

THESIS

DEVELOPMENT OF AN ELECTROCOAGULATION BASED TREATMENT TRAIN FOR
PRODUCED WATER WITH HIGH CONCENTRATIONS OF ORGANIC MATTER

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ABSTRACT

DEVELOPMENT OF AN ELECTROCOAGULATION BASED TREATMENT TRAIN FOR PRODUCED WATER WITH HIGH CONCENTRATIONS OF ORGANIC MATTER

Well stimulation in the form of hydraulic fracturing has made unconventional oil and gas extraction economically feasible, significantly increasing the number of producing oil and gas wells in the United States in the last several decades. Both the hydraulic fracturing process and shale play development has created a large amount of oil and gas associated wastewater. Deep well injection or disposal wells are the preferred and most widely used method for managing produced water. This industry standard both eliminates valuable water resources from the hydrologic cycle and can be linked to the increasing frequency of seismic events in parts of the United States. This paper investigates water treatment processes in the context of beneficial reuse towards irrigation. Treating produced water on well pad locations followed by agricultural use within close proximity minimizes trucking costs and environmental impacts as well as recycles industrial wastewater back into the hydrologic cycle. High concentrations of salts and organic matter must be removed in addition to other contaminants (Benzene, Boron, Calcium, and Magnesium) from produced water collected from Noble Energy's Wells Ranch Central Processing Facility (CPF) before being applied towards a secondary use. Electrocoagulation coupled with a strong oxidant creates a more effective coagulation process prior to ultrafiltration, granular activated carbon and reverse osmosis processes. Organic matter removal and its potential for significant fouling of reverse osmosis membranes remains a major challenge as concentrations of total organic carbon in Noble Energy CPF produced water are typically around

1,500 mg/L after ultrafiltration. Four treated produced water effluent qualities generated in the CSU Environmental Engineering lab, in addition to freshwater were used to irrigate two non-food crops. Switchgrass and canola were arranged at the CSU greenhouse and watered using a drip irrigation system. The fate of regulated volatile organics and impact of salt accumulation are the primary parameters of interest for impaired water usage. This study is constructed to provide a baseline for the development of a larger scale pilot designed to treat produced water from an operator's storage tanks and used to irrigate nearby agricultural land. The concentration of dissolved organic carbon can be linked directly to the economic feasibility and operational challenges of treatment, both in the context of pretreatment and required maintenance for reverse osmosis. Although produced water from gel-based hydraulic fracturing in the Denver-Julesburg can be very difficult to treat, beneficial reuse should be an important consideration for future shale play development in Colorado and other parts of the United States.

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1. INTRODUCTION

Well stimulation in the form of modern hydraulic fracturing practices has made oil and gas extraction economically feasible from shale formations, creating a shale boom in the United States. An average 2.5 million gallons of process injection water in addition to formation water flows backs over the lifetime of a well (Freyman, 2014). This industrial waste water, referred to as produced water, generally contains high concentrations of salts, carcinogenic organic compounds, and a wide range of other chemical constituents. Current industry practices involve injecting produced water back into a subsurface formation at designated deep injections wells. Alternative shale water management strategies such as treating produced water for secondary uses promotes recycling valuable water resource, as well as mitigated potential risks associated with disposal wells. This thesis can be divided into two sections: 1) Produced water treatment 2) Application of treated produced water effluent used as irrigation water for beneficial reuse. Different unit processes, particularly electrocoagulation, were used to treat water at the Environmental Engineering Laboratory at CSU. Produced water treated to different water quality effluent levels was then used to irrigate non-food crops, switchgrass and canola, at the CSU greenhouse for a period of 3-4 months. Produced water was collected from Noble Energy's Wells Ranch Central Processing Facility over a 6 month period and was representative of flow back water from gel-based fracturing fluids. Wells Ranch is located in the Denver-Julesburg Basin with the Niobrara shale formation. Chapter 2 provides background information for this study as a Literature Review. Chapter 3 provides the materials and methodology used, experimental results and a synthesis of those results to draw a set of conclusions for this research. The emphasis of this thesis is produced water treatment. The irrigation study provides a

research purpose and context for the treatment processes evaluated. This thesis is a unique collaboration between a water solutions company called Water Tectonics, and CSU senior design engineering projects. Irrigation management and reverse osmosis testing were the two contributions made by these senior design groups. Bench scale electrocoagulation and ultrafiltration technologies were provided by Water Tectonics along with several collaborative phone calls with their CEO and project leaders. Chapter 4 outlines the large potential for process optimization and future work that can be built on this research.

2. LITERATURE REVIEW

2.1 Unconventional Oil and Gas in the U.S.

Energy usage is an essential component to both the current standard of living and economic growth in the United States. In 2014 the United States produced 87.39 quadrillion BTUs of fuel and consumed 98.48 quadrillion. EIA projects that U.S. production will equal consumption by 2030 as both slowly increase to roughly 105 quadrillion BTUs (EIA, 2015). Although population growth and development continue to demand energy from a wide and diverse range of sources; natural gas, petroleum, and related liquids still make up 63% of the total U.S. energy consumption (EIA, 2015). As the United State depletes it's easy to access conventional reservoirs, unconventional shale extraction has significantly increased the amount of oil and gas available for production.

The resource pyramid found in figure 1 provides a useful tool for understanding the mass availability of oil and gas reservoirs, the difference is quality and the integration of current economic feasibility (Holditch, 2006). A conventional reservoir refers to oil and gas that has migrated from a hydrocarbon rich source rock and accumulated in a concentrated area. The top portion of the pyramid identifies these resources as high quality, easy to develop, and available in smaller in volumes. Unconventional reservoirs are shown further down the pyramid. These are lower quality and more expensive to extract but spatially extensive. The notation "md" is a unit of formation permeability (Holditch, 2006). In 2013, 87% of the global oil production came from conventional reservoirs and 3% unconventional. Unconventional production is projected to rise to 12% by 2040 (University of Michigan, 2015). Natural gas is projected to provide 29% of the total U.S. energy consumption by 2040 (EIA, 2015). Unconventional shale gas and tight gas

are expected to make up 71% of the domestic dry gas production by 2035 (Sieminski, 2012). These projections show that there is currently an economic incentive to develop shale resources, and that demand will only continue to increase.

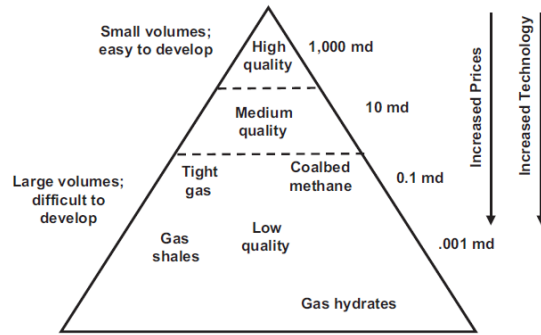


Figure 2-1: Resource Pyramid (Holditch, 2006)

The United States is ranked 2nd in the world for “technically recoverable shale oil resources” at 58 billion barrels and is ranked 4th for shale gas at 665 trillion cubic feet (EIA, 2013). It is important to differentiate these estimates from economically recoverable resources which are determined by operational costs, oil and gas prices, and well production rates (EIA, 2013). Major U.S. shale plays include the Marcellus, Bakken, Eagle Ford, Permian, Anadarko-Woodford, Granite Wash, Haynesville, Utica and the Niobrara. Typically these shale plays stretch across large areas but also require horizontal drilling practices that maximize shale surface area in order to be economically feasible.

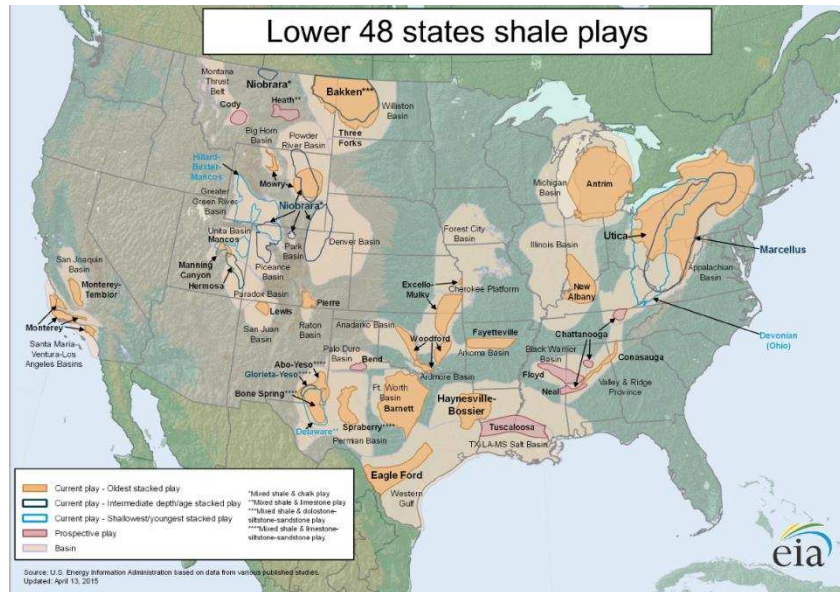


Figure 2-2: U.S. Shale Play Map (EIA, 2015)

2.1.1 Hydraulic Fracturing

Hydraulic fracturing is a form of well stimulation that has made oil and gas extraction from shale rock economically feasible in addition to the advancement in horizontal drilling (Holditch, 2006). An unconventional reservoir is a tight shale formation with low hydraulic conductivity. Hydraulic fracturing is the process of injecting a fracturing fluid into a wellbore at extremely high pressures to induce fractures or cracks in the rock. This significantly increases the permeability and porosity of the formation and ultimately hydrocarbon recovery. In this case, the source rock also functions as the reservoir rock. Hydraulic fracturing fluids consist of 90 percent water, 9 percent sand/proppant, and 1 percent chemical additives (Anadarko, 2015). Table 2-1 describes the composition of hydraulic fracturing fluid and the function of each additive.

Table 2-1: Hydraulic Fracturing Fluid Composition (Anadarko, 2015)

Additive	Purpose	Downhole Result	Other Common Uses
Acid	Helps dissolve minerals and initiate cracks in the rock	Reacts with minerals present in the formation to create salts, water and carbon dioxide	Swimming pools, chemical cleaners
Corrosion Inhibitor	Protects casing from corrosion	Bonds to metal surfaces (pipe), any remaining product not bonded is broken down by micro-organisms and consumed or returned in produced water	Pharmaceuticals, acrylic fibres and plastics
Biocide	Eliminates bacteria in the water that can cause corrosive by-products	Reacts with micro-organisms that may be present in the treatment fluid and formation	Disinfectant, sterilizer for medical and dental equipment
Breaker	Allows a delayed breakdown of gels	Reacts with the crosslinker and gel once in the formation, reaction produces ammonia and sulfate salts	Hair colouring, disinfectant, manufacture of common household plastics
Clay Stabiliser	Temporary or permanent clay stabiliser to lock down clays in the shale structure	Reacts with clays in the formation through a sodium-potassium exchange, reaction results in sodium chloride (salt)	Low sodium table salt substitute, medicines, intravenous fluids
Crosslinker	Maintains viscosity as temperature increases	Combines with the breaker in the formation to create salts	Laundry detergents, hand soaps, cosmetics
Friction Reducer	Reduces friction effects between the water and the pipe	Remains in formation where temperature and exposure to breaker allows micro-organisms to consume	Cosmetics, make-up, nail and skin products
Gel	Thickens the water in order to suspend the proppant and sand	Combines with breaker in the formation to enhance fluid return to the borehole	Cosmetics, baked goods, ice cream, toothpaste, sauces, salad dressings
Iron Control	Helps to prevent precipitation of metal oxides	Reacts with the minerals in the formation to create simple salts, carbon dioxide and water which, are returned in produced water	Food additive, beverages, lemon juice
Non-Emulsifier	Used to break or separate oil and water mixtures	Generally returns in produced water, in some shale formations, can return via produced natural gas	Laundry detergents, dishwasher detergents, carpet cleaners
pH Adjusting Agent	Maintains effectiveness of other additives such as crosslinkers	Reacts with acidic agents in the treatment fluid to maintain a neutral (non-acidic, non-alkaline) pH, produces salts, water and carbon dioxide, returns in produced water	Detergent, washing soda, water softener, soap
Scale Inhibitor	Prevents build-up of scale in pipe and formation	Product attached to the formation, majority of the product returns with produced water, remainder consumed by micro-organisms	Household cleaners, de-icers, paints
Surfactant	Reduces surface tension of the treatment fluid in the formation and helps improve fluid recovery from the well post stimulation	Some made to react with the formation, some to be returned with produced water, or some enter the produced natural gas	Glass cleaner, multi-surface cleaner, antiperspirant, deodorants, hair-colour

Creating optimal fracture geometry and producing an effective viscosity for delivery of the proppant into the fractures are essential components to a complex engineered fluid system. As target viscosity varies, so does the fluid composition (Zhu, 2012). Three types of fracturing fluids can be identified by their relative target viscosity.

- Slickwater (Water-frac)

Hydraulic fracturing fluid with no viscosity enhancing additives. Slickwater fluids consist of water, proppant, and minimal concentrations of other additives such as friction reducers. Slickwater fluids are used primarily for gas producing fields but not exclusively (Vidic, 2013).

- Cross-linked Polymer (Gel-frac)

A gelling agent, crosslinking agent, and pH buffering agent are added to water to significantly increase the viscosity for maximum proppant delivery under high temperatures and pressure. Gelling agents are typically guar-based or cellulose-based such as hydroxyethyl cellulose or carboxymethyl cellulose (Vidic, 2013). These polymers are cross-linked using inorganic metals like Boron, Zirconium and Titanium. Borate-based salts are the most prevalently used crosslinking agents.

- Hybrid

A Hybrid fracturing fluid would consist of combining a slickwater fluid and cross-linked gel for each stage of the horizontal production zone (Sick, 2014)

2.1.2 Water Usage

The Ceres report on “Hydraulic Fracturing & Water Stress: Water Demand by the Numbers” estimates that 97.5 billion gallons of water were used for U.S. oil and gas operations during the time period of January 1, 2011 to May 31, 2013. This amounts to an average of 2.5

million gallons of water used per well (Freyman, 2014). Water usage can be divided into two categories: drilling operations and the hydraulic fracturing process. Of those 2.5 million gallons, over 95 % is used for hydraulically fracturing horizontally drilled wells (Goodwin, 2012). This creates massive operational demand for water management both upstream and downstream of oil and gas production. This also means that both freshwater acquisition/conveyance along with wastewater disposal are two key pieces to shale resource development. For the time period analyzed by the Ceres report, almost half of the wells drilled were in areas of “high or extremely high water stress” (Freyman, 2014). Combined with population growth, competing water use, groundwater depletion, drought and climate change; shale play development in water stressed environments is both prevalent and highly encourages better management practices.

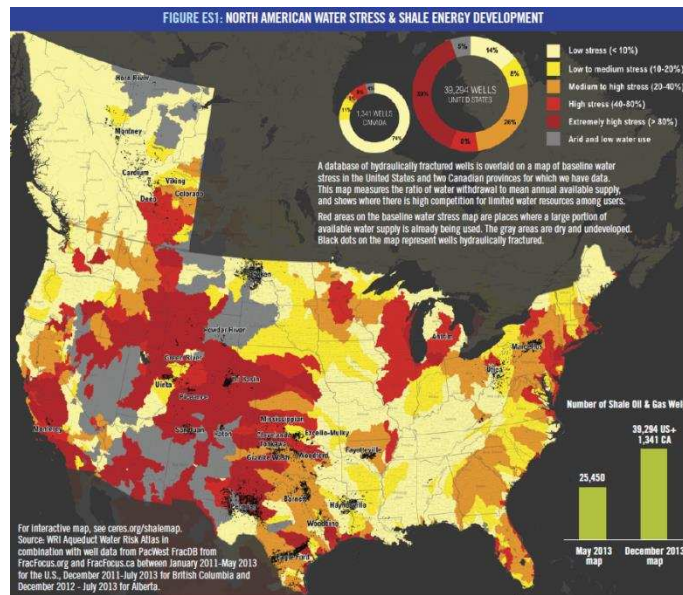


Figure 2-3: Shale Play Development in Water Stressed Regions (Freyman, 2014)

This study focuses on the Denver Julesburg Basin and primarily Weld County, Colorado. Defined as a region of “extremely high water stress”, 1.3 billion gallons of water were used for hydraulic fracturing operations in 2012. Noble Energy and Anadarko are the two primary operators in this region (Freyman, 2014). This problem can be seen as a unique opportunity for

the oil and gas industry to encourage recycling and reuse of wastewater, coupled with smarter acquisition of fresh and non-fresh water resources.

2.1.3 Shale Water Management Alternatives

In 2012, U.S. onshore wells generated over 20 billion barrels of produced water (Veil, 2012). Although Section 2.2 will address the characterization of produced water, it will be useful to know three key components; high salinity, oil and grease and toxic chemicals. The most commonly used produced water management strategies are listed below; percentages are for total U.S. produced water (Veil, 2012).

- Injection for Enhanced Oil Recovery (45.1%)

A large portion of produced water is re-injected into wells as a method of enhanced oil recovery (EOR). Techniques such as water flooding or steam flooding are used to recover additional oil in gas typically in conventional reservoirs (Veil, 2012). Although this is a form of recycling, this waste product still needs to be managed further after this second use

- Injection for Disposal (38.9%)

The majority of unconventional produced water is permanently disposed using deep injection wells or disposal wells. Injection wells are regulated by the Environmental Protection Agency (EPA) as part of the Underground Injection Control (UIC) program. Produced water falls under Class II Disposal wells, used for oil and gas related fluids. State Agencies like the Colorado Oil and Gas Conservation Commission (COGCC) will even enforce stricter regulations at a state level. Disposal wells are located in approved regions where the receiving subsurface formation has been approved for the injection of

wastewater. The EPA issues permits with specifications for "Construction, Operation, Monitoring & Testing, Reporting, and Closure Requirements (EPA, 2016)".

- Surface Discharge (5.4%)

State agencies receive authorization to issue permits for surface water discharge under the National Pollutant Discharge Eliminations System and the Clean Water Act (EPA, 2015).

Only a small portion of onshore wells contribute to this percentage. Surface water discharge of unconventional produced water requires significant treatment to reach acceptable effluent standards (Veil, 2012).

- Evaporation Ponds (3.4%)

Evaporation Ponds are essentially holding ponds that use the power of sun in arid climates to separate water from all other suspended and dissolved solids, primarily salts. Open pits filled with produced water do present major air quality problems due to the presence of volatile organic compounds (VOC's). Potential for leaking is also an issue.

- Offsite Commercial Disposal (6.7%)

Oil and gas companies will pay a commercial facility a fee per barrel in addition to their own transportation costs to accept and dispose of their produced water. These private companies own infrastructure to either treat the water for a secondary use or for deep well injection. 98% of the water sent for offsite commercial disposal was directed towards privately owned disposal wells (Veil, 2012).

