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Treatment of Produced Waters by Electrocoagulation and Reverse Osmosis

Topical Report

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ABSTRACT

Two oil field produced waters and one coal bed methane produced water from Wyoming were treated with electrocoagulation and reverse osmosis. All three produced waters would require treatment to meet the new Wyoming Department of Environmental Quality requirements for effluent discharge into a class III or IV stream. The removal of radium 226 and oil and grease was the primary focus of the study.

Radium 226 and oil and grease were removed from the produced waters with electrocoagulation. The best removal of radium 226 (>84%) was achieved with use of a non-sacrificial anode (titanium). The best removal of oil and grease (>93%) was achieved using a sacrificial anode (aluminum). By comparison, reverse osmosis removed up to 87% of the total dissolved solids and up to 95% of the radium 226.

INTRODUCTION

The extraction of oil and gas from subterranean formations also produces an aqueous stream that must be disposed of or put to beneficial use. In Wyoming this aqueous stream may be highly saline and may contain dissolved hydrogen sulfide, residual hydrocarbons, turbidity, dissolved radium, or other undesirable components. The oil and gas industry in Wyoming produces a large amount of water that could be put to beneficial use if properly treated. The volume of water produced in Wyoming through oil and gas extraction in 1988 was 1.729 billion barrels or 73 billion gallons. The liberation of methane from a coal-bearing formation also requires the extraction of large volumes of groundwater in order to lower the hydrostatic pressure in the formation. The quality of coal bed methane produced water ranges from near drinking water quality to toxic wastewaters with salinity higher than sea water (U.S. Department of the Interior 1990).

All oil and gas produced waters in Wyoming must meet requirements established by the Wyoming Department of Environmental Quality (WDEQ) to be discharged into a receiving body of water or onto the land surface. Separate regulations exist for the type of receiving water or land surface receiving the discharge, whether it be a cold water fishery, a groundwater aquifer, or a dry gulch. Produced waters that exceed the established limit for a given parameter must be treated until the level of that component is brought below the limit, or the water cannot be discharged. An alternative, and most common, disposal method for produced water is to reinject the water into a subterranean formation that has poor quality water (> 10,000 mg/L total dissolved solids). However, reinjection is expensive and treatment of the produced waters for discharge may often be less costly and could produce an aqueous stream that has beneficial uses. The treated produced water could be used for livestock watering, agriculture, game and fish propagation, tertiary recovery, and boiler/heat exchanger feed. Many parts of Wyoming have water shortages and would benefit from the use of a discharged produced water of acceptable quality. The current limitations for discharge of a produced water into a class III or IV stream are shown in Table 1. A class III stream is defined by the WDEQ as any surface water that supports, or has the potential to support non-game fish. A class IV stream is defined as a surface water that does not have the hydrologic or natural water quality potential to support fish (WDEQ 1984).

The toxicity of a discharge is currently determined by the Wyoming whole effluent toxicity program. An acute toxicity test is run on the discharge. In this test fathead minnows and a small crustacean (Ceriodaphnea dubia) are exposed to 100% effluent for a period of 96 and 48 hours, respectively. If greater than 20% mortality occurs during the exposure period, the discharge is considered toxic (Cox 1989).

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Table 1. National Pollutant Discharge Elimination System Permit Limitations

Parameter	Value
TDS	5000 mg/L
Oil & Grease	10 mg/L
pH	6.5-8.5
Radium 226	60 pc/L
Chlorides	2000 mg/L
Sulfates	3000 mg/L
Toxic Substances	Concentrations below levels toxic to aquatic life

Objective

The principal objective of this study was to evaluate electrocoagulation and reverse osmosis as water treatment technologies designed to upgrade produced water for beneficial use as opposed to reinjecting the water into the oil-bearing strata. Three produced waters were obtained and evaluated. Two waters were associated with oil production; the other water resulted from coal bed methane production. In the case of the water samples from oil production, the oil companies will be required to further treat this produced water to meet new discharge requirements for radium and other toxic compounds. The water was characterized before and after treatment to establish the change in the physical-chemical properties of the water induced by the treatment process.

