membrane damage. When IEX precedes RO in this manner, the RO waste brine which is high in the exchange ions from the resin can successfully recharge the ion exchange bed [22]. This is one example of how multiple treatment process units can work together to achieve greater overall treatment levels.

High TDS levels can only be processed by an IEX column for a short time before the resin exchange ions are spent. This will result in low production levels of treated water [22]. These production levels are not economically sustainable. Ideally the TDS value of feed wastewater should not exceed 1000 mg/L [26]. However, WAC resins can handle TDS values in excess of 3000 mg/L. Although handling slightly higher values of TDS, WAC resins require regeneration by hydrochloric acid solution followed by sodium hydroxide solution. The use of these corrosive solutions calls for corrosion resistance in the ion exchange column as well as the surrounding piping [14]. These measures will increase the overall cost of the IEX system.

Performance models and cost

Empirical data for IEX performance is rarer than RO performance data.

The first set of data involves both anion and cation exchange. The cation exchange is performed by a permutite resin consisting of sodium alumino silicate. The permutite is pretreated with acid to gain exchangeable hydrogen cations. The permutite is highly capable of removing sodium cations in solution. The anion exchange is performed by hydrotalcite (HTC) which consists of layered double hydroxides with exchangeable anions. Lime pretreatment precedes the IEX treatment. Permutite converts the basic pH to an acidic pH while the HTC increases the pH. Overall the process reduces the pH by 60% from 12.4 to 5 [28]. Table 7 has the IEX TDS input and output values for this process.

Table 7
IEX TDS inputs and outputs[28].

Step	TDS Input Value	Percent Reduction	TDS Output Value
Permutite Cation Removal	8,000 mg/L	67.5%	2,600 mg/L
HTC Anion Removal	2,600 mg/L	76.9%	600 mg/L

Since HTC primarily removes chloride ions, the assumption is made that the process removes 75% of chloride ions.

A second set of IEX data was found using EMIT Water Discharge Technology, LLC technology which employs the DOWEX G-26 SAC resin. This process also uses lime pretreatment[27]. The approximate TDS reduction is 76.0%. The data values are given in Table 8.

Table 8
SAC IEX process inputs and outputs[27].

Parameter	Input Value	Output Value	Percent Reduction
Sodium	486 mg/L	12 mg/L	97.5%
Calcium	22.2 mg/L	113 mg/L	-409%
Magnesium	13.2 mg/L	0.92 mg/L	93.0%
Potassium	13.5 mg/L	0.95 mg/L	93.0%
Chloride	18 mg/L	42 mg/L	-133%

IEX is a relatively simple process and therefore has a low level of operational energy use which corresponds to a lower overall process cost [28]. One source gives the cost of removing most sodium cations using natural zeolites as \$6.30/m^3 [29].

Thermal treatment

Both RO and IEX have upper limits to the TDS levels of input water. Thermal processes can treat produced water with very high levels of TDS.

Process

The premise of thermal treatment involves adding or removing thermal energy to the wastewater solution to facilitate the separation of the water from the contaminants. One thermal technique is referred to as Rapid Spray Evaporation™ (RSE). In RSE, a fine spray of wastewater enters a heated chamber with such conditions as to cause the pure water to evaporate leaving waste brine particles on filters in the chamber. The water vapor eventually condenses to give the treated solution [27]. Rather than adding heat to cause separation, freeze/thaw evaporation (FTE) removes heat to cause separation. The produced water is again separated into small drops before adding to an ice pile where pure water crystals freeze and a brine solution is removed as a liquid. The frozen water is recovered after thawing. The brine solution remains a liquid due to the contaminants lowering the freezing point of the solution. FTE does use a significant amount of land on which to form the ice pile and the process is primarily feasible in the winter months[30]. These thermal processes take advantage of the depressed freezing points and elevated boiling points of brine solutions compared to pure water to separate very pure water from the waste solutions. Thermal processes have fewer constraints than either RO or IEX processes and are capable of treating high TDS levels.

Performance models and cost

RSE can treat produced water streams with TDS values as high as 160,000 mg/L. Costs are estimated to be around \$0.25/m^3 of treated water. RSE is a developing technology and data does not exist for hydrocarbon and boron removal. However, the percent reduction can be considered high given the high percent reductions for the other contaminants. Table 9 gives the RSE process inputs and outputs.

Table 9
RSE process inputs and outputs[27].