- Beneficial Reuse (0.6%)

Blending recycled produced water with freshwater for use in hydraulic fracturing fluid is the primary application for beneficial reuse. Other small uses include irrigation and road application for dust and ice management (Veil, 2012). The target blended or treated water quality is extremely important for beneficial reuse purposes.

- Colorado Shale Water Management

The COGCC maintains records for produced water management from all operators. Over 60% of oil and gas associated water was injected for EOR or disposal in 2012. Roughly 10% for surface discharge, 9% for evaporation and 6 % for offsite commercial disposal. The 12% used for beneficial reuse went towards subsequent fracturing fluids (Veil, 2012).

2.1.4 Negative Impacts of Current Management

Challenges associated with shale water management address direct, cumulative, and future negative impacts.

- The overuse of Class II Disposal Wells has serious implications associated with unsustainable water use, capacity and induced seismicity. Once wastewater has been injected into a designated disposal well, it has been removed permanently from the hydrologic cycle. With increasing pressure on water resources and shale development in areas of high water stress, disposal wells are wasting valuable water resources. Both freshwater used for hydraulic fracturing fluid and produced water extracted from the formation are wasted opportunities for reuse. Although surrounded by some controversy, it is well accepted in the scientific community that deep injection wells are causing earthquakes (Ellsworth, 2013). A change in fault loading caused can be attributed to a

change in the stress regime due to a large volume of fluids injected into a formation is called induced seismicity. The number of earthquakes of magnitude 3 or greater has significantly increased in eastern and central United States since 2011. The last challenge is the question of capacity. As many disposal wells become safely filled to maximum capacity, the option of disposal disappears to oil and gas operators.

- Trucking produced water to a disposal well, treatment facility, or other management location has considerable costs. From a social perspective, trucking causes unwanted traffic and noise to places with shale development. From an environmental and public health perspective, trucking impacts air quality through diesel emissions. In addition to air pollution, increased traffic is could be causing millions of dollars in road repairs.

2.2 Produced Water Characterization

Although produced water is a general term often used to refer to the bulk of wastewater generated from an oil and gas well; there is a distinction between flowback, transition, and produced water for shale play development. These are typically defined by a well's temporal trends for both quality and quantity.

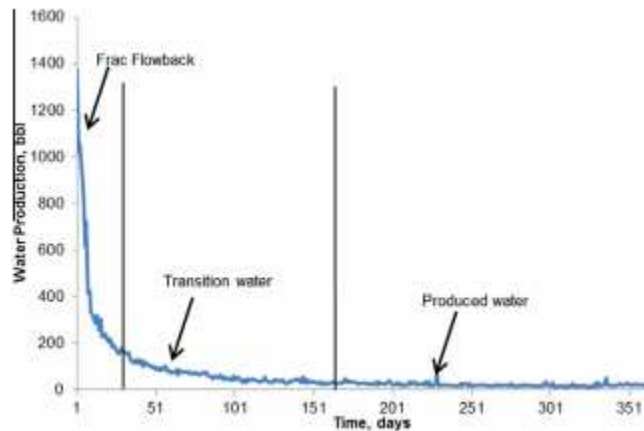


Figure 2-4: Water Production Model for 86 Wells in Weld County, CO (Bai et al., 2015)

Flowback consists primarily of the base water used for hydraulic fracturing. Once a well is perforated and fractured, this water will immediately begin to return to the surface. Flow back will contain the majority of chemical additives used in the fracturing fluid along with high concentrations of organic matter attributed to the broken down cross-linked polymers in gel-fracs. Water-fracs will produce flowback with much lower concentrations of organic matter (Sick, 2014). Produced water is the naturally present water that exists in a shale formation along with oil and gas. There is a large amount spatial variability for produced water since it is representative of a specific geologic formation. Transition water is a blend of the two. Well age is often used to estimate what kind of water is flowing from an unconventional well. The following water quality characterization will use produced water as an umbrella term but will also provide ranges to account for the temporal variability.

2.2.1 Produced Water Quality

Produced water is characterized by its total dissolved solids (TDS), total suspended solids (TSS), oil and grease, inorganic and organic constituents.

- Total Dissolved Solids (TDS)

TDS is primarily a measure of salinity as sodium chloride (NaCl) originating from the geologic formation. Other major dissolved inorganic ions such as bicarbonate, carbonate, calcium, magnesium, and sulfate constitute TDS as well as dissolved organic carbon (DOC).

- Total Suspended Solids (TSS)

This is a measure of both particles and colloids present in the water. Turbidity is a rough approximation of TSS which indicates sand, silt, clay, emulsified oil droplets, and other particulate matter.

- Total Organic Carbon (TOC)

Organic Matter can be divided into two categories; formation-based and residual fracturing fluid. Aromatic compounds, phenols, carboxylic acids, and aliphatic hydrocarbons are the primary soluble organics found in produced water associated with the shale play. This includes highly regulated benzene, toluene, ethyl benzene, and total xylenes (BTEX), oil and grease, and total petroleum hydrocarbons (TPH). Some of the soluble organics like benzene are considered volatile organic compounds (VOC'S) and present a public health and air quality risk. The other portion of organic matter consists of broken down polymer chains; guar or cellulose based. This can account for a large concentration of total organic carbon in regions where gel-fracs are commonly used (Sick, 2014).

- Hardness

Hardness or scaling compounds include divalent cations calcium and magnesium

- Metals

Metals found in produced water are typically barium, iron, lead, manganese, strontium, and zinc. Heavy metals cadmium, chromium, nickel, vanadium and copper have also been found in low concentrations (Li, 2013)

- Naturally Occurring Radioactive Materials (NORMs)

Radioactive material such as radium and uranium are naturally occurring. These compounds are dissolved in produced water and brought to the surface. Although found in low concentrations, accumulation of these materials is an environmental health and safety concern. States regulate the management of oil field waste with NORMs (USGS, 1999).

Although the physical characteristics and chemical constituents are similar, spatial variability exists with unconventional produced water. Each shale play in the U.S. has its own produced water quality unique to the geologic formation, temperature, and depth. The fracturing fluid composition also has significant influence on flowback and transition type water which accounts for large volumes (Bai, 2015 and Sick, 2014).

Table 2-2: Marcellus Shale Produced Water Quality (Vidic et al., 2013)

	minimum	maximum	average	number of samples
TDS (mg/L)	680	345,000	106,390	129
TSS (mg/L)	4	7,600	352	156
oil and grease (mg/L)	4.6	802	74	62
COD (mg/L)	195	36,600	15,358	89
TOC (mg/L)	1.2	1530	160	55
pH	5.1	8.42	6.56	156
alkalinity (mg/L as CaCO ₃)	7.5	577	165	144
SO ₄ (mg/L)	0	763	71	113
Cl (mg/L)	64.2	196,000	57,447	154
Br (mg/L)	0.2	1,990	511	95
Na (mg/L)	69.2	117,000	24,123	157
Ca (mg/L)	37.8	41,000	7,220	159
Mg (mg/L)	17.3	2,550	632	157
Ba (mg/L)	0.24	13,800	2,224	159
Sr (mg/L)	0.59	8,460	1,695	151
Fe dissolved (mg/L)	0.1	222	40.8	134
Fe total (mg/L)	2.6	321	76	141
gross alpha ^a (pCi/L)	37.7	9,551	1,509	32
gross beta ^a (pCi/L)	75.2	597,600	43,415	32
Ra ²²⁸ (pCi/L)	0	1,360	120	46
Ra ²²⁶ (pCi/L)	2.75	9,280	623	46
U ²³⁵ (pCi/L)	0	20	1	14
U ²³⁸ (pCi/L)	0	497	42	14

^aData for Northeast Pennsylvania only.

Table 2-3: Niobrara Shale Produced Water:
Slickwater vs. Cross-linked Gel Flowback (Sick, 2014)

Parameter	Unit	Well B (Hybrid)			Well D (Slickwater)			Well G (Cross-Linked Gel)		
		Average	Range		Average	Range		Average	Range	
pH	-	6.95	6.75	– 7.18	6.99	6.78	– 7.22	7.06	6.79	– 7.46
Conductivity	mS/cm	45.1	34.8	– 51.1	44.8	29.8	– 51.1	40.6	24.8	– 50.4
TOC	mg/L	1,187	943	– 1,662	284	222	– 440	1,334	1,027	– 1,735
DOC	mg/L	1,042	831	– 1,375	248	214	– 340	1,189	820	– 1,431
COD	mg/L	4,624	3,175	– 7,120	2,354	950	– 3,750	4,943	4,050	– 8,825
Turbidity	NTU	295	119	– 763	262	124	– 489	247	115	– 490
UV254	Abs.	1.567	0.746	– 2.670	0.719	0.352	– 2.163	1.613	0.967	– 2.412
Alkalinity	mg/L CaCO ₃	623	534	– 710	581	428	– 778	653	574	– 782
TS	mg/L	30,960	23,427	– 35,520	30,056	18,620	– 34,830	27,332	18,087	– 34,500
TDS	mg/L	30,352	22,913	– 34,680	29,871	18,187	– 33,840	27,029	17,380	– 33,460
TSS	mg/L	155	41	– 339	144	40	– 220	148	38	– 322
TVS	mg/L	2,268	1,533	– 3,518	2,104	960	– 4,320	1,995	992	– 3,247
VDS	mg/L	2,177	1,333	– 3,420	1,961	733	– 3,810	1,930	870	– 2,700
VSS	mg/L	101	32	– 238	74	17	– 137	106	27	– 285
Al	mg/L	3.3	2.1	– 5.0	3.2	1.7	– 5.0	2.2	1.1	– 3.4
Ba	mg/L	24	14	– 37	27	12	– 39	14	6	– 28
B	mg/L	34	26	– 39	23	19	– 26	37	29	– 44
Ca	mg/L	574	355	– 1,014	562	275	– 1,002	471	213	– 927
Fe	mg/L	45	25	– 103	41	20	– 72	50	33	– 82
K	mg/L	101	72	– 161	76	57	– 89	112	87	– 143
Mg	mg/L	85	54	– 136	84	40	– 133	72	34	– 132
Na	mg/L	10,761	7,349	– 18,608	11,173	9,583	– 12,637	9,430	6,063	– 12,428
Si	mg/L	41	29	– 49	56	40	– 67	40	28	– 51
Sr	mg/L	81	44	– 165	80	32	– 167	68	25	– 157
Zr	mg/L	0.78	0.30	– 1.83	0.22	0.12	– 0.46	0.27	0.16	– 0.42
Br	mg/L	80	54	– 102	79	48	– 102	70	45	– 93
Cl	mg/L	16,190	11,400	– 20,570	16,883	12,150	– 19,580	14,686	9,010	– 19,050
HCO ₃	mg/L	553	418	– 722	493	320	– 838	525	360	– 716
NH ₄	mg/L	36	25	– 43	33	24	– 38	35	24	– 41
SO ₄	mg/L	15	4	– 29	20	1	– 89	43	2	– 210
Oil and grease	mg/L	123	40	– 435	68	17	– 304	153	10	– 872
GRO	mg/L	208	47	– 910	127	33	– 356	243	49	– 1,392
DRO	mg/L	76	10	– 273	54	12	– 248	124	7	– 762
ORO	mg/L	8	7	– 12	15	5	– 34	23	5	– 77
TPH	mg/L	281	55	– 1,068	180	48	– 398	378	56	– 2,231
BTEX	mg/L	50	26	– 100	39	19	– 63	52	26	– 135

2.3 Treatment Processes

Water treatment processes are essential components to shale water management as the need for beneficial reuse will only increase and the finite number of class II disposal wells will begin to reach capacity. A wide range of chemical, biological, and physical treatment techniques have been applied to oil and gas associated water. Primary goals of produced water treatment are: oil/water separation, solid/liquid separation, organic matter removal, softening, and desalination (Ahmadun, 2009). Other processes may include disinfection, ion specific exchange, and removal of other contaminants such as dissolved gases and NORMs. Table 2-8 outlines applied technologies and their corresponding function.

Table 2-4: Oilfield Water Treatment Methods (Compiled from Ahmadun, 2009)

Unit Process	Type	Mechanism	Purpose
Centrifuge	Physical	Centrifugal Force	Separate free oil from water
Corugated Plate Separator		Density Variation	Separate free oil from water
Hydroclone		Centrifugal Force & Air Bubble Attachment	Separate free oil from water
Dissolved Air Flootation (DAF)		Air Bubble Attachment	Separate free oil from water and solids removal. Solids should have a specific gravity < 1.0
Sand Filtration		Size Exclusion /Attachment	suspended solids removal. Reduction in metals with pretreatment i.e. pH adjustment
Porous Media		Adsorption	Primarily soluble organic matter removal, but also dissolved metals. Media can include activated carbon, zeolite, resins, organoclay, and others.
Settling Basin		Gravity	Remove suspended solids and floccs. Settling velocity of individual particles must high enough for feasible retention time
Evaporation		Phase Change	Energy Intensive. Removes water from most contaminants (especially salts) as vapor, then re-condenses. Distillation processes, steam generators, mechanical vapor recompression.
Electrodialysis (ED)		Ionic charge attraction	Remove salts in lower TDS water. Cations and anions attach to +/- charged membrane

Unit Process	Type	Mechanism	Purpose
Softening	Chemical	Chemical Precipitation	Increased pH to precipitate calcium, magnesium, sulfides, iron, and barium.
Ion-exchange Resins		Ion Exchange	Exchange ions for another with a greater affinity to undergo hydrolysis
Coagulation/Flocculation		Particle Destabilization, Brownian Forces, Aggregation of floc	Solid/Liquid Separation. Chemical addition of polymers or trivalent metals (Fe and Al) to destabilize particles and colloids. Aggregated floccs settle or
Chemical Oxidation		Electron donors and acceptors	Chemicals added to break up organic matter and change speciation of metals through oxidation
Electrochemical		Oxidation/Reduction	Electrocoagulation utilizes electric current to donate and accept electrons. Water is reduced as metal plates are oxidized releasing ion in aqueous state
Fenton Process		Hydroxyl Radical Generation through Oxidation/Reduction	Chemical oxygen demand (COD) and oil removal.
Demulsifier		Oil Droplet Destabilization	Alkali, Surfactants, and Polymers (ASP) used to break up natural emulsion process.

Unit Process	Type	Mechanism	Purpose
Trickling Filter	Biological	Biodegradation	Significant removal of chemical oxygen demand (COD), total organic carbon (TOC), total petroleum hydrocarbons (TPH). Seeded or naturally occurring microorganism break down contaminants and use as a food source. Aerobic processes consume large amounts of oxygen for COD removal.
Aerated Lagoon			
Continuous Flow Activated Sludge			
Sequencing Batch Reactor (SBR)			
Biologically Aerated Filter (BAF)			

Unit Process	Type	Mechanism	Purpose
Microfiltration	Membranes	Size Exclusion	Removes suspended solids. Pore size 0.1 - 5 um
Ultrafiltration		Size Exclusion	Remove suspended solids and colloids. Pore size 0.1 - 0.01 um
Nanofiltration		Size Exclusion/Diffusion	Removes suspended solid, colloids, and some multivalent ions. Pore size 0.01 - 0.001 um
Reverse Osmosis		Differential Concentration Gradient	Removes small colloids and aqueous salts. Water is forced a semi-permeable membrane. ~ 0 Dalton MWCO Rejection. TDS/small ion removal

Pore Size (Membrane Research Environment, 2015)

Many unit processes are used as a pretreatment for subsequent processes such as polymeric membrane technology. Pre-oxidation and coagulation are two processes that can reduce irreversible fouling and improve contaminant removal through low pressure membranes,

microfiltration and ultrafiltration (Huang et al, 2008). Also if pre-treatment is ineffective, reverse osmosis cannot be economically feasible. Membrane fouling, reduced flux and chemical membrane cleaning processes can increase costs significantly (Ahmdun, 2009). The main barrier to produced water treatment is the significant capital cost as well as operation and maintenance. When applied at a large scale, desalination processes can cost between \$0.75 - \$1.25 a barrel (DOE, 2013). Depending on demand, commercially operated disposal wells range from \$0.50 - \$2.50 a barrel, with roughly \$1.00 per barrel per hour trucking time (McCurdy, 2011). Proximity to disposal wells, the cost of disposal wells and ability to optimize treatment costs control water management strategies. Although a more cost effective strategy is minimized onsite treatment for use in fracturing fluid, the number of new wells being developed has likely declined due to the low price of oil (McCurdy, 2011). Some examples of applied produced water treatment trains are listed below with variability for both influent water quality and location.

- Acidified>Degasified>Coagulation/Flocculation>Sedimentation>packed bed media filtration> Brackish Water Reverse Osmosis (Duraismy. 2013)
- Blended with supersaturated ozonized water>Electrochemical precipitation>Activated Carbon filter>Reverse Osmosis (Duraismy, 2013)
- Dissolved Air Flootation>Acid Cracking>Coagulation>5 um and 1 um filtration>Micro/Ultrafiltration>Nanofiltration/Reverse Osmosis (Cakmakci et al., 2008)
- Walnut Shell Filter>Warm Lime Clarifier>Cooling>Trickling Filter>Pressure Filter>Ion exchange>Reverse Osmosis (Ahmdun, 2009)
- Oil Skim Tanks>Coagulation/Polymer>Dissolved Air Flootation>Aerated Biologically Active Storage Ponds (Lobato, 2015 CSU Gas Symposium)

- Strong Oxidation> Contact/Settling Basin>10 um filtration>Deep Injection Well Disposal (Hill, 2015)

2.3.1 Coagulation/Flocculation

Coagulation/flocculation is the process of using chemical precipitation or synthetic polymers to remove both suspended solids and colloidal particles in an accelerated amount of time. Suspended solids and colloidal particles are small enough to be considered neutrally buoyant in water. The majority of particles found in water have a negative surface charge and remain stable due to the repulsive forces that prevent them from attaching to each other to grow larger and settle naturally (Chetty, 2012). The primary mechanism of coagulation is particle destabilization. Positively charged trivalent metal ions (Fe^{+3} or Al^{+3}) are often added to balance the particles' surface charges to a point where Van der wal's attraction is able to take over. Flocculation is the process of aggregating both the destabilized particles and metal hydroxides into larger clumps or "flocs" that can be settled rapidly. Flocculation is mostly achieved through a slow mixing step. A secondary but also effective method of coagulation is called sweep coagulation (Esmailirad, 2015). This utilizes a larger dose of chemical precipitants to form large flocs which will essentially pull out particles. Surface charge balance is not necessary for sweep coagulation. Inorganic metal compounds and synthetic polymers are predominantly used for coagulants.