Conventional water treatment methods have been proven successful for the treatment of produced waters, but such treatment is often not economically feasible. In this study, the use of electrocoagulation as an alternative treatment method was investigated. The use of electrocoagulation as a water treatment technology has not been thoroughly studied in the reference literature since its conception; however, with the current increase in environmental regulation it may be a feasible alternative to conventional treatment systems.

In the electrocoagulation process, the aqueous stream is passed through a region of electric potential, thereby initiating physical-chemical reactions. The precipitate or "floc" that is formed settles out of the water and is separated and disposed of, thus altering the physical-chemical properties of the water.

The use of reverse osmosis as a treatment alternative for produced water was also investigated. The results of the reverse osmosis treatment process are compared with the results of the electrocoagulation treatment process with consideration given to economic feasibility of the processes and the intended use of the discharged produced water.

Produced Waters Studied

Three produced waters were located that contained the specific qualities outlined below. In each case, samples were collected and contained according to the sampling procedures outlined in 1990 U.S. Environmental Protection Agency (EPA) Standard Methods for the specific analysis performed.

The initial step was to find an oil-produced water that was currently being discharged and had radium 226 levels near or above the current WDEQ discharge limit of 60 pc/L into a Class III or IV stream. With information supplied by the Wyoming Oil and Gas Commission and WDEQ, a suitable produced water sample was obtained from an oil producer in central Wyoming. Samples were taken at the EPA sampling point from the discharged aqueous stream and then transported back to Western Research Institute (WRI) for characterization. The EPA sampling point is downstream from an oil and water separating system that employs a coagulating chemical followed by a hydrocell unit.

The second sample was also an oil produced water obtained from central Wyoming. The oil producer composited waters from two separate oil-producing formations before discharging. No treatment existed upstream from the sampling point other than a gravity-aided water-oil separation tank.

The third produced water was obtained from a coal bed methane production well in southern Wyoming. Samples were taken from a pond near the production well and were transported back to WRI. The produced water had been pumped directly from the production well to the pond, without pretreatment.

BACKGROUND

Electrocoagulation

Electrocoagulation is a process in which an aqueous stream containing colloidal particles and sparingly-soluble salts are coagulated when passed through an electrical field. Physical and chemical processes occurring during electrocoagulation facilitate the removal of suspended and dissolved solids within the solution.

The coagulated particles aggregate and form flocs. As the floc begins to settle, other colloidal suspended particles are entrapped or adsorbed on the floc and can also be removed from the solution.

According to classical electric double layer theory, for colloidal suspended particles to aggregate and form flocs, the attractive forces between the particles must exceed the repulsive forces. Most colloidal suspended particles in water are positively or negatively charged and they therefore will attract or repulse one another. Repulsive forces due to an electric charge are known as electric potential forces. The surface charge on the particle is usually measured in terms of Zeta

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potential, which influences the electric potential forces. The electric potential forces decrease rapidly in magnitude as the distance from the particle increases. Electrocoagulation is believed to lower the Zeta potential on a particle by facilitating the release of ions, which will react with the surface of the charged particle. As the Zeta potential decreases, the repulsive forces between particles decrease, allowing the particles to remain in closer proximity (Thortec International 1988).

All particles have an attractive force known as Van der Waals forces. Van der Waals forces are small in magnitude over larger distances but increase rapidly as two particles approach each other (e.g., <10 angstroms). If the Zeta potential and repulsive forces of a charged particle have been weakened by the electrocoagulation process, Van der Waals forces may be strong enough to aggregate particles, thereby causing a floc to form. This process would be aided by hydrodynamic and thermodynamic forces within the electrocoagulation unit which facilitate particle movement and inter-particle contact.

During electrocoagulation, trivalent metal ions are released into the solution when a sacrificial anode such as aluminum or iron is used. These trivalent ions are positively charged and will adsorb onto negatively charged colloids. Large particle masses can be formed as negatively charged particles are joined together by the metal ions and polymeric hydroxo complexes. The resulting mass of particles will tend to settle out of the solution (Renk 1988). Chemical coagulation using aluminum and iron salts results in the same mechanisms for the aggregation of colloidal particles to form heavy flocs