Parameter	Input Value	Output Value	Percent Reduction
TDS	130,000 mg/L	440 mg/L	99.7%
Sodium	25,000 mg/L	160 mg/L	99.4%
Calcium	79 mg/L	1.6 mg/L	98.0%
Magnesium	490 mg/L	1.7 mg/L	99.7%
Chloride	5,000 mg/L	90 mg/L	98.2%

Oilfields in Wyoming have successfully applied the FTE technology to treat produced water. For most contaminants, FTE results in a 90% reduction. Table 10 gives data values for percent reduction of process inputs and outputs The cost is estimated to be around \$0.13/m^3 product water [30].

Table 10
FTE process inputs and outputs[27].

Parameter	Input Value	Output Value	Percent Reduction
TDS	9,790 mg/L	1,000 mg/L	89.8%
Total hydrocarbons	39.1 mg/L	3.1 mg/L	92.0%

Analysis

This analysis provides tools for high-level decision making. A process design engineer assigned to the two hypothetical oilfield cases presented in Table 4 could use the method in this analysis to narrow down which process technologies have potential for a specific case. This analysis will also eliminate from consideration process technologies which are unsuitable for the case.

Reverse osmosis

RO cannot treat the case I oilfield from Table 4. RO requires a TDS value of less than 40,000 mg/L; case I has a TDS value of 148,000 mg/L.

Case II can be treated by RO due to its TDS value of only 3700 mg/L. However, this is probably not ideal due to the high chloride ion concentration. Plugging the TDS value into Eq. (1) gives a maximum 95.7% RO recovery. A set of data values were chosen due to the relative closeness of the input values to those of case II. Using the empirical process values for RO across a thin-film spiral round cross-flow membrane at an applied pressure of 19 bar (Table 6) gives the results outlined in Table 11. Even while trying to maximize RO recovery in order to maximize irrigation water production, significant volumes of waste are formed with RO. Given the volume of waste, the cost for the process is assumed to be: \$14/m^3. Table 11 shows that RO did not successfully treat the case II water for irrigation water reuse. The two parameters that met acceptable post-treatment levels were chloride and pH. TDS levels were overtreated and are too low for irrigation water use. Hydrocarbon and boron levels remain too high for irrigation water use.

Table 11
RO process inputs and outputs for oilfield case II.

Parameter	Input Value	Percent Reduction	Output Value	Irrigation Water Constraints	Acceptable (Yes/No)
Total hydrocarbons	200 mg/L	76.2%	47.5 mg/L	10 mg/L maximum	No
TDS	3,700 mg/L	95.5%	166.5 mg/L	320-600 mg/L	No
Chloride	500 mg/L	96.8%	15.8 mg/L	150 mg/L maximum	Yes
Boron	1.8 mg/L	39.3%	1.1 mg/L	0.5 mg/L maximum	No
pH	8.2	13.0%	7.1	6 to 9	Yes

Ion exchange

IEX cannot treat the case I oilfield from Table 4. IEX requires a low TDS value; case I has a TDS value of 148,000 mg/L.

Case II can be treated by IEX, because its TDS value of 3700 mg/L is relatively close to the ideal maximum of 1000 mg/L TDS. The higher TDS value (>3000 mg/L) requires the use of a WAC resin. Using the empirical process values for IEX through a column with permutite and HTC resins (Table 8) gives the results outlined in Table 12. The cost is approximated as $6.30/m^3 treated water. Table 12 shows that IEX did not successfully treat the case II water for irrigation water reuse. The only parameter that met acceptable post-treatment levels was chloride. TDS and pH levels were slightly overtreated and are too low for irrigation water use. Hydrocarbon and boron levels remain too high for irrigation water use.

Table 12
IEX process inputs and outputs for oilfield case II.

Parameter	Input Value	Percent Reduction	Output Value	Irrigation Water Constraints	Acceptable (Yes/No)
Total hydrocarbons	200 mg/L	0%	200 mg/L	10 mg/L maximum	No
TDS	3,700 mg/L	92.5%	277.5 mg/L	320-600 mg/L	No
Chloride	500 mg/L	75.0%	125 mg/L	150 mg/L maximum	Yes
Boron	1.8 mg/L	0%	1.8 mg/L	0.5 mg/L maximum	No
pH	8.2	60%	3.3	6 to 9	No

Thermal treatment

Case I can be treated by RSE which can treat produced water streams with TDS values as high as 160,000 mg/L. Costs are estimated to be around \$0.25/m^3 of treated water. Using the empirical process values for RSE water treatment (Table 9) gives the results outlined in Table 13. Table 13 shows that RSE successfully treated 80% of the parameter of the case I water for irrigation water reuse. The only parameter that did not meet acceptable post-treatment levels was chloride. TDS, hydrocarbon, boron, and pH levels all achieved acceptable levels for irrigation water use.