2.3.2 Electrocoagulation

Electrocoagulation (EC) is an alternative to chemical coagulation. Although the mechanisms are the same, iron or aluminum ions are released as water passes through a series of electrically charged metals plates. Figure 2-9 describes the series of oxidation reduction reactions

as an electric current circulates between the cathode and anode. Both hydrolysis of metals ions and electrolysis of water are essential to the electrochemistry and theory behind EC.

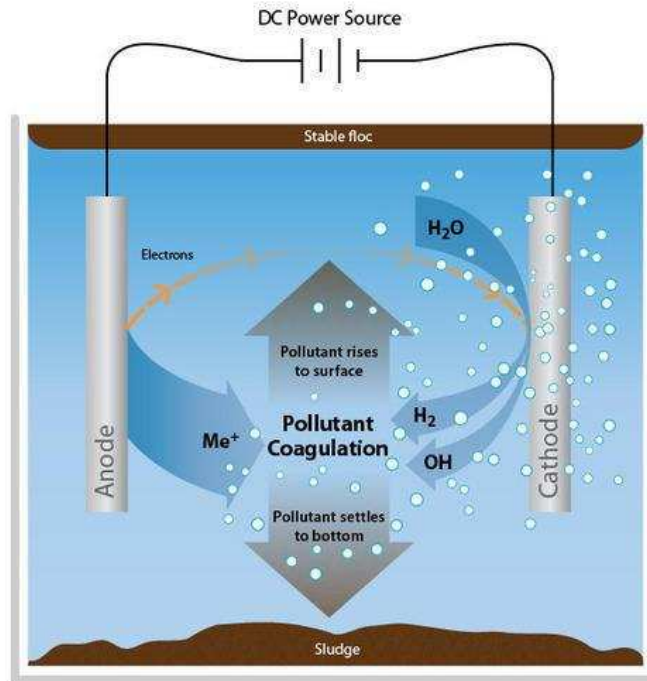
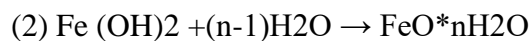
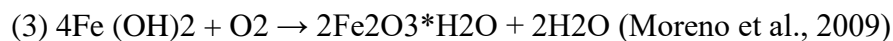


Figure 2-5: Electrocoagulation Anode & Cathode Schematic (Geo Enviro Solution, 2016)

Ferrous Hydroxide:



Ferric Hydroxide:



Electrocoagulation was first applied to wastewater treatment in 1889 as a method of in situ coagulation (Vepsäläinen, 2012). Recently there has been an increased interest in this technology due to potential lower operating costs, reduced chemicals on site, hydrogen gas generation, and effectiveness of contaminant removal. In addition to TSS reduction there has been research linking EC to increased removal rates for boron, oil in water emulsions, and COD (Sayinera,

2008 & Canizares, 2008). Hydrogen gas generated as water is reduced from the cathode has the ability to float the metal hydroxide floc as an alternative to settling. If the specific gravity of the sludge generated is less than one, hydrogen gas coupled with dissolved air floatation (DAF) could be more cost effective than conventional settling. One major challenge for the application of produced water is the high concentrations of organic matter, measured as total organic carbon (TOC). High TOC can cause ineffective electrocoagulation as charged organic matter is thought to adsorb and desorb from metal hydroxide particles (Esmailirad, 2015).

2.4 Research Purpose

Research is often sparked by a problem and the need for a solution. In this case, the problem stated below is complicated economically, socially, and scientifically. A gap has been created for research to begin mapping potential alternatives. If a single solution existed for every different geographic location and produced water quality, it would have already been applied to all situations.

Problem: Water usage in the shale extraction sector can demand large volumes in water stressed regions. Current practices primarily use deep injection wells as a method of disposal; this limits the reuse of a valuable resource and increases the risk of anthropogenic-influenced seismic events.

Primary Objectives

- i) Understand electrocoagulation in the context of water with high organic matter concentrations
- ii) Develop an electrocoagulation based treatment train in order to provide treated effluent for a beneficial reuse irrigation study
 - Clearly identify unit process goals in terms of contaminant removal

- Define successes, challenges, and failures for process optimization

Secondary Objectives

iii) Describe irrigation study as a first step to building a pilot scale experiment aimed at treatment of produced water for agricultural related beneficial reuse.

3. PRODUCED WATER TREATMENT FOR BENEFICIAL REUSE IRRIGATION STUDY

3.1 Introduction and Background

The scope of the research objectives can be divided into 1) Water Treatability 2) Soil and Crop Analysis. Although the primary focus of this paper is to evaluate a combination of treatment processes, the irrigation study plays an essential role by providing context and target effluent goals and considerations. For this project, produced water was collected from Noble Energy's Wells Ranch Central Processing Facility (CPF) in Weld County, Colorado. This wastewater was then treated at the Colorado State University Environmental Engineering Lab and transported to a greenhouse located at the CSU's Environmental Research Center (ERC). The water was then used to provide four different levels of treated water quality and integrated into a drip irrigation system watering two different types of crops for a 3-4 month growing period. Crop growth, soil quality and water quality were key parameters monitored for this period of time. The treatability component of this project utilized CSU's unique relationship with a commercial water treatment solution company, Water Tectonics. Water Tectonics provided a WaveIonics bench scale unit and Hummel hollow fiber ultrafiltration membranes for process testing. Water Tectonics provided unit process knowledge and a platform for treatability discussions while CSU collected and characterized CPF produced water, ran preliminary jar tests, and evaluated potential treatment train processes which were scaled up to approximately 30 gallons per week.

3.2 Materials and Methodology

3.2.1 Location

Figure 3-1 shows the Wells Ranch CPF, storage tank sampled, and surrounding area. Weld County is located in the Denver Julesburg Basin in which oil and gas operators are developing the Niobrara shale formation.

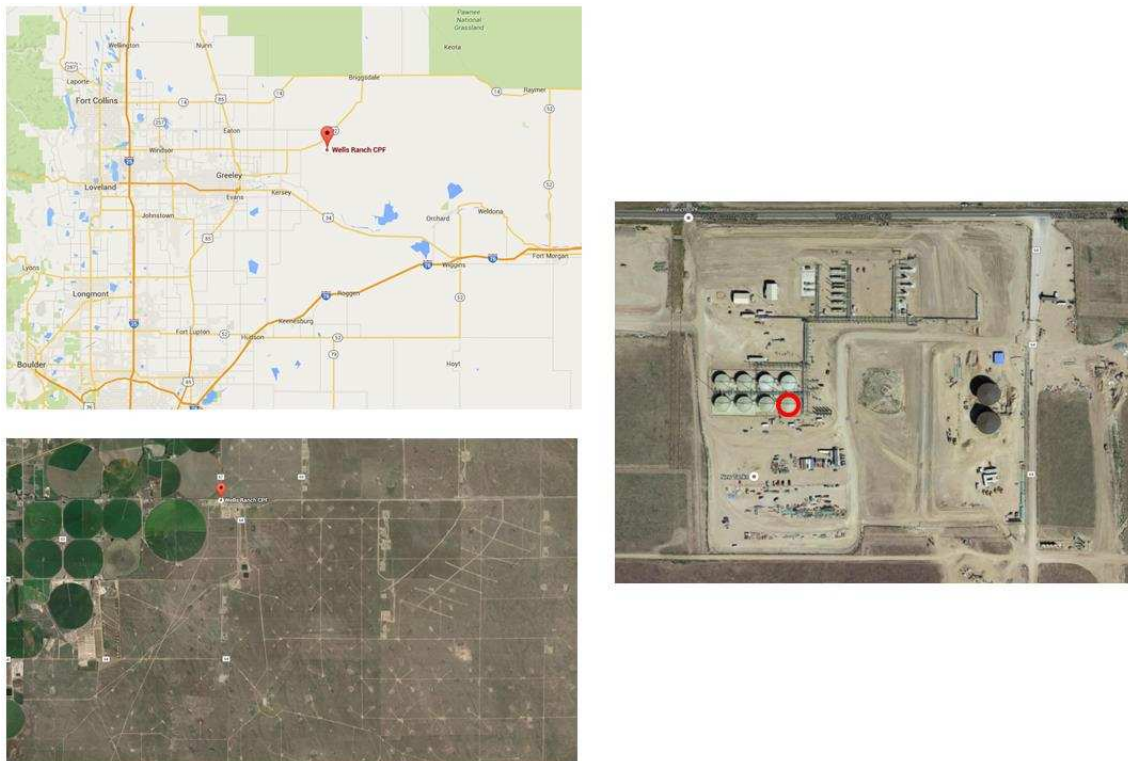


Figure 3-1: Noble Energy Wells Ranch Central Processing Facility in Weld County, CO (Google Maps, 2016)

Produced water was collected from the southeast corner tank. As a central processing facility, wells from the entire area are blended and flow into these tanks as a combination of both produced and flowback water (Schauer, 2015)

3.2.2 CPF Produced Water Quality

Produced water was collected from the CPF weekly or biweekly for preliminary treatability jar testing and for irrigation use. In the context of beneficial reuse and meeting specific target water quality goals; treatment processes were selected to remove particles, dissolved organic matter, and salts. For this reason; turbidity, total organic carbon (TOC), and total dissolved solids (TDS) are the primary parameters used to evaluate initial raw water quality, determine the range of treatment dosage and quantify the effectiveness of each process.

Table 3-1: Wells Ranch CPF Produced Water Quality

CPF Produced Water Quality					
Parameter	Minimum	Maximum	Average	# Data Points	Time Period
Turbidity (NTU)	120	1,428	322	12	10/27/2015 - 4/8/2016
TOC (mg/L)	1,200	2,173	1,783	11	
TDS (mg/L)	13,600	27,539	21,978	12	
pH	6.5	6.7	6.6	3	
ORP (mV)	-88	-23	-58	3	
Ca (mg/L)	190	270	227	4	
Mg (mg/L)	ND	36	22	4	
HCO ₃ (mg/L)	600	750	660	3	
Na (mg/L)	6300	6900	6526	4	
Cl (mg/L)	11,000	17,000	13,000	4	
B (mg/L)	19	22	25	4	
BTEX (mg/L)	9	42	25	3	
ND *Not Detected					

Although there is a temporal variability to CPF produced water quality, typically this water has a turbidity of 120 – 380 NTU, a TOC concentration of 1500 – 2200 mg/L, and a TDS of 20,000 – 25, 000 mg/L. TDS consists primarily of sodium chloride but also a range of others salts such as bicarbonate, sulfate and others. Large concentrations of TOC indicate significant concentrations of broken down cross-linked polymers or residual fracturing fluid in additions to hydrocarbon sources. Figure 3-4 shows that almost 1,300 mg/L of dissolved organic matter

passes through a 1,000 Dalton ultrafilter. Emulsified and free floating oil droplets will be typically no smaller than 1 μm . (Lake, 2006). Size exclusion was performed using two different methods 1) Amicon Stirred Ultrafiltration Cell Model 8400 (400 mL capacity) 2) Mann + Hummel Ultrafiltration Unit described in section 3.2.3 (30 L minimum). The Amicon Stirred Ultrafiltration Unit used Millipore Ultrafiltration Discs at an operating pressure less than 55 psi. Filters were rinsed by running 400 mL of deionized water through each new filter.

- Millipore Ultracel 1 KDA Ultrafiltration Disc (CAT. NO. PLAC07610)
 - Membrane Material: Regenerated Cellulose (RC)
 - Filter Diameter: 76 mm
- Millipore Biomax 50 KDA Ultrafiltration Disc (CAT. NO. PBQK07610)
 - Membrane Material: Polyethersulfone (PES)
 - Filter Diameter: 76 mm

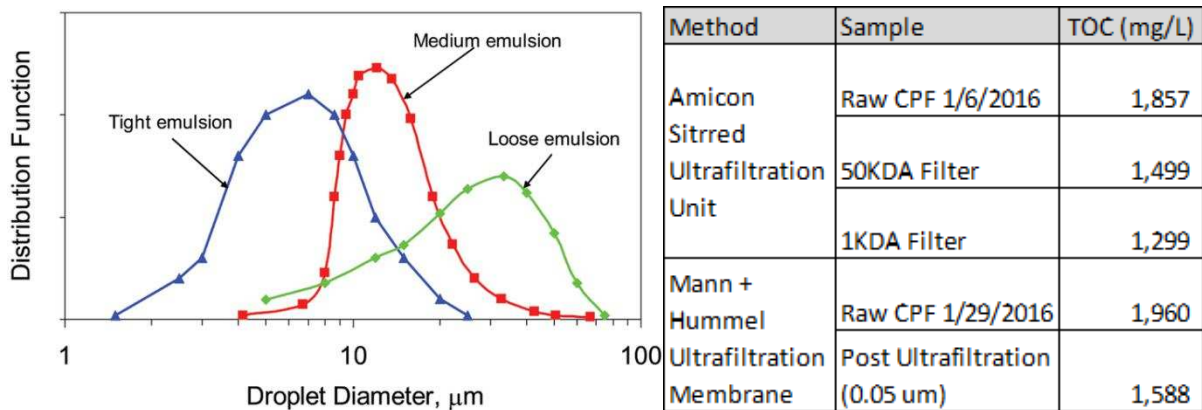


Figure 3-2: Organic Matter Size Exclusion of CPF Produced Water & Emulsified Oil Droplet Size (Lake, 2006)

The higher range of turbidity and TOC measurements occurred when there was visually more emulsified and free floating oil in the produced water sample. Methods for turbidity, TOC, TDS, pH, ORP, and water quality ions measured using an outside analytical laboratory are found below.

- Turbidity

Hach 2100N Turbidimeter used to measure turbidity compliant with EPA Method 180.1.

- Total Organic Carbon (TOC)

Shimadzu TOC-V CSH Total Organic Carbon Analyzer. TOC = Total Carbon (TC) - Inorganic Carbon (IC) method used for analysis. The TOC-V CSH uses a combustion catalytic oxidation method at 720 C to oxidize carbon in a gaseous state which is detected through the nondispersive infrared sensor (NDIR).

- pH & Oxidation Reduction Potential (ORP)

Hach HQ40d Multi probe. IntelliCAL ORP-REDOX and IntelliCAL pH probes.

- Total Dissolved Solids (TDS)

Gravimetric Solids Analysis using Hach USEPA approved method 8163. TDS measurements were taken from filtrate with particles 1.5 um or smaller.

- Analytical Water Chemistry

ALS Global Environmental Laboratory was used for all additional water analysis. Water samples were collected into ALS provided sample containers with corresponding preservatives. ALS measured benzene, toluene, ethyl benzene, total xylenes (BTEX),

gasoline range organics (GRO), diesel range organics (DRO), trace metals (Al, B, Ba, Ca, Fe, K, Mg, Mn, Na, Si, Sr, Zn), and anions (Br, Cl, HCO₃, SO₄, PO₄).



Figure 3-3: Wells Ranch CPF Produced Water

Other chemical constituents of interest include barium, boron, calcium, magnesium, sulfate, carbonates, gasoline range organics (GRO), diesel range organics (DRO), benzene, toluene, ethyl benzene, and xylene (BTEX). Calcium, magnesium, sulfate, and carbonates are all major precipitants and can cause major operational issues related to scaling. Carbonates also make up alkalinity or acid buffering capacity. Alkalinity is proportional the cost of acid/base used for pH adjustment. BTEX and GRO (C₆-C₁₀) are considered volatile organic compounds along with DRO (C₁₀-C₁₅) which is considered carcinogenic. The volatile organic compounds are hydrocarbon based and strictly regulated as they originate from oil and gas production.

3.2.3 Bench Scale Unit Processes

Electrocoagulation

Jar testing utilized two metal plates connected to a power supply, one anode and one cathode, as the first phase of the treatability study. A continuous flow electrocoagulation unit for second phase testing used the same power supply in addition to a SHURflo diaphragm pump (model No. 8000-953-238). This unit consisted of six stacked iron plates and anode/cathode electrolytic cell connection points. A “WaveIonics: Electrocoagulation Treatment Technology” power supply built Water Tectonics was used with Water Tectonics fabricated electrocoagulation units with iron plates (Continuous Flow & Batch). Although there is a lack of equivalence between the jar testing plates and the large continuous flow through unit based on amperage, surface area, and contact time; there was an empirical relationship between the "relative" comparison of treatment techniques (i.e. softening before EC is much more effective than after EC for both jar tests and continuous flow unit). EC was selected as a unit process due to its advantages of 1) requiring significantly less dosage than chemical coagulant addition 2) significantly less iron sludge generation than ferric chloride addition 3) no dosing pumps or chemicals required on potential pilot site locations

Table 3-2: Electrocoagulation Method Equivalence

Sample	EC Method	turbidity (NTU)	TOC (mg/L)	Dosage
Raw CPF 1.6.16	n/a	148	1857	n/a
pH 9.5/EC/DAF	Jar Test	45.8	1679	400 mL, 52 seconds, 1 amp
pH 9.5/EC/DAF	Continuous Flow Unit	98.5	1719	0.75 gpm, 6 amps

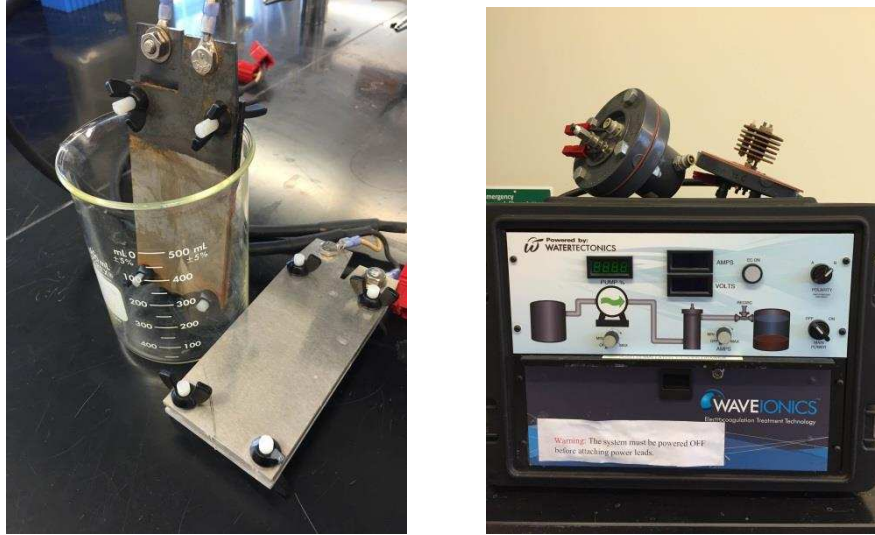


Figure 3-4: WaveIonic Electrocoagulation Bench Scale Unit: Continuous Flow & Batch

Solid/liquid separation methods included flocculation followed by settling and dissolved air floatation. Jar tests used a Phipps and Bird 900 Model Jar Tester at a paddle speed of 15 rpm for flocculation. 60 liter batches for treated for irrigation used a "" mixer at a paddle speed of 50 rpm for flocculation. Dissolved air floatation (DAF) was simulated by adding a measure volume of deionized water with microbubbles to produced water after a coagulant had been added. The microbubbles were generated by adding deionized water to a pressurized vessel at 80 psi. Connected to the pressurized vessel was an outlet hose with and adjustable on/off lever.

Ultrafiltration

A Mann + Hummel UA420-BT housing and UA420-E hollow fiber filter was selected for ultrafiltration. The nominal pore size is 0.05 um and membrane material a hydrophilic modified polyacrylonitrile (PAN). The same SHURflo diaphragm pump (model No. 8000-953-238) was used to pump to water at a flow rate of 0.5 gpm post electrocoagulation and solid/liquid separation.



Figure 3-5: Hollow Fiber Ultrafiltration Unit

Granular Activated Carbon

Three columns were constructed using 3" and 4" diameter PVC piping, caps, nozzles, and plastic tubing. Tubing exited the bottom of each column and ran upward to the entrance of the next column. This was done to simulate a submerged GAC bed and plug flow conditions. Acid washed 12x30 mesh activated charcoal coconut shell was used for adsorption media (Charcoal House, GAC1230C-AW). The three columns were assembled in series with a total empty bed contact time (EBCT) of 7.96 hours.

- Total volume of 3 columns = 23894.59 cubic cm
- Flow rate (Masterflex 1/s peristaltic pump) = 50 mL/min
- Volume of columns filled with GAC / flow rate = residence time



Figure 3-6: Granular Activated Carbon Columns in Series at CSU Laboratory

Isotherms were generated using the same GAC1230C-AW adsorption media. Ten different masses of GAC (5-50% by mass) were measured and each combined with a 400 mL of ultrafiltration brine. Each 400 mL beaker of ultrafiltration brine and coconut charcoal was mixed at a paddle speed of 25 rpm for 1 hour using the same Phipps and Bird jar test described above. The brine/GAC mixture was then filtered using a 6 um Whatman #3 filter to remove suspended inorganic carbon particles before measuring TOC.

Reverse Osmosis

Sterlitech SEPA CF Cell Crossflow Filtration Unit was used for reverse osmosis (RO) testing. GE Osmonics flat sheet RO membranes were selected to evaluate different membrane materials and operating pressures. Both the AG and SE series were looked at closely (Sterlitech, 2016 & GE, 2016).

- AG-series
 - Membrane Material: Polyamide
 - Typical Operating Pressure/Flux: 200 psi/10-20 GFD
 - Maximum Operating Pressure: 450 psi (with tape) and 600 psi (with outer wrap)
 - Salt rejection: 95.5 % as NaCl
 - Application: Brackish Water

- SE-series
 - Membrane Material: Thin Film
 - Typical Operating Pressure/Flux: 425 psi/5-20 GFD
 - Maximum Operating Pressure: 600 psi with temperatures below 35 C
 - Salt rejection: 98.9 % as NaCl
 - Applications: Industrial/Wastewater

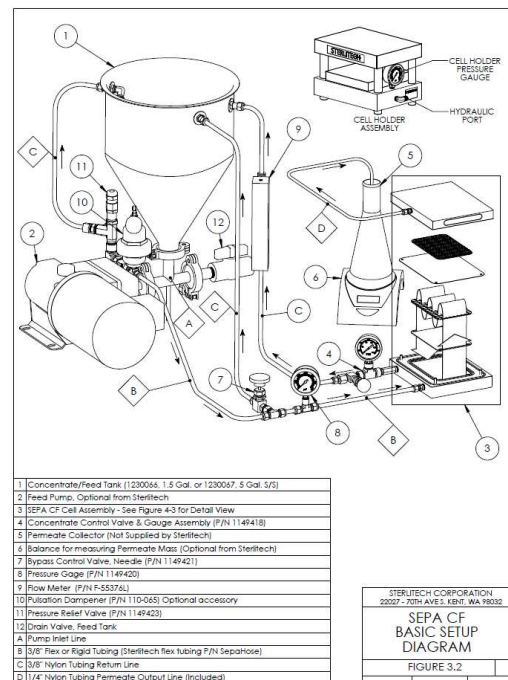


Figure 3-7: Sterlitech SEPA CF Cell Crossflow Filtration Unit and Flow Diagram (Sterlitech Corporation, 2016)

3.2.4 Greenhouse Experiment

Biofuel crops switchgrass and canola were chosen for the irrigation study. 5 different water qualities were chosen to irrigate the crops using a drip irrigation system. Greenhouse controls such as temperature and humidity were selected to best simulate "August" conditions in Colorado. Triplicates for each water quality and type of crop were assigned a randomized position as part of a grid system. Barrier plants watered using freshwater surrounded all test plants in order to minimize variability in what is considered a microclimate environment. Barrier plants are intended to keep conditions consistent with all thirty test pots since the perimeter may experience different conditions (i.e. temperature, humidity, air pressure differentials).

CANOLA							SWITCHGRASS						
Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier
Barrier	Control	3500 mg/L TDS with Organics	400 mg/L TDS with low Organics	400 mg/L TDS with low Organics	Control	Barrier	Barrier	Control	Control	400 mg/L TDS with low Organics	400 mg/L TDS with low Organics	3500 mg/L TDS with low Organics	Barrier
Barrier	3500 mg/L TDS with low Organics	Raw UF Brine	3500 mg/L TDS with Organics	Raw UF Brine	3500 mg/L TDS with Organics	Barrier	Barrier	3500 mg/L TDS with Organics	3500 mg/L TDS with low Organics	Raw UF Brine	3500 mg/L TDS with Organics	Raw UF Brine	Barrier
Barrier	3500 mg/L TDS with low Organics	400 mg/L TDS with low Organics	Control	Raw UF Brine	3500 mg/L TDS with low Organics	Barrier	Barrier	400 mg/L TDS with low Organics	Control	Raw UF Brine	3500 mg/L TDS with Organics	3500 mg/L TDS with low Organics	Barrier
Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier	Barrier

Figure 3-8: Greenhouse Experiment Grid System and Water Quality Designation (Stone et al., 2016)

The five experimental waters used included a freshwater control, and produced water treated to four different water quality effluent levels. Due to significant volume limitations of the bench scale reverse osmosis unit, produced water was treated through all other unit processes except RO and then diluted with freshwater to meet target TDS levels. All crops were irrigated with

freshwater (control) for the first 4 weeks after seeds were planted and then switched to their corresponding water quality.

- Control: Horsetooth Reservoir water. There was a direct water supply connection from the reservoir to the greenhouse
- Raw UF Brine: Produced water post ultrafiltration. High TOC and high TDS levels.
- 3500 mg/L TDS with organics: Produced water post ultrafiltration and diluted to 3500 mg/L TDS using Horsetooth water. Organics were not removed after ultrafiltration.
- 400 mg/L TDS with low Organics: Produced water post ultrafiltration and post GAC column organic removal. Diluted to 400 mg/L TDS using Horsetooth water. Very low levels of organics present (<1 mg/L).
- 3500 mg/L TDS with low organics: Produced water post ultrafiltration and post GAC column organic removal. Diluted to 3500 mg/L TDS using Horsetooth water. Very low levels of organics present.



Figure 3-9: Greenhouse Canola and Switchgrass Irrigation Arrangement

Plant biomass measurements were made after harvesting crops. Plant leaves and stems were separated from the roots and dried in large paper bags at 60 degrees C for 48 hours. Plants were allowed to cool for 15 minutes before bags were weighted (Stone et al, 2016). Soil salinity was measured by diluting soil samples by mass with a dilution factor of 4. Mixture of de-ionized water and soil was shaken and allowed to sit for 24 hours. The salt saturated dilution water was then used to follow the gravimetric measurement procedure outlined in section 3.2.2.

Hydrocarbon-based organics were measured in the soil by ALS Global Environmental Laboratory using ALS selected sampling containers. Soil in pots were dug up and mixed before soil sample analysis.

3.3 Results

3.3.1 Electrocoagulation

Suspended solids and colloid removal are the goal of electrocoagulation. This solid/liquid separation step is a pre treatment before filtration to reduce fouling for low pressure membranes and maintain acceptable performance levels (i.e. low transmembrane pressure drop). Jar testing compared chemical coagulation, polymer addition, bentonite clay coagulant aids, electrocoagulation, oxidants, pH adjustments, flocculation & settling, dissolved air floatation (DAF) and several combinations of these methods. Although chemical coagulation using ferric chloride and softening was effective when used together, high alkalinity levels increased the amount of sodium hydroxide necessary for pH adjustment as well as excessive iron floc sludge generation. Turbidity removal over 80% for the addition of hydrogen peroxide led to more pre oxidation testing using the continuous flow EC unit. Although softening/electrocoagulation/dissolved air floatation (pH 9.5/EC/DAF) had turbidity removal rates

of 69, 54, and 82 percent; when scaled up the turbidity removal rate for this process was only 33 percent.

When scaled up, the addition of hydrogen peroxide (Sigma-Aldrich CAS No. 7722-84-1) caused electrocoagulation to be a more effective process. Figure 3-11 shows a dose of 0.004% hydrogen peroxide by volume followed by electrocoagulation, flocculation, and settling removed 89% of raw turbidity.

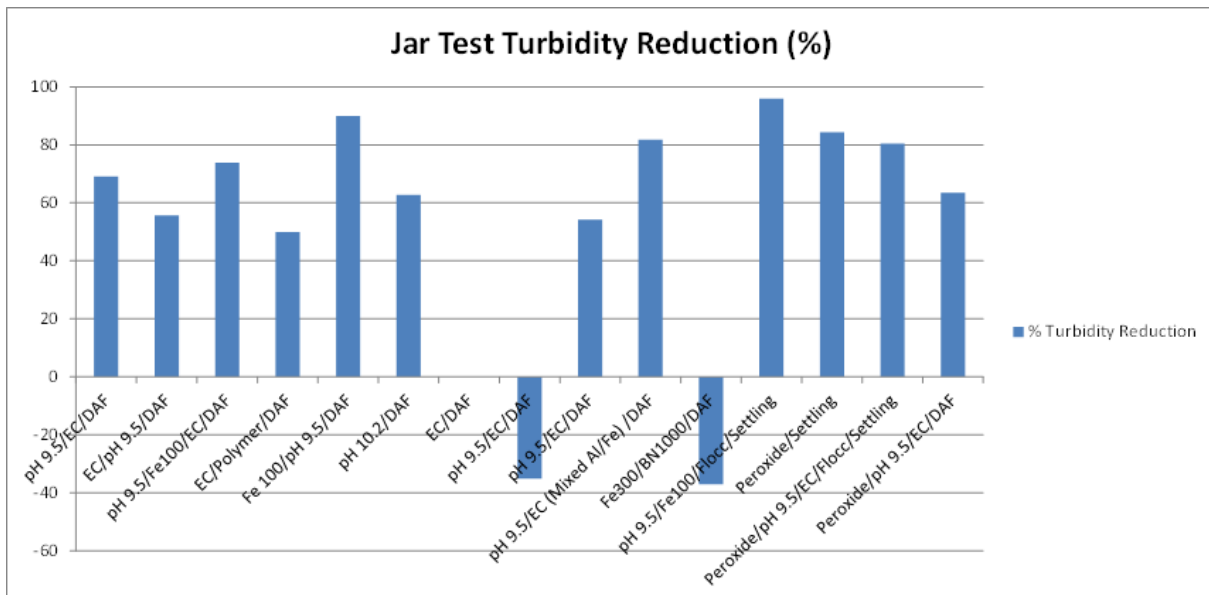


Figure 3-10: Chemical and Electrocoagulation Jar Test Turbidity Removal for CPF Water

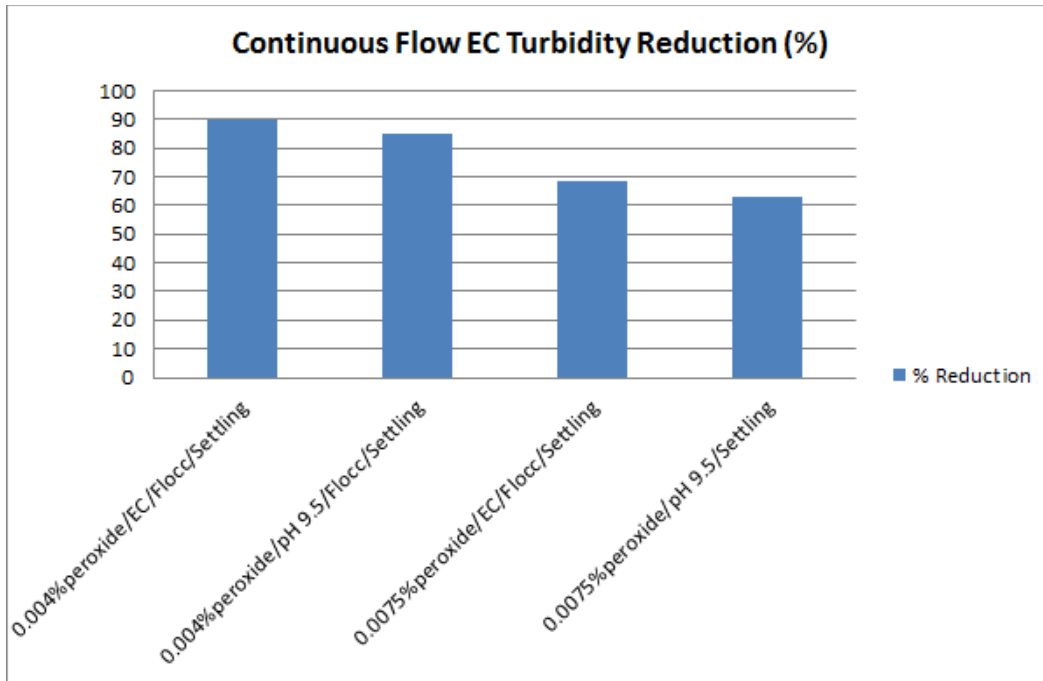


Figure 3-11: Continuous Flow Electrocoagulation and Pre-oxidation Turbidity Removal for CPF Water

Hydrogen peroxide used as a pre-oxidant before electrocoagulation is effective for two reasons. The primary reason is related to the speciation of aqueous iron and its oxidation states. Figure 3-12 describes these underlying mechanisms to determine the speciation of iron since it is the added coagulant. The secondary reason is an empirical observation related to settling velocity, outlined in Figure 3-14.

Sample	pH	ORP (mV)	ORP (V)	Eh (V)	TOC (mg/L)	Turbidity (NTU)	Comments
Raw CPF	6.21	-54.2	-0.0542	0.1563	1759	191	directly from storage tank 2.27.2016
Raw CPF	7.54	114.2	0.1142	0.3247			25 rpm for 20 hours, no peroxide
Peroxide	7.73	255.5	0.2555	0.466			25 rpm for 20 hours, peroxide
EC only	7.81	-163.1	-0.1631	0.0474	1302	123	1 hr flocculation, 1 hr settling
Peroxide/EC	7.84	251.7	0.2517	0.4622	1240	16.6	1 hr flocculation, 1 hr settling

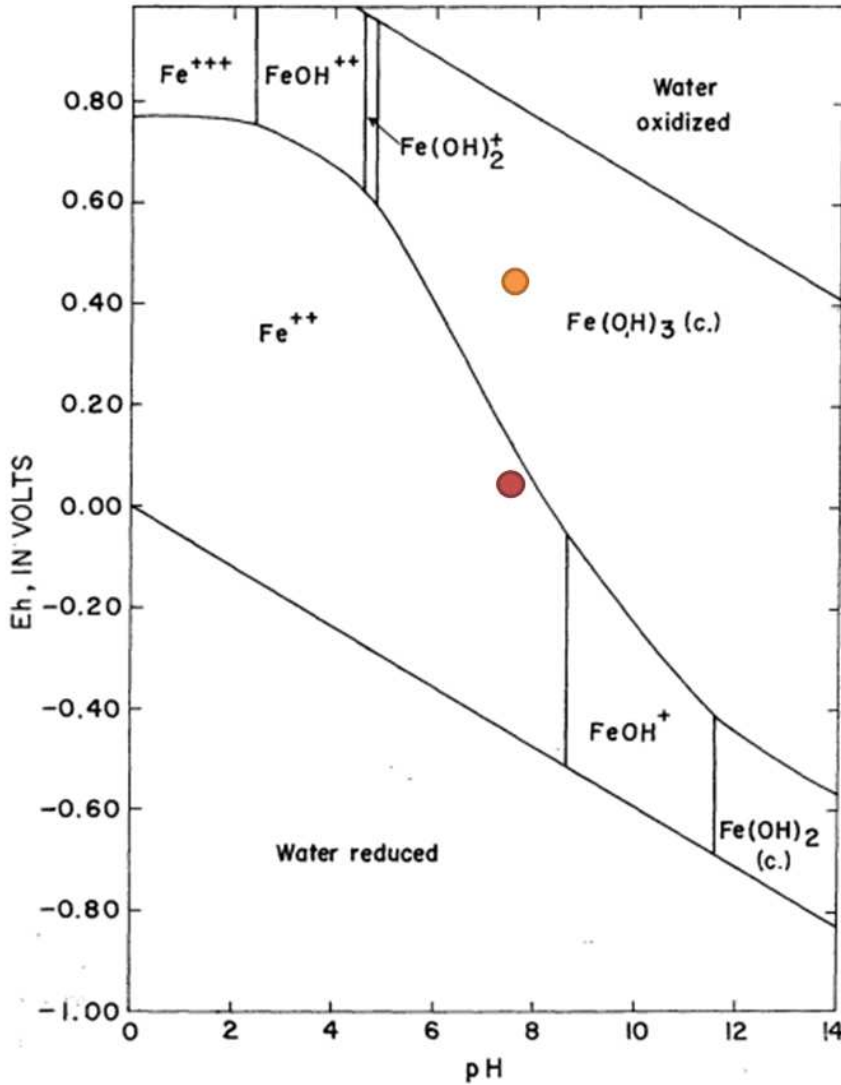


FIGURE 1.— Stability-field diagram for aqueous ferrio-ferrous system.