Table 13
RSE process inputs and outputs for oilfield case I.

Parameter	Input Value	Percent Reduction	Output Value	Irrigation Water Constraints	Acceptable (Yes/No)
Total hydrocarbons	4.69 mg/L	99.0%	0.05 mg/L	10 mg/L maximum	Yes
TDS	148,000 mg/L	99.7%	444 mg/L	320-600 mg/L	Yes
Boron	4.6 mg/L	98.0%	0.1 mg/L	0.5 mg/L maximum	Yes
pH	6.4	-	6.4	6 to 9	Yes
Chloride (Cl^-)	91,200 mg/L	98.2%	1642 mg/L	150 mg/L maximum	No

Case II can be treated by FTE, because its TDS value of 3700 mg/L is relatively close to the experimental feed value of 10000 mg/L TDS. Using the empirical process values for FTE (Table 10) gives the results outlined in Table 14. The cost is approximated as $0.13/m^3 treated water. Table 14 shows that RSE successfully treated 80% of the parameters in the case II water for irrigation water reuse. Hydrocarbon levels were the only parameter that did not meet acceptable post-treatment levels. TDS, chloride, boron, and pH levels all achieved acceptable levels for irrigation water use.

Table 14
FTE process inputs and outputs for oilfield case II.

Parameter	Input Value	Percent Reduction	Output Value	Irrigation Water Constraints	Acceptable (Yes/No)
Total hydrocarbons	200 mg/L	92.0%	16 mg/L	10 mg/L maximum	No
TDS	3,700 mg/L	89.8%	377 mg/L	320-600 mg/L	Yes
Boron	1.8 mg/L	90.0%	0.2 mg/L	0.5 mg/L maximum	Yes
pH	8.2	-	8.2	6 to 9	Yes
Chloride (Cl^-)	500 mg/L	90.0%	50 mg/L	150 mg/L maximum	Yes

CHAPTER IV

CONCLUSIONS

This research had the goal of analyzing the suitability and performance of several desalination processes for the purpose of converting produced water into irrigation water. This is a complex goal due to the immense variety found in produced water qualities, the specific needs and constraints of each process, and the immense variety found in crop and soil needs from irrigation water. Due to the complexity of designing a process that meets all of the treatment needs and falls withing all of the system constraints, this research pursues a high-level process analysis. The high-level process analysis gives results to direct the design engineer toward processes that have potential to successfully treat the water and away from processes that cannot successfully treat the water.

There were two case studies developed for this research. Case I involves an oilfield with produced water high in TDS and low in hydrocarbon content. The high TDS values automatically removed the possibility of treatment by RO and IEX. Both of these processes have a constraint on the maximum amount of TDS in the process feed stream. This leaves the thermal treatment RSE as the only option for processing the case I oilfield water. RSE successfully treats most of the water parameters for irrigation use. RSE only failed in bringing chloride concentrations under the maximum of 150 mg/L. A process designer could then focus on using RSE for case I. The next steps in the design process would involve looking for any pretreatment and posttreatment options that would result in all of the parameter values being in the acceptable ranges. One such option could involve using IEX as a postreatment which could lower the chloride levels to within the acceptable maximum.

Case II involves an oilfield high in hydrocarbon content and low in TDS levels. The RO and IEX treatment methods were able to treat the water, but did not achieve acceptable values with the exception of lowering chloride levels. Both RO and IEX overtreated the TDS levels and resulted in TDS levels below the acceptable range. In order to reach acceptable TDS levels, the RO and IEX must be followed up with posttreatment processes that could increase the TDS. FTE was also able to treat the case II oilfield and achieved acceptable levels for all of the parameters except for the hydrocarbon level. A process design engineer working with case II would choose to further pursue using the FTE treatment method.

These case studies demonstrate how the process design engineer can use a high-level process analysis to narrow down treatment options for each oilfield water source and irrigation water destination. The results of the literature review demonstrated thermal treatments to be suitable for a wide range of produced water qualities. The thermal treatments had very high percent reduction values for each parameter. RO and IEX have stricter constraints on feed stream contaminant levels and are less successful in reaching acceptable levels for produced water parameters.

In the future this work can be extended to include a detailed economic analysis for each process. Additionally, the analysis can look at the ability of multi-unit processes to treat the produced water. For instance, the RSE process combined with IEX posttreatment could be studied. More processes can be studied to expand the treatment options that can be included in the high-level process analysis.

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