Sample	Iron (mg/L)
Raw CPF	27.9
Post H2O2/EC	51.9
Actual Coagulant Dose	24
Theoretical Coagulant Dose	37.62

Figure 3-12: Eh-pH Plot for Electrocoagulation versus Pre-oxidation/Electrocoagulation (U.S. Department of the Interior, 1962)

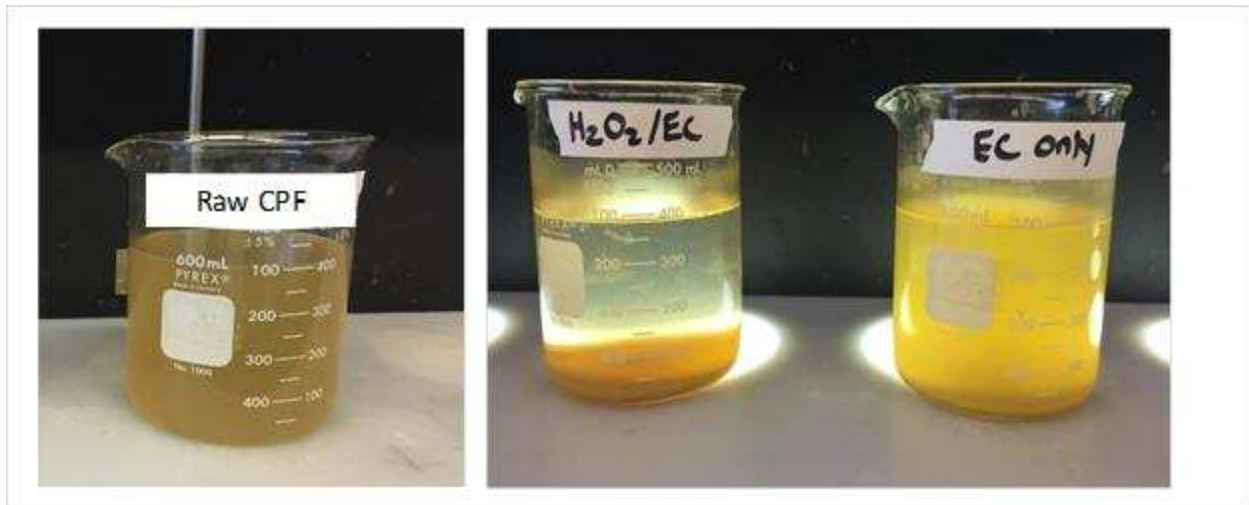


Figure 3-13: Flocculation and Settling for Electrocoagulation Versus Oxidation/Electrocoagulation

Oxidation Reduction Potential (ORP) and pH control the speciation of ionic compounds, particularly iron, in an aqueous state. For a Hach IntelliCAL ORP-REDOX probe:

$$E_h = E + E_{ref}$$

- E_h = Oxidation Reduction Potential, Standard Hydrogen Electrode (mV)
- E = Measured Oxidation Reduction Potential, ORP probe specific (mV)
- E_{ref} = Reference potential = 210.5 mV at 20 C for a Hach IntelliCAL ORP-REDOX probe

Electrocoagulation first oxidizes stable iron (zero valent iron) into ferrous as a result of the electrically charged anode/cathode, then ferrous is oxidized to ferric. Ferrous (Fe^{2+}) exists predominantly in a dissolved state while ferric (Fe^{3+}) reacts with hydroxide to produce solid phase ferric hydroxide, a strong coagulant. Ferrous can react to produce ferrous hydroxide although ferric hydroxide has a stronger positive surface charge and is therefore a more effective coagulant. Figure 3-12 shows that electrocoagulation significantly lowers the oxidation reduction potential of the produced water being treated. By adding hydrogen peroxide, a strong oxidizing

environment is created as the ORP increases from -53 mV to $+255$ mV, and decreases only to $+250$ mV after electrocoagulation. If an oxidant is not added, the ORP drops below -150 mV after electrocoagulation. At a pH of around 7.8, the hydrogen peroxide acts an oxidizing agent to transform ferrous into ferric. For irrigation water treatment and Figure 3-10, a dose of 0.005% hydrogen peroxide by volume was used.

Table 3-3: Relative Settling Velocity of Different Oxidation Contact Times

Sample (30 L Batches)	Settled Turbidity (NTU)	ORP (mV)	Settling
Raw CPF 3/22/16	402	<100	n/a
3 hours continuous mix	40	>300	Very Poor, 3 days
20 hours continuous mix	25	~250	Very Good, 1 hour

During water treatment for irrigation, it was observed that although adding hydrogen peroxide created an extremely positive ORP value, a short pre-oxidation contact time could be associated with "poor" settling and a long pre-oxidation contact time with "good" settling. This may be attributed to the oxidation of organic matter measured as TOC. High concentrations of TOC coupled with "desirable" flocculation and settling conditions after a 20 hour oxidation time indicate that hydrogen peroxide may also be oxidizing and breaking up organic matter so that it cannot adsorb and desorb from metal hydroxide particles (Esmailirad, 2015).

3.3.2 Ultrafiltration

Ultrafiltration removed most emulsified oil droplets still present after electrocoagulation and settling, but large concentrations of TOC still remained. Most of the TOC post ultrafiltration consisted primarily of residual cross linked polymers, but also small concentrations of volatile organics like BTEX that are a large concern for environmental compliance and regulation. As a

particle removal step, turbidity post ultrafiltration was either close to or less than 1 NTU consistently.

Table 3-4: Water Quality Sequence of Raw CPF Produced Water Through Ultrafiltration and Granular Activated Carbon Processes

Sample	TOC (mg/L)	TDS (mg/L)	Ca (mg/L)	HCO ₃ (mg/L)	Na (mg/L)	Cl (mg/L)	B (mg/L)	Fe (mg/L)
Raw	1960	n/a	200	630	6400	12000	22	29
Post Ultrafiltration	1588	24,000	200	590	6300	12000	22	0.27
Post GAC	350	16,993	27	180	5400	9800	ND	ND

Sample	Benzene (ug/L)	Toluene (ug/L)	Ethylbenzene (ug/L)	Total Xylenes (ug/L)	BTEX (ug/L)
Raw	5200	3200	160	820	9380
Post Ultrafiltration	1900	1200	62	320	3482
Post GAC	45	76	6.9	39	166.9

sample	TOC (mg/L)	turbidity (NTU)	pH	ORP (mV)
Raw	2128	172	6.68	-65.3
Peroxide/EC/Flocc/settled	1855	23.9	6.51	282.7
UF	1571	1.1	6.68	282.2
GAC	350	1.6	7.35	87

3.3.3 Granular Activated Carbon

Granular Activated Coconut Charcoal was used as an organic compound removal process. Through adsorption and other complexing processes, boron was also removed. Although bench scale testing met the goal of providing low organic matter water to be diluted for irrigation, the breakthrough time of the GAC columns was very rapid and only small volumes could be produced with influent conditions from 900 to 1600 mg/L TOC concentration. An arbitrary goal of less than 50 mg/L was set to prevent membrane fouling during RO testing although practical applications would call for TOC to be as close to zero as possible to be operationally feasible. Even with an effluent TOC concentration of 31.5 mg/L, BTEX was measured at 19.3 ug/L. Benzene has a molecular weight of 78.11 g/mole and is a concern for passing through RO membranes.

Table 3-5: CPF Produced Water Contaminant Removal Through GAC and RO:
BTEX and Boron

Sample	TDS (mg/L)	TOC (mg/L)	Benzene (ug/L)	Toluene (ug/L)	Ethylbenzene (ug/L)	Total Xylenes (ug/L)	BTEX (ug/L)
Post GAC	24360	31.6	5	9.6	ND	4.7	19.3
Post RO	4580	7.588	ND	ND	ND	ND	ND

Sample	TOC (mg/L)	B (mg/L)
Post GAC 1	150	ND
Post GAC 2	350	ND
Post GAC 3	32	ND

A Freundlich Adsorption Isotherm was generated with the following values (EPA, 2016):

- Coefficient of determination: $R^2 = 0.9664$
- Adsorption capacity parameter $(\text{mg/g})(\text{L/mg})^{1/n}$: $K = 0.013741979$
- Adsorption intensity parameter (unitless): $1/n = 1.8464$

Isotherm testing determined equilibrium loading (Q_e) and equilibrium concentration values (C_e) used to calculate:

- Average equilibrium loading (mg TOC removed / g GAC) = $Q_e = 7.75$
- GAC required for 5,000 bbl/ day pilot (target TOC at 15 mg/L) = 786 cubic meters

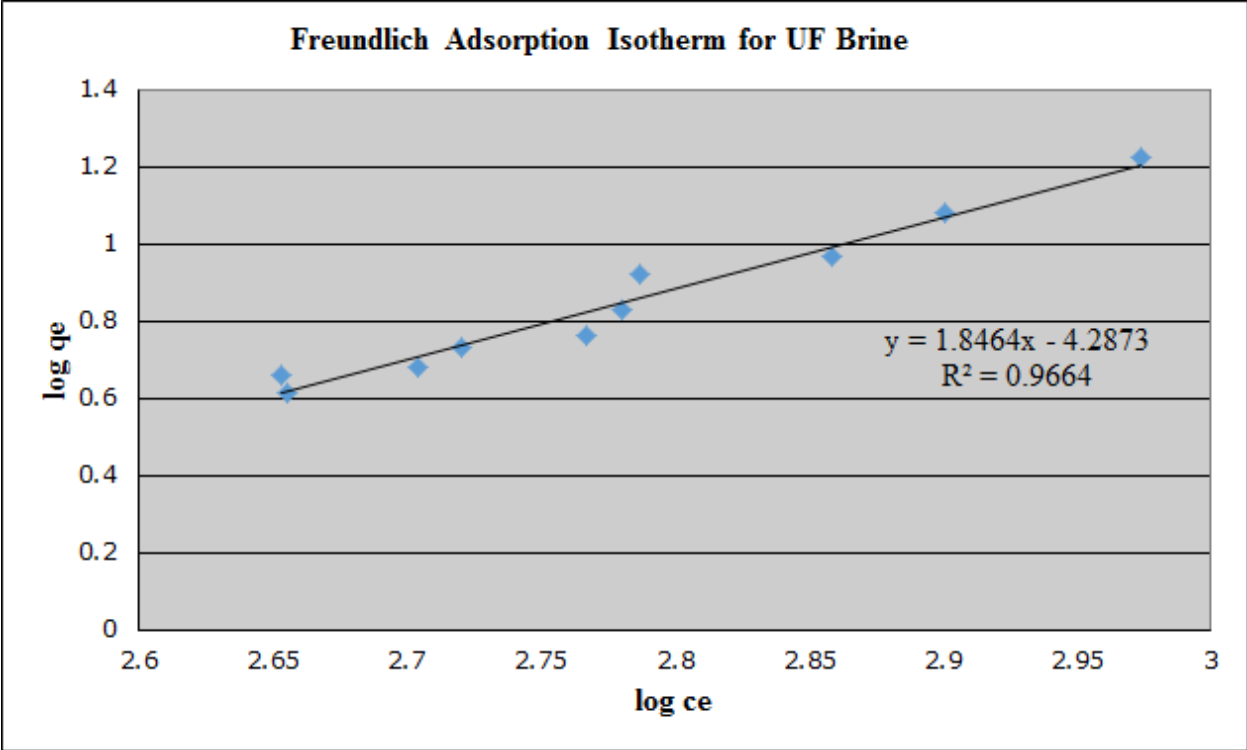


Figure 3-14: Freundlich Adsorption Isotherm for CFP Produced Water Post Ultrafiltration

With an influent concentration of approximately 1,500 mg/L TOC and a target effluent of at 15 mg/L TOC to avoid RO membrane fouling, GAC does not appear to be a feasible organic removal process. Either slickwater or hybrid fracturing fluid flowback should be the preferred wastewater for treatment options, or an alternative process must be used (biological or advanced chemical).

3.3.4 Reverse Osmosis

AG-series membranes were selected to run the majority of tests based on the lower recommended operating pressures and lower breakthrough of organic matter when compared to the SE-series. The fourth run found in table 3-14 shows a TDS removal rate of 81%. BTEX concentrations for this permeate were non-detectable. During the second run in table 3-14, a significantly reduced flux (permeate flow rate) was observed, possibly indicated fouling at a

TOC feed concentration of over 200 mg/L. Since target TDS levels would be under 500 mg/L, a multi-stage reverse osmosis operation would be implemented in the field. Figures 3-13 and 3-14 show that as the feed water becomes more concentrated with rejected salts, the increased concentration gradient allows for more TDS breakthrough. Increased concentrations can also lead to scaling issues reducing flux. Both TDS breakthrough and reduced flux can be seen as a function of time as the feed water becomes more concentrated. Low flux values were measured ranging from 0.13 -0.60 L/min/m² for AG membrane testing (Shackelford et al., 2016).

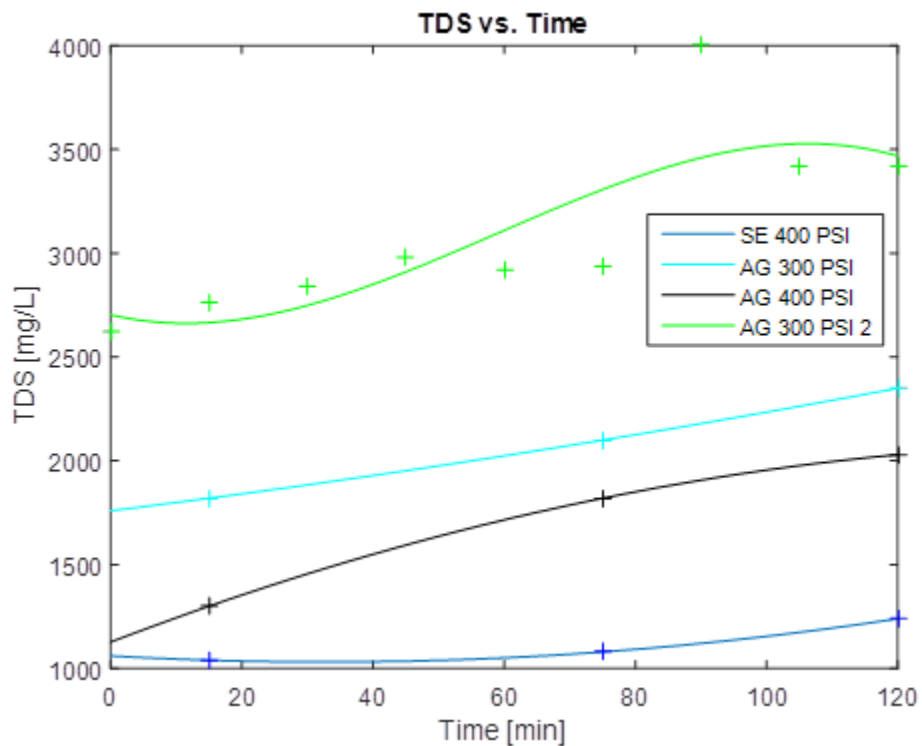


Figure 3-15: Reverse Osmosis Testing for Totals Dissolved Solids Versus Time (Shackelford et al., 2016)

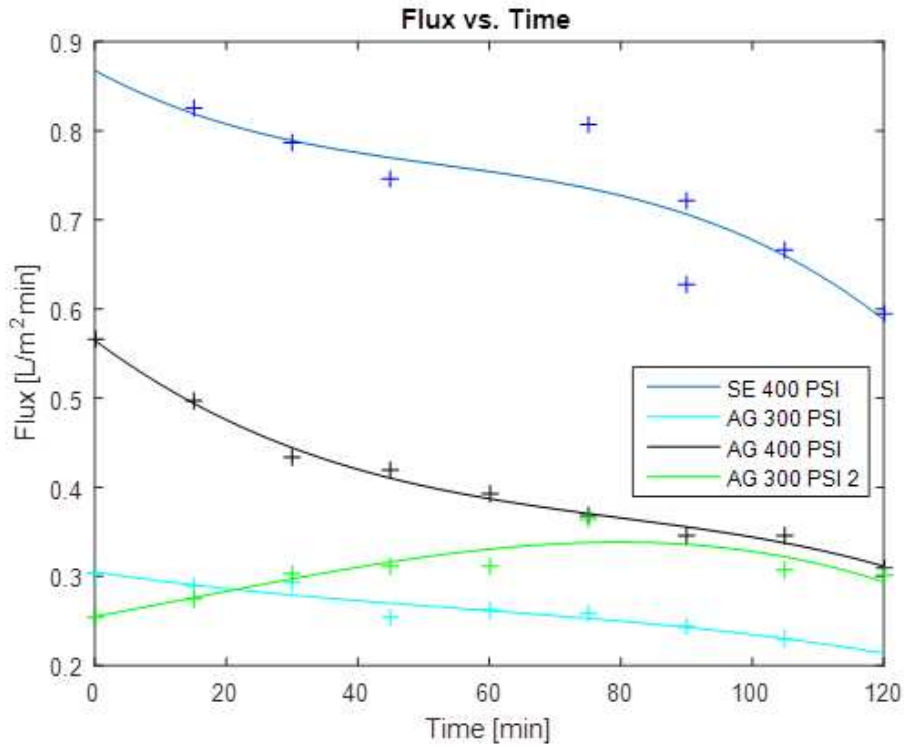


Figure 3-16: Reverse Osmosis Testing for Membrane Flux versus Time (Shackelford et al., 2016)

Table 3-6: Permeate TDS and TOC Concentrations for Crossflow Reverse Osmosis Testing of Pretreated Produced Water

membrane type	Feed TDS (mg/L)	Feed TOC (mg/L)	Permeate TOC (mg/L)	Permeate TDS (mg/L)	Pressure	comments
SE*		150	105	1120	400	Large TOC breakthrough
AG*		223	99	2350	300	Low flux implies rapid fouling
AG*		137	62	2030	400	
AG	24360	31.6	7.588	4580	300	BTEX: Feed = 19.3 mg/L & Permeate = ND
AG		60.11	14.88	3100	300	

*Data points used in Shackelford et al. graphs

Figure 3-16 shows the results of GE's Membrane System Design Software, Winflows 3.3.1. The AG-series membrane was selected. CPF produced water treated through GAC was used as the feed water quality being modeled using Winflows 3.3.1. The recommended operating pressure was 265 psi with a permeate TDS of 5676 mg/L as a single pass.

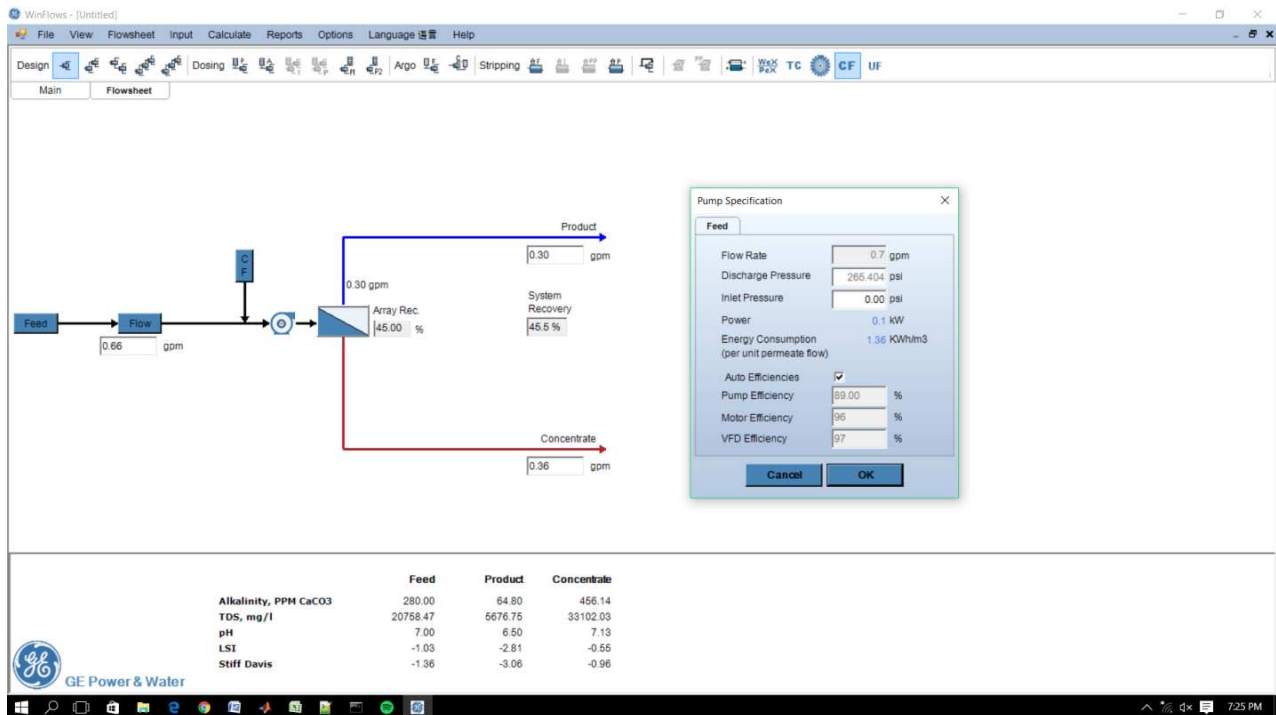


Figure 3-17: GE Winflows 3.3.1 Modeling Software Results for Reverse Osmosis of Pre-treated CPF Produced Water, AG-series (Shackelford, 2016 & GE Power, 2016)

3.3.5 Treated Effluent for Irrigation

Table 3-17 shows water quality parameters for the four different waters used to irrigate. Due to the heterogeneous nature of produced water throughout the treatment process, target TDS and TOC levels were not met exactly but were modeled so that the actual parameters appropriately and relatively simulated the target parameters. Larger concentrations of TOC can be correlated with elevated BTEX levels.

Table 3-7 Irrigation Water Quality Applied to Switchgrass and Canola Crops

Irrigation Water	Watering Period	TDS (mg/L)	TOC (mg/L)	B (mg/L)	BTEX (ug/L)
3500 Low Organics	5	3660	36.98	ND	2.6
400 Low Organics		470	3.2	ND	ND
3500 High Organics		3650	200.4	3.7	151.5
Ultrafiltration Brine		21930	1262	23	1623
3500 Low Organics	6	5820	16.97	ND	5.3
400 Low Organics		360	5.17	ND	6.6
3500 High Organics		6080	346.3	5.9	815.8
Ultrafiltration Brine		22180	1233	22	2612
3500 Low Organics	7	3440	2.05	ND	8.7
400 Low Organics		480	1.19	ND	ND
3500 High Organics		3520	125.6	3.2	297
Ultrafiltration Brine		25660	9795	22	2327

Appendix E includes both basic standards for organic constituents (BTEX) and constituent limits for irrigation water. The EPA drinking water secondary standard is 500 mg/L for TDS (EPA, 2016). Municipal surface discharge allows an incremental increase of 400 mg/L TDS from the surface water baseline or 1 ton/day for industrial discharge under Colorado Discharge Permit System Regulations (CDPHE, 2016). The sodium adsorption ratio is also an important parameter to determine the quality of water used for irrigation.

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{+2}] + [Mg^{+2}]}{2}}}$$

(Lesch & Suarez, 2009)

Week 6 SAR values for 3500 low organics, 400 low organics, 3500 high organics, and ultrafiltration brine are 87.5, 4.5, 57.0, and 104.0 respectively. Concern for salt accumulation occurs when SAR values are larger than 3 (BOR, 2011). Significant damage can occur to clay-type soils with SAR values greater than 9 (Landschoot, 2016). Both 400 low organics and 3500 low organics were in compliance with BTEX regulations, particularly the 5 ug/L limit for

benzene; 3500 high organics and ultrafiltration brine are significantly out of regulation for benzene.

3.3.6 Crop and Soil Analysis

Biomass and plant height measurements clearly show the negative impact of irrigating with high salinity water (ultrafiltration brine). On the opposite end of the spectrum, the control (Horsetooth Reservoir water) promoted the most growth which was also expected. Although there was variability throughout the growing period; 3500 low organics, 400 low organics, and 3500 high organics all performed similarly in terms of plant height for switchgrass and canola. For switchgrass biomass measurements, 400 low organics had 32% and 3500 low organics 25% more biomass growth than 3500 high organics. For canola biomass measurements, 3500 low organics was 31% and 42% larger than 3500 high organics and 400 low organics respectively.

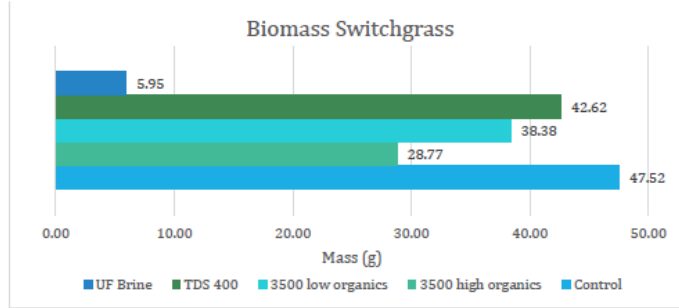


Figure 27 Biomass of tested switchgrass given in grams

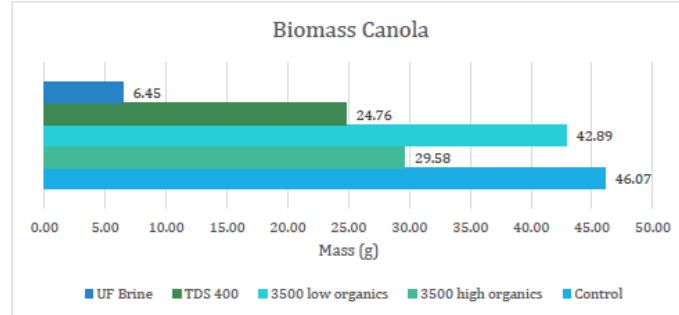


Figure 28 Biomass of tested canola given in grams

Figure 3-18: Biomass Measurements for Canola and Switchgrass by Irrigation Water Quality (Stone et al, 2016)

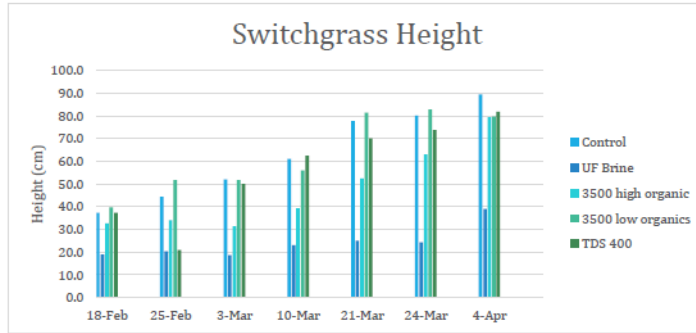


Figure 21 Graph showing variable switchgrass height by date

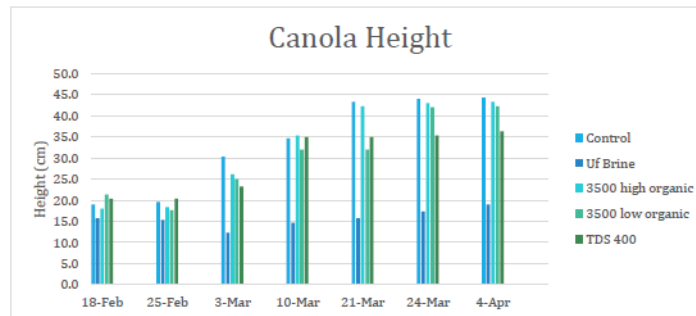


Figure 22 Graph showing variable canola height by date

Figure 3-19: Crop Height Measurements for Canola and Switchgrass by Irrigation Water Quality (Stone et al, 2016)

Table 3-8: Final Total Dissolved Solids Soil Measurements for Canola and Switchgrass

Canola					Switchgrass				
Water Quality Type	TDS (mg/L)	Average TDS (mg/L)	Standard Deviation	Coefficient of Variation	Water Quality Type	TDS (mg/L)	Average TDS (mg/L)	Standard Deviation	Coefficient of Variation
Horsetooth	16,640	9,200	6,948	0.76	Horsetooth	6,000	8,480	2,702	0.32
Horsetooth	8,080				Horsetooth	11,360			
Horsetooth	2,880				Horsetooth	8,080			
3500 w/ Organics	1,520	4,880	2,998	0.61	3500 w/ Organics	19,360	8,533	9,443	1.11
3500 w/ Organics	5,840				3500 w/ Organics	2,000			
3500 w/ Organics	7,280				3500 w/ Organics	4,240			
3500 w/out Organics	8,320	6,293	1,800	0.29	3500 w/out Organics	6,480	22,827	17,172	0.75
3500 w/out Organics	5,680				3500 w/out Organics	21,280			
3500 w/out Organics	4,880				3500 w/out Organics	40,720			
400 Low Organics	3,360	6,800	3,039	0.45	400 Low Organics	23,120	12,507	9,460	0.76
400 Low Organics	7,920				400 Low Organics	9,440			
400 Low Organics	9,120				400 Low Organics	4,960			
Ultrafiltration Brine	10,560	10,267	441	0.04	Ultrafiltration Brine	16,880	45,787	34,023	0.74
Ultrafiltration Brine	10,480				Ultrafiltration Brine	37,200			
Ultrafiltration Brine	9,760				Ultrafiltration Brine	83,280			

The high coefficients of variation values show variability in soil salt accumulation for irrigation triplicate pots. There was significantly more salt accumulation for the canola ultrafiltration brine, and slightly more accumulation for the switchgrass. Values ranged from 4,000 to 12,000 mg/L for the rest of the water quality types. Larger coefficient of variation values may be due to variability for where salt accumulation spatially occurred in the pot.

All fifteen pots for canola were tested for BTEX, GRO and DRO. All fifteen soil samples were measured as "Not Detected" for BTEX, GRO and DRO.

3.4 Conclusion

Conclusions can be made about the feasibility of the treatment train applied, the mechanistic processes behind electrocoagulation, empirical observations of treatment unit process performance and the knowledge gained through the first phase of a produced water reuse irrigation study.

- Even with produced water and flowback being blended at the Wells Ranch Central Processing Facility, total organic carbon (TOC) is still high with an average concentration of 1,783 mg/L.
- The addition of a strong oxidant such as hydrogen peroxide makes electrocoagulation a much more effective process. Creating a higher oxidation reduction potential (ORP) affects the speciation of iron as a coagulant, producing ferric as the dominant species instead of ferrous. Oxidizing organic matter also minimizes interference between organic compounds and metal hydroxides; allowing the floc to settle within a reasonable amount of time.
- Mann Hummel Ultrafiltration membranes are able to effectively remove emulsified oils and particulate matter in CPF produced water. Size exclusion shows that there is a large concentration of small organic matter post ultrafiltration (pore size of 0.05 μm).
- Granular activated carbon is not an economical and operationally feasible organic removal process for the high TOC produced waters coming from Noble Energy's Wells Ranch Central Processing Facility.
- High TOC concentrations will foul reverse osmosis membranes, decreasing flux. Benzene is also likely to breakthrough into the RO permeate at TOC concentrations above 150 mg/L.

- Although GE AG-series membranes had effective TDS removal rates for CPF pretreated produced water at a feed rate of 2.5 L/min; low permeate flux, demand for multi-stage RO filtration vessels, and the need for descalant additives are three challenges for reverse osmosis.
- Switchgrass and canola were able to grow under most water quality conditions, except for ultrafiltration brine which had an extremely negative impact on crop growth and soil salt accumulation. Much more soil, plant and drainage water analysis should occur to determine the specific impacts of each water quality.
- Organics (BTEX, GRO and DRO) were not detected in the soil for canola after the first crop rotation. Organics compounds were either biodegraded, photo degraded, or present in drainage water but were not retained in the soil. More testing needed to confirm any of these results, especially the potential contamination of irrigation runoff.
- Economical and feasible irrigation reuse will either require flowback/produced water with much lower concentrations of total organic carbon. This could be a result of slickwater/hybrid fractured wells or using produced water either from another formation a part from the Niobrara in the Denver Julesburg Basin or possibly a different operator.
- Long term impacts of irrigating with treated produced water are highly unknown. This includes salt accumulation and the fate of other inorganic and organic contaminants.

4. FUTURE WORK

There is a lot of future work that can be done in this area of study, both produced water treatment and impaired wastewater reuse for irrigation purposes. This experimental design was to provide a first phase set up to evaluate the treatment and application of "clean" effluent as well as to establish a set of significant parameters. Future work would entail using a professional water treatment solutions vendor, low organic water, a steady influent waste stream, agricultural land within close proximity, and treating water all the way through reverse osmosis field operation units. The upper limit for a pilot scale would be around 5,000 barrels a day.

Future work with electrocoagulation research would be to investigate 1) oxidant accelerators to reduce oxidation contact time 2) Using a shorter oxidation contact time followed by flocculation and a well-constructed continuous flow bench scale dissolved air floatation (DAF) unit.

For the irrigation study, deeper investigation into the degradation or fate of regulated organic contaminants (BTEX, GRO, and DRO) from application to runoff or uptake. Currently a second crop rotation is being looked at to evaluate the impact of longer term salt and low organic accumulation.

There is still a lot of opportunity for process optimization with electrocoagulation dosage and reverse osmosis testing. RO testing was very limited due to the difficulty of producing water with both low organic carbon and inorganic carbon (GAC residual). Scaling due to the presence of calcium and magnesium is a major concern for reverse osmosis. Solutions need to be investigated whether that is ion exchange resins, softening, or industrial descalant chemical additives. More membrane types could also be tested.

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APPENDIX

Appendix A: Water Quality Data and Collection

Table A-1: Sample Handling Guidelines for EPA Certified Lab Analysis (ALS Global Environmental Laboratory, 2016)



Sample Handling Guidelines

General Inorganic Parameters							
Parameters	Method	Water			Soil/Sludge		
		Preservative	Container	Holding Time	Preservative	Container	Holding Time
Acidity	E305.1	4°C	250 mL / P	14 Days		Matrix Not Applicable	
Alkalinity (Total, Carbonate, Bicarbonate, Hydroxide)	E310.1, SM230B	4°C	250 mL / P	14 Days		Matrix Not Applicable	
Ammonia	E350.1, SMA500	4°C, H ₂ SO ₄ to pH <2	125 mL / P	28 Days	4°C	4oz WMG	28 Days
Anions: Br, Cl, F, SO ₄ / NO ₂ , NO ₃ , o-PO ₄	E300.0, SW9056	4°C	125 mL / P	28 Days / 48 Hours	4°C	4oz WMG	28 D / 48 H from Prep
Fluoride	E340.2, SMA500, SW9214	4°C	125 mL / P	28 Days	4°C	4oz WMG	28 Days from Prep
Nitrite	E354.1	4°C	125 mL / P	48 Hours	4°C	4oz WMG	48 Hours from Prep
Chromium VI (Hexavalent Cr)	SW7196A(aq, so), SW7196A/3060A (so)	4°C	125 mL / P	24 Hours	4°C	4oz WMG	24 Hours from Prep
Cyanide (Total)	E335.2, SW9010B, SW9013B, SW9014	4°C, NaOH to pH >12	125 mL / P	14 Days	4°C	4oz WMG	14 Days
Cyanide (Amenable to Chlorination)	E335.2, SW9010B, SW9013B, SW9014	4°C, NaOH to pH >12	125 mL / P	14 Days		Matrix Not Applicable	
Cyanide (Weak Acid Dissociable)	SMA500	4°C, NaOH to pH >12	125 mL / P	14 Days	4°C	4oz WMG	14 Days
Hardness	E130.2, SM2340	4°C	125 mL / P	14 Days		Matrix Not Applicable	
Nitrate + Nitrite as N	E353.2	4°C, H ₂ SO ₄ to pH <2	125 mL / P	28 Days	4°C	4oz WMG	28 Days
Perchlorate	E314.0	4°C, 1/3 headspace	250 mL / P	28 Days	4°C	4oz WMG	28 Days
Phosphorus, Total	E365.2, SMA500	4°C, H ₂ SO ₄ to pH <2	125 mL / P	28 Days		Matrix Not Applicable	
Phosphate, Ortho	E365.2, SMA500	4°C	125 mL / P	48 Hours		Matrix Not Applicable	
Positive pH, Sodium Adsorption Ratio, Electrical Conductivity	USDA460		Matrix Not Applicable		N/A	Quart Size Baggie	N/A
pH	E150.1, SW9040, SW9045	4°C	125 mL / P	4 Days from Receipt	4°C	4oz WMG	4 Days from Receipt
Solids, Dissolved (TDS)	E160.1, SM2540C	4°C	250 mL / P	7 Days		Matrix Not Applicable	
Solids, Suspended (TSS)	E160.2, SM2540D	4°C	250 mL / P	7 Days		Matrix Not Applicable	
Solids, Total (TS)	E160.3, SM2540B	4°C	250 mL / P	7 Days		Matrix Not Applicable	
Solids, Volatile (TVS)	E160.4, SM2540E	4°C	250 mL / P	7 Days		Matrix Not Applicable	
Specific Conductance	E120.1, SW9050, SM2510B	4°C	125 mL / P	4 Days from Receipt		Matrix Not Applicable	
Sulfide	E376.1, SMA500	4°C, ZnAc, NaOH to pH >9	250 mL / P	7 Days		Matrix Not Applicable	
Total Organic Carbon (TOC)	E415.1 (aq), 9060 (aq), Walkley Black (so)	4°C, H ₂ SO ₄ to pH <2	125 mL / Amb G	28 Days	4°C	4oz WMG	28 Days
Metals Parameters							
Parameters	Method	Water			Soil/Sludge		
		Preservative	Container	Holding Time	Preservative	Container	Holding Time
Metals	E200.7, SW6010B, E200.8, SW6020A	4°C, HNO ₃ to pH<2	250 mL / P	6 Months	4°C	4oz WMG	6 Months
Mercury	E245.1, SW7470 (aq), SW7471 (so)	4°C, HNO ₃ to pH<2	250 mL / P	28 Days	4°C	4oz WMG	28 Days
Hardness	Calculation from Ca & Mg Results	4°C, HNO ₃ to pH<2	250 mL / P	6 Months		Matrix Not Applicable	
Sodium Adsorption Ratio (SAR)	Calculation from Ca, Mg, & Na Results	4°C, HNO ₃ to pH<2	250 mL / P	6 Months		Matrix Not Applicable	
Organic Parameters							
Parameters	Method	Water			Soil/Sludge		
		Preservative	Container	Holding Time*	Preservative	Container	Holding Time*
Chlorinated Herbicides	SW8151A	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
EDB and/or DBCP	8260	4°C, HCl to pH<2, ZH	3 x 40 mL / V-TLS	14 Days		Matrix Not Applicable	
Glycols (ethylene and propylene)	SW8015D	4°C	3 x 40 mL / V-TLS	7 / 14 Days	4°C	4oz WMG / TLC	14 Days
Lipids	SOP 672		Matrix Not Applicable		Frozen	8oz WMG / TLC	28 Days
Methane, Ethane, Ethene, Propane	RSK175	4°C, HCl to pH<2, ZH	3 x 40 mL / V-TLS	14 Days		Matrix Not Applicable	
Moisture	ASTM 2216		Matrix Not Applicable		4°C	4oz WMG / TLC	14 Days
Organochlorine Pesticides	E608, SW8081A	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
Organophosphorus Pesticides	SW8141	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
PCBs	E608, SW8082	4°C	1000 mL / TLC-Amb G	None	4°C	4oz WMG / TLC	None
Polynuclear Aromatic Hydrocarbons	SW8270D, SW8270D-SIM	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
Semivolatile Organics (Base/Neutrals/Acids)	E625, SW8270D, SW8270D-SIM	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
Total Petroleum Hydrocarbons							
DRO and/or MO	SW8015M, CAL-LUFT	4°C, HCl to pH<2, ZH	3 x 40 mL / V-TLS	14 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
DRO	TX1005	4°C, HCl to pH<2, ZH	3 x 40 mL / V-TLS	14 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
GRO	SW8015, CAL-LUFT	4°C, HCl to pH<2, ZH	3 x 40 mL / V-TLS	14 Days	4°C	4oz WMG / TLC	14 Days
Oil and Grease	E1664 (aq), SW9071 (so)	4°C, H ₂ SO ₄ to pH<2	1000 mL / TLC-Amb G	28 Days	4°C	4oz WMG	28 Days
Volatile Organics	ES24.2, E624, SW8260C	4°C, HCl to pH <2, ZH	3 x 40 mL / V-TLS	14 Days	4°C	4oz WMG / TLC	14 Days
BTEX and/or MTBE	ES24.2, E624, SW8260C	4°C, HCl to pH <2, ZH	3 x 40 mL / V-TLS	14 Days	4°C	4oz WMG / TLC	14 Days
Volatile Organics	S035A/SW8260C		Matrix Not Applicable		4°C	3 ENCORE Samplers	48 H to Analysis or Freezing
Volatile Organics	S035A/SW8260C		Matrix Not Applicable		4°C / sodium bisulfate	1 Terracone Sampler	14 Days

*Where two holding times are provided, the first value indicates holding time to extraction, the second value indicates holding time between extraction and analysis.

Table A-2: Water Quality Parameter Database for Multiple-Type Waters Used During Irrigation Study

Sample ID	Date (Raw Produced Collected from CPF)	Watering Period	Gravimetric Analysis		
			Alkalinity (mg/L as CaCO3)	TOC (mg/L)	TDS (mg/L)
Horsetooth Water			37	ND	310
UF Brine	1/22/2016	2	580	1438	21,500
GAC Brine			360	150	13,320
3500 low organics			130	37	3,500
SE permeate			59	105	1,120
Raw			630	1960	
UF	1/29/2016	3	590	1588	24,000
3500 low organics			81	37	3,500
GAC			280	350	16,993
Raw UF Brine	2/12/2016	5		1262	21,930
3500 low organics				36.98	3,660
400 low organics				3.2	470
3500 high organics				200.4	3,650
Raw	2/26/2016	6			
Raw UF Brine				1233	22,180
3500 low organics				16.97	5,820
400 low organics				5.17	360
3500 high organics				346.3	6,080
Feed Water				31.6	24,360
AG Permeate 3.1 (300 psi)				7.588	4,580
Raw UF Brine	3/14/2016	7		9795	25,660
3500 low organics				2.05	3,440
400 low organics				1.19	480
3500 high organics				125.6	3,520

Sample ID	Watering Period	EPA certified Lab Results											
		Al (mg/L)	Ba (mg/L)	B (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	Si (mg/L)	Sr (mg/L)	Zn (mg/L)
Horsetooth Water				ND	12		ND	1.8		3.3			
UF Brine	2	ND	8	21	190	0.24	94	25	0.3	6,600	29	36	0.15
GAC Brine		ND	ND	ND	11	ND	190	31	ND	3,500	1.8	0.45	ND
3500 low organics		ND	ND	ND	11	ND	37	14	ND	1,000	0.69	0.26	ND
SE permeate		ND	ND	ND	ND	ND	25	2.2	ND	510	0.3	0.025	ND
Raw	3	ND	16	22	200	29	96	27	0.37	6400	45	39	0.048
UF		ND	8	22	200	0.27	96	27	0.32	6300	32	38	ND
3500 low organics		ND	ND	ND	14	ND	79	17	ND	1200	0.72	0.28	0.031
GAC	4	ND	0.17	ND	27	ND	300	64	ND	5400	1.6	0.89	ND
Raw UF Brine	5			23									
3500 low organics				ND									
400 low organics				ND									
3500 high organics				3.7									
Raw	6												
Raw UF Brine				22	220		100	29		6,200			
3500 low organics				ND	14		170	13		1,900			
400 low organics				ND	11		4.5	2.2		62			
3500 high organics				5.9	75		28	11		2,000			
Feed Water				ND									
AG Permeate 3.1 (300 psi)			ND										
Raw UF Brine	7			22	220		110	30		1,600			
3500 low organics				ND	13		190	8.4		1,000			
400 low organics				ND	10		5.8	2		38			
3500 high organics				3.2	47		14	7.1		1,000			

Sample ID	Watering Period											
		Br (mg/L)	Cl (mg/L)	SO4 (mg/L)	PO4 (mg/L)	HCO3 (mg/L)	Benzene (ug/L)	Toluene (ug/L)	Ethylbenzene (ug/L)	Total Xylenes (ug/L)	BTEX (ug/L)	
Horsetooth Water			3.2	3.9		37						
UF Brine	2	130	13,000	55		580	2400	1300	70	380	4150	
GAC Brine		49	6,000	120		130	47	67	4.8	26	144.8	
3500 low organics		17	2,000	28		69	10	13	0.9	4.9	28.8	
SE permeate		7.1	850	6.5		ND	7.7	1.7	ND	ND	9.4	
Raw	3	130	12000	40	ND	630	5200	3200	160	820	9380	
UF		140	12000	43		590	1900	1200	62	320	3482	
3500 low organics		18	2000	56		74	11	15	1	5.7	32.7	
GAC		92	9800	230		180	45	76	6.9	39	166.9	
Raw UF Brine	5						960	530	23	110	1623	
3500 low organics							1.3	1.3	ND	ND	2.6	
400 low organics							ND	ND	ND	ND	0	
3500 high organics							100	43	1.5	7	151.5	
Raw	6			44	ND							
Raw UF Brine			12,000				1500	840	42	230	2612	
3500 low organics			3,500				2.4	2.9	ND	ND	5.3	
400 low organics			110				3	3.6	ND	ND	6.6	
3500 high organics			3,600				580	200	5.8	30	815.8	
Feed Water							5	9.6	ND	4.7	19.3	
AG Permeate 3.1 (300 psi)							ND	ND	ND	ND	0	
Raw UF Brine	7		6,900				1400	570	57	300	2327	
3500 low organics				2,000				4.2	4.5	ND	8.7	
400 low organics				71				ND	ND	ND	0	
3500 high organics				2,300				200	78	3	16	

Table A-3: Final Irrigation Effluent Quality Dilution Calculations

Watering Period	Sample	date	dilution water TDS (mg/L)	initial brine TDS (mg/L)	turbidity (NTU)	initial brine TOC (mg/L)	Final TOC (mg/L)	measured TOC (mg/L)	Volume dilution water (L)	Volume of Brine (L)	Total Volume (L)	target WQ TDS (mg/L)	measured TDS (mg/L)	dilution factor
1	Raw	12/4/2016			120	1650								
	3500 LOW ORGANICS	1/21/2016	310	15,787		478	101.6637034		41.72766468	11.27233532	53	3500		4.7017764
	400 LOW ORGANICS	1/21/2016	310	15,787		478	2.868254956		52.68197173	0.318028269	53	400		166.65185
	3500 HIGH ORGANICS	1/21/2016	310	21,650		1353	215.9438635		44.54100165	8.458998349	53	3500		6.2655172
	UF Brine	1/21/2016		21,650		1353								
2	Raw	1/22/2016			167	2173								
	3500 LOW ORGANICS	1/29/2016	310	13320		150	37.20839813		39.85303266	13.14696734	53	3500		4.031348
	400 LOW ORGANICS	1/29/2016	310	13320		150	1.049766719		52.62908243	0.370917574	53	400		142.88889
	3500 HIGH ORGANICS	1/29/2016	310	21500		1438	232.2407857		44.44036047	8.55963953	53	3500		6.1918495
	UF Brine	1/29/2016		21500		1438								
3	Raw	1/29/2016			288	1960								
	3500 LOW ORGANICS	2/8/2016	310	13320		150	37.20839821		9.700313453	3.2	12.90031345	3500.000007		4.031348
	400 LOW ORGANICS	2/8/2016	310	13320		150	1.049766719		52.62908243	0.370917574	53	400		142.88889
	3500 HIGH ORGANICS	2/8/2016	310	24000		1588	229.1973577		45.35046602	7.649533979	53	3500		6.9285266
	UF Brine	2/8/2016		24000		1588								
4	Raw	2/5/2016			172	2128								
	3500 LOW ORGANICS	2/12/2016	310	16993		350	68.35853791		55.62084641	13.5	69.12084641	3499.999999		5.1200627
	400 LOW ORGANICS	2/12/2016	310	16993		350	1.928610788		52.70795322	0.292046776	53	400		181.47778
	3500 HIGH ORGANICS	2/12/2016	310	23166		1558	233.3561837		45.06169593	7.938304066	53	3500		6.676489
	UF Brine	2/12/2016		23166		1558								
5	Raw	2/12/2016			260	n/a								
	3500 LOW ORGANICS	2/22/2016	310	19800		223	36.92167956	36.98	44.2248923	8.775107697	53	3500	3660	6.0398119
	400 LOW ORGANICS	2/22/2016	310	19800		223	1.04167748	3.2	52.75242643	0.247573571	53	400	470	214.07778
	3500 HIGH ORGANICS	2/22/2016	310	21930		1262	200.6469298	200.4	44.57346491	8.426535088	53	3546.743421	3650	6.2896552
	UF Brine	2/22/2016		21930		1262		1262					21930	
6	Raw	2/26/2016			191	1759								
	3500 LOW ORGANICS	3/1/2016	310	13740		76	18.15485997	16.97	40.33937397	12.66062603	53	3500	5820	4.1862069
	400 LOW ORGANICS	3/1/2016	310	13740		76	0.512206081	5.17	52.64280365	0.357196346	53	400	360	148.37778
	3500 HIGH ORGANICS	3/1/2016	310	13600		1401	375.9096644	346.3	38.77929178	14.22070822	53	3500	6080	3.7269592
	UF Brine	3/1/2016		13600		1401		1233					22180	
7	Raw	3/14/2016			376	1598								
	3500 LOW ORGANICS	3/17/2016	310	21860		23.69	3.510638841	2.05	45.14589031	7.854109692	53	3500	3440	6.7480596
	400 LOW ORGANICS	3/17/2016	310	21860		23.69	0.099046237	1.19	52.7784107	0.221589302	53	400	480	239.18122
	3500 HIGH ORGANICS	3/17/2016	310	25013.33		1027	138.3715297	125.6	45.85911288	7.140887122	53	3500	3520	7.422047
	UF Brine	3/17/2016	310	25013.33		1027		9795					25,660	
8	Raw	3/22/2016			242	1643								
	3500 LOW ORGANICS	3/31/2016	310	15006.66667		14.44	3.134288954	5.7	41.49603085	11.50396915	53	3496.865711	3380	4.6071055
	UF Brine	3/31/2016	310	25373.33333		1192		1192					26220	

Table A-4: Feed Water Quality Input for Winflows Reverse Osmosis Modeling (Shackelford, 2016 & GE Power, 2016)

Water Type

Feed Water Analysis
 Select Water Source: Brackish Surfacewater (Conventional)
 Select Water Type: User Defined

Ion	mg/l	meq/l	ppm as CaCO ₃
Calcium (Ca)	27.00	1.3474	67.43
Magnesium (Mg)	31.00	2.5809	127.66
Sodium (Na)	7844.89	341.2306	17076.37
Potassium (K)	190.00	4.8596	243.19
Ammonia - N (NH ₄)	0.00	0.0000	0.00
Barium (Ba)	0.17	0.0025	0.12
Strontium (Sr)	0.89	0.0203	1.02
Iron (Fe)	0.00	0.0000	0.00
Manganese (Mn)	0.00	0.0000	0.00
Total Cations	8093.95	350.0114	17515.80
Sulfate (SO ₄)	230.00	4.7885	239.63
Chloride (Cl)	12000.00	338.4763	16938.54
Fluoride (F)	0.00	0.0000	0.00
Nitrate (NO ₃)	0.00	0.0000	0.00
Bromide (Br)	92.00	1.1514	57.62
Phosphate (PO ₄)	0.00	0.0000	0.00
Boron (B)	0.00	0.0000	0.00
Silica (SiO ₂)	1.60	0.0001	0.00
Hydrogen Sulfide (H ₂ S)	0.00	0.0000	0.00
Bicarbonate (HCO ₃)	340.46	5.5797	279.23
Carbon Dioxide (CO ₂)	28.15	0.0000	0.00
Carbonate (CO ₃)	0.46	0.0153	0.77
Total Anions	12664.52	350.0114	17515.79

Parameters

Total Alkalinity (ppm CaCO₃): 280.00
 TDS (mg/l): 20758.47
 pH: 7.00
 Temperature (C): 25.00
 SDF: 4.00
 Recovery (%): 45

Saturation Data (Feed Water)

BaSO₄: 104.15 %
 CaF₂: 0.00 %
 CaSO₄: 0.21 %
 SiO₂: 1.28 %
 SrSO₄: 0.30 %
 Struvite: 0.000 %
 LSI: -1.03
 Stiff-Davis Index: -1.36
 Osmotic Pressure: 231.90 psi
 Conductivity at 25C: 33499 μS/cm
 Density: 1011.6 kg/m³

Note: - Alkalinity is user-input
 Execute 'Balance' button first, if required, click on 'Add Sodium/Chloride'

Buttons: Export, Import, Multiple Feed, Design Guidelines, Add Sodium, Add Chloride, Clear Values, Balance, Cancel, OK

Appendix B: Supplementary Calculations

Table B-1: Theoretical Dosage for Electrocoagulation (Nielsen, 2015)

Continuous Flow EC dosing Calculator		Batch Treatment (Jar Test) EC dosing Calculator	
Operating Amps	6	Operating Amps	1
Operating Time (seconds)	60	Operating Time (seconds)	52
Flow per cell (gpm)	0.75	Sample Volume (mL)	400
# of iron electrodes	6	# of iron electrodes	1
# of aluminum electrodes	0	# of aluminum electrodes	0
% Fe	100%	% Fe	100%
% Al	0%	% Al	0%
Coulombs	360	Coulombs	52
Faradays	0.004	Faradays	0.001
moles e ⁻	0.004	moles e ⁻	0.001
moles Fe	0.002	moles Fe	0.000
moles Al	0.000	moles Al	0.000
grams Fe released	0.104	grams Fe released	0.015
grams Al released	0.000	grams Al released	0.000
mg Fe/L	36.6963	Fe Dose (mg/L)	37.6217
mg Al/L	0.00	Al Dose (mg/L)	0.00
Charge Loading (F/m ³ /min)	1.314	Charge Loading (F/m ³)	1.347
Charge Rate (Coulombs/gpm)	480.00	Dosing Factor (x)	4.10
Dosing Factor (x)	4		

Table B-2: Isotherm Generation Calculations (EPA, 2015)

% GAC	mass of adsorbent (m)(g)	TOC (mg/L)	% reduction	mass removed (ab	qe x/m (mg removed/g GAC)
0	0	1276	0	0	0
5	20	942.4	26.14420063	333.6	16.68
10	40	795.8	37.63322884	480.2	12.005
15	60	722.2	43.40125392	553.8	9.23
20	80	613	51.95924765	663	8.2875
25	100	603.3	52.71943574	672.7	6.727
30	120	585	54.15360502	691	5.758333333
35	140	525.9	58.78526646	750.1	5.357857143
40	160	506	60.34482759	770	4.8125
45	180	450.2	64.71786834	825.8	4.587777778
50	200	452.3	64.55329154	823.7	4.1185

% GAC	Ce	1/qe	1/ce	log ce	log qe	Ce/qe	Ce	Ce/qe
0	1276							
5	333.6	0.2	0.002998	2.523226	0.69897	66.72	0.002998	56.4988
10	480.2	0.1	0.002082	2.681422	1	48.02	0.002082	66.28905
15	553.8	0.066667	0.001806	2.743353	1.176091	36.92	0.001806	78.24485
20	663	0.05	0.001508	2.821514	1.30103	33.15	0.001508	73.96682
25	672.7	0.04	0.001487	2.827821	1.39794	26.908	0.001487	89.68337
30	691	0.033333	0.001447	2.839478	1.477121	23.03333	0.001447	101.5919
35	750.1	0.028571	0.001333	2.875119	1.544068	21.43143	0.001333	98.15491
40	770	0.025	0.001299	2.886491	1.60206	19.25	0.001299	105.1429
45	825.8	0.022222	0.001211	2.916875	1.653213	18.35111	0.001211	98.1303
50	823.7	0.02	0.001214	2.915769	1.69897	16.474	0.001214	109.8215

MANN+HUMMEL UA420-BT (Ultrafiltration Cartridge)

MANN+HUMMEL UA420-BT Ultrafiltration cartridge typically removes suspended solids, including high molecular-weight substances such as organic and inorganic compounds. It also acts as a barrier for the control of bacteria, viruses, spores, algae and parasites.

The **MANN+HUMMEL UA420-BT** design is based on years of water filtration expertise, in-house R&D, engineering and manufacturing skills combined with stringent German automotive standards. Customers use **UA420-BT** to effectively treat surface / borehole and process water.

The **UA420-BT** cartridge are designed with these features:

- Hydrophilic / low fouling of membranes
- High flow rates at low pressure utilization
- Robust fibers producing quality permeate water
- Small footprint/ mobile device

Membrane Specifications	
Structure	Hollow Fiber
Membrane Material	Hydrophilic Modified PAN
Surface Area (nominal)	6 m ² / 65 ft ²
Housing Material and Caps	PVC Transparent Housing
Potting	Epoxy
Inlet / Outlet Dimensions	1" NPT (Female thread)
Weight (Shipping)	7 kg / 16 lbs
Refill Element Weight	3 kg / 6.6 lbs

Membrane Performance*	
Filtrate Flux	Up to 120 LMH*
Nominal Pore Size	50 nm
Bacteria Rejection	> Log 6
Feed TSS	Max 350 mg/L
Feed Turbidity	Max 300 NTU

* Depending on feed water quality and operating conditions

Also available in:	
UA420-E	Fiber element only
UA420-BB	Blue housing

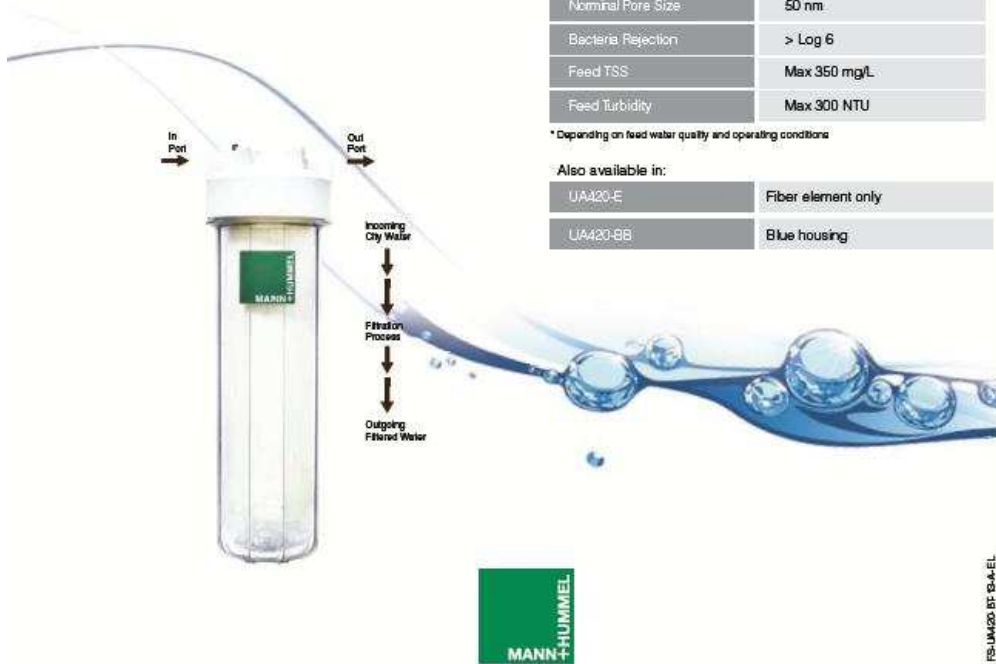


Figure C-1: Ultrafiltration Membrane and Housing Specifications (MANN+HUMMEL, 2012)

SPECIFICATIONS	
US Standard Sieve	12X30
Mesh Size:	
Greater than 12	4% maximum
Less than 30	4% maximum
Total Surface Area	minimum 1200 m ² /g
Iodine Number (mg/g)	1100 minimum
Hardness number	98 minimum
Moisture	5% maximum as packed
Apparent Density (g/cc)	0.51 typical
Back Washed & Drained Density (lbs/ft ³)	28-28.5 typical
Water Soluble Ash	Less than 0.5%
pH	5-8

Figure C-2: GAC1230C-AW Granular Activated Coconut Shell Charcoal Specifications (Charcoal House, 2016)

Table 1: Element Specification

Membrane	A-Series, Thin-Film Membrane (TFM*)
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Model	Average permeate flow gpd (m ³ /day) ^{1,2}	Average NaCl rejection ^{1,2}	Minimum NaCl rejection ^{1,2}
AG2540TM	710 (2.7)	99.5%	99.0%
AG4025T	1,600 (6.0)	99.5%	99.0%
AG4026F	1,600 (6.0)	99.5%	99.0%
AG4040C	2,400 (9.1)	99.5%	99.0%
AG4040FM	2,400 (9.1)	99.5%	99.0%
AG4040TM	2,400 (9.1)	99.5%	99.0%
AG8040C	9,900 (37.3)	99.5%	99.0%
AG8040F	9,600 (36.3)	99.5%	99.0%
AG8040F 400	10,500 (39.8)	99.5%	99.0%
AG8040N	9,600 (36.3)	99.2%	98.5%
AG8040N 400	10,500 (39.8)	99.2%	98.5%
AG8340F 400	10,500 (39.8)	99.5%	99.0%

¹ Average salt rejection after 24 hours operation. Individual flow rate may vary +/- 20%.

² Testing conditions: 2,000 ppm NaCl solution at 225 psi (1,551 kPa) operating pressure, 77°F (25°C), pH 7.5 and 15% recovery.

Table 3: Operating and CIP parameters

Typical Operating Pressure	200 psi (1,379 kPa)
Typical Operating Flux	10-20GFD (15-35LMH)
Maximum Operating Pressure	Tape 450 psi (3,103 kPa) Other outerwrap: 600 psi (4,137 kPa)
Maximum Temperature	Continuous operation: 122°F (50°C) Clean-In-Place (CIP): 122°F (50°C)
pH Range	Optimum rejection: 7.0-7.5, Continuous operation: 4.0-11.0, Clean-In-Place (CIP): 2.0-11.5
Maximum Pressure Drop	Over an element: 12 psi (83 kPa) Per housing: 50 psi (345 kPa)
Chlorine Tolerance	1,000+ ppm-hours, Dechlorination recommended
Feedwater	NTU < 1 SDI < 5

Figure C-3: GE AG-Series Reverse Osmosis Membrane Specifications (GE Power, 2015)

Table 1: Element Specification

Membrane		S-Series, Thin-Film Membrane (TFM*)	
Model	Average permeate flow gpd (m3/day)l ^{1,2}	Average NaCl rejection ^{1,2}	Minimum NaCl rejection ^{1,2}
SE2540F30	550 (2.1)	99%	97.5%
SE2540F50	370 (1.4)	99%	97.5%
SE8040C30	8,500 (32.2)	99%	97.5%

¹Average salt rejection after 24 hours operation. Individual flow rate may vary ±25%.

²Testing conditions: 2,000ppm NaCl solution at 425psi (2,930kPa) operating pressure, 77°F (25°C), pH6.5 and 15% recovery.

Table 3: Operating and CIP Parameters

Typical Operating Flux	5-20 GFD (8-34 LMH)
Maximum Operating Pressure	600psi (4,137kPa) if T < 95°F (35°C) 435psi (3,000kPa) if T > 95°F (35°C)
Maximum Temperature	Continuous Operation: 122°F (50°C) Clean-In-Place (CIP): 122°F (50°C)
pH Range	Optimum rejection Range 5.5-7.0 Continuous Operation: 2.0-10.0 Clean-In-Place (CIP): 1.0-10.5
Maxime Pressure Drop	Over an element: 15psi (103kPa) Per housing: 60psi (414kPa)
Chlorine Tolerance	500+ ppm-hours, dechlorination recommended
Feedwater	NTU < 1 SDI < 5

**Figure C-4: GE SE-Series Reverse Osmosis Membrane Specifications
(GE Power & Water, 2014)**

Appendix D: Jar Test Pictures

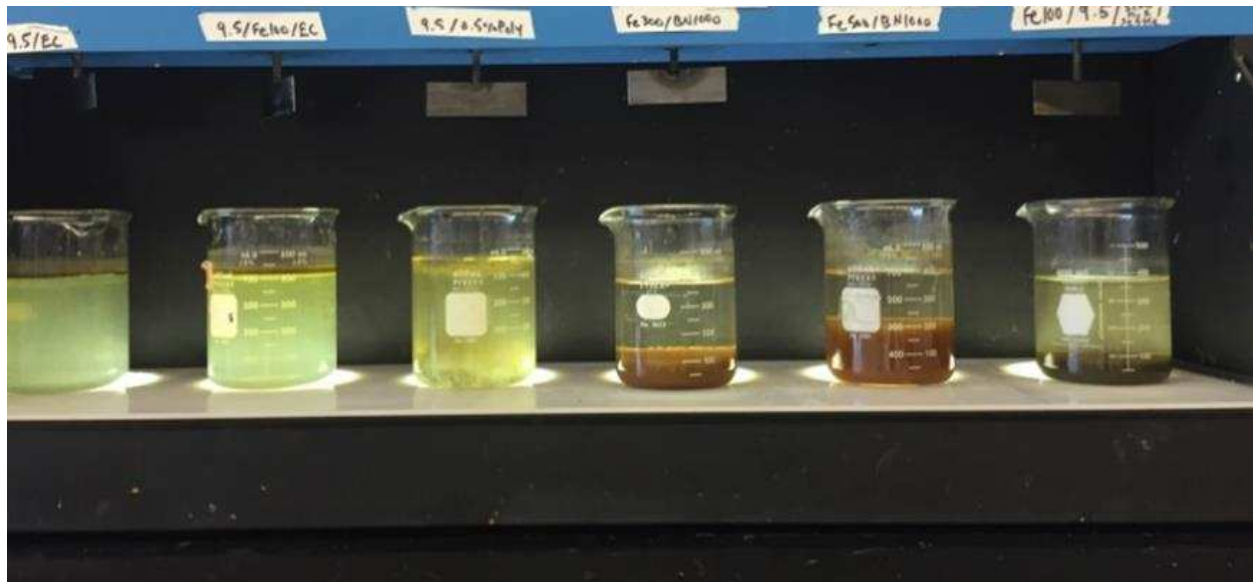


Figure D-1: Sludge Generation from Use of Ferric Chloride During Jar Tests

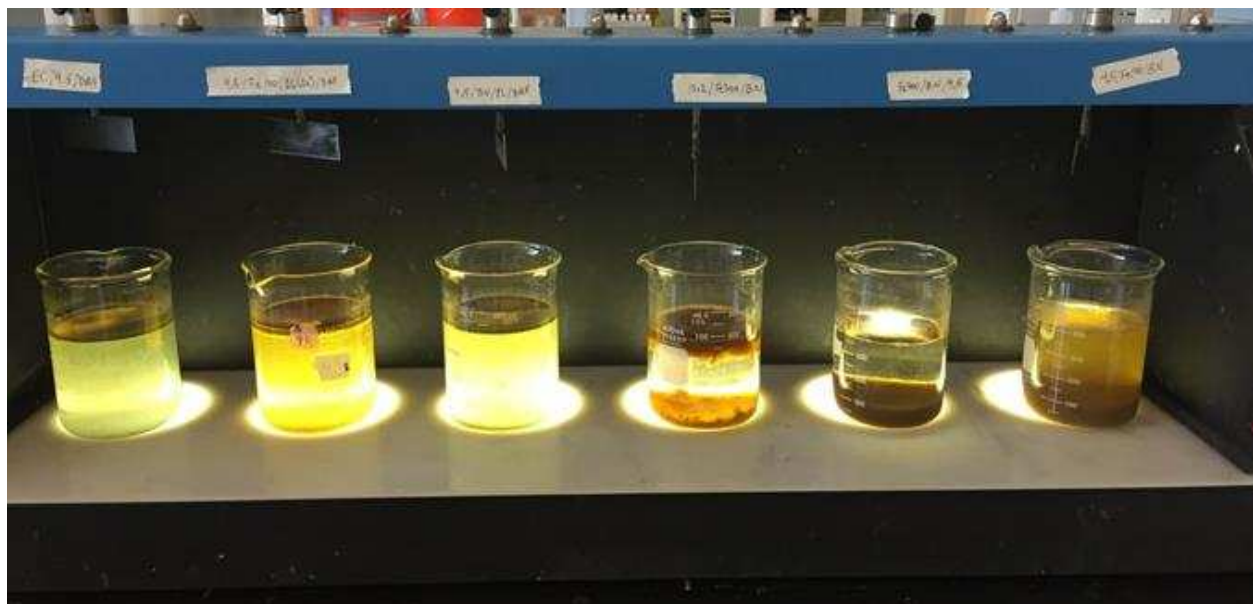


Figure D-2: Jar Test Comparison between Chemical Coagulation and Electrocoagulation

Appendix E: Water Constituent Regulations and Limitations

Table E-1: Basic Standards for Organics Chemicals under Regulation No. 31 (CDPHE, 2016)

BASIC STANDARDS FOR ORGANIC CHEMICALS (in micrograms per liter)						
Parameter	CAS No.	Human Health Based ¹			Aquatic Life Based ⁴	
		Water Supply ²	Water+Fish ³	Fish Ingestion ⁵	Acute	Chronic
Acenaphthene	83-32-9	420	420	--- ¹⁰	1,700	520
Acetochlor	34256-82-1	140	---	---	---	---
Acetone	67-64-1	6300	---	---	---	---
Acrolein	107-02-8	3.5	3.5	9.3	68	21
Acrylamide ^{C,13}	79-06-1	0.022	---	---	---	---
Acrylonitrile ^C	107-13-1	0.065	0.051	0.25	7,500	2,600
Alachlor	15972-60-8	2 ^M	2	140	---	---
Aldicarb	116-06-3	7 ^M	---	---	---	---
Aldicarb Sulfone	1646-88-4	7 ^M	---	---	---	---
Aldicarb Sulfoxide	1646-87-3	7 ^M	---	---	---	---
Aldrin ^C	309-00-2	0.0021	4.9X10 ⁻⁵	5.0X10 ⁻⁵	1.5	---
Aniline ^C	62-53-3	6.1	---	---	---	---
Anthracene (PAH)	120-12-7	2,100	2,100	40,000	---	---
Aramite ^C	140-57-8	1.4	---	---	---	---
Atrazine	1912-24-9	3 ^M	---	---	---	---
Azobenzene ^C	103-33-3	0.32	---	---	---	---
Benzene ^{C,12}	71-43-2	2.3 to 5 ^M	2.2	51	5,300	---

BASIC STANDARDS FOR ORGANIC CHEMICALS (in micrograms per liter)						
Parameter	CAS No.	Human Health Based ¹			Aquatic Life Based ⁴	
		Water Supply ²	Water+Fish ³	Fish Ingestion ⁵	Acute	Chronic
Endosulfan, alpha	959-98-8	42	--- ¹⁰	---	0.11	0.056
Endosulfan, beta	33213-65-9	42	--- ¹⁰	---	0.11	0.056
Endosulfan sulfate	1031-07-8	42	--- ¹⁰	---	0.11	0.056
Endothall	145-73-3	100 ^M	---	---	---	---
Endrin	72-20-8	2 ^M	--- ¹⁰	---	0.086	0.036
Endrin aldehyde	7421-93-4	2.1	0.29	0.30	---	---
Epichlorohydrin ^C	106-89-8	3.5	---	---	---	---
Ethylbenzene ¹¹	100-41-4	700 ^M	530	2,100	32,000	---
Ethylene dibromide ^{C,12} (1,2 – dibromoethane)	106-93-4	0.02 to 0.05 ^M	---	---	---	---
Ethylene glycol monobutyl ether (EGBE) (2-Butoxyethanol)	111-76-2	700	---	---	---	---
Ethylhexyl phthalate (BIS-2) ^{C,12} (DEHP)	117-81-7	2.5 to 6 ^M	1.2	2.2	---	---
Fluoranthene (PAH)	206-44-0	280	130	140	3,980	---
Fluorene (PAH)	86-73-7	280	280	5,300	---	---
Folpet ^C	133-07-3	10	---	---	---	---
Furmecyclo ^C	60568-05-0	1.2	---	---	---	---
Glyphosate	1071-83-6	700 ^M	---	---	---	---
Guthion	86-50-0	---	---	---	---	0.01

BASIC STANDARDS FOR ORGANIC CHEMICALS (in micrograms per liter)						
Parameter	CAS No.	Human Health Based ¹			Aquatic Life Based ⁴	
		Water Supply ²	Water+Fish ³	Fish Ingestion ⁸	Acute	Chronic
Tetrachloroethylene (PCE) ^C	127-18-4	5 ^M	5	62	5,280	840
Toluene ^{11, 12}	108-88-3	560 to 1,000 ^M	510	5,900	17,500	---
Toxaphene ^{C, 12}	8001-35-2	0.032 to 3 ^M	0.00028	--- ¹⁰	0.73	0.0002
Tributyltin (TBT)	56573-85-4	---	---	---	0.46	0.072
Trichloroacetic acid	76-03-9	0.52	---	---	---	---
Trichlorobenzene 1,2,4- ¹¹	120-82-1	70 ^M	35	--- ¹⁰	250	50
Trichloroethane 1,1,1 (1,1,1-TCA)	71-55-6	200 ^M	---	---	---	---
Trichloroethane 1,1,2 (1,1,2-TCA) ^{11, 12}	79-00-5	2.8 to 5 ^M	2.7	71	9,400	---
Trichloroethylene (TCE)	79-01-6	5 ^M	2.5	30	45,000	21,900
Trichloropropane 1,2,3- ^{C, 13}	96-18-4	3.7E-4	---	---	---	---
Trichlorophenol 2,4,5	95-95-4	700	700	3,600	---	---
Trichlorophenol 2,4,6 ^C	88-06-2	3.2	1.4	2.4	---	970
Trichlorophenoxypropionic acid (2,4,5-tp) (Silvex)	93-72-1	50 ^M	---	---	---	---
Trihalomethanes	(total) ⁷	80	80	---	---	---
Vinyl Chloride ^{C, 12}	75-01-4	0.023 to 2 ^M	0.023	2.3	---	---
Xylenes (total) ¹²	1330-20-7	1,400 to 10,000 ^M	---	---	---	---

Table E-2: Constituent Limits for Irrigation Water (BOR, 2011)

Table 9. Constituent limits for irrigation water (adapted from Rowe and Abdel-Magid, 1995)

Constituent	Long-term Use (mg/L)	Short-term Use (mg/L)
Aluminum (Al)	5	20
Arsenic (As)	0.1	2
Beryllium (Be)	0.1	0.5
Boron (B)	0.75	2
Cadmium (Cd)	0.01	0.05
Chromium (Cr)	0.1	1
Cobalt (Co)	0.05	5
Copper (Cu)	0.2	5
Fluoride (F)	1	15
Iron (Fe)	5	20
Lead (Pb)	5	10
Lithium (Li)	2.5	2.5
Manganese (Mn)	0.2	10
Molybdenum (Mo)	0.01	0.05
Nickel (Ni)	0.2	2
Selenium (Se)	0.02	0.02
Vanadium (V)	0.1	1
Zinc (Zn)	2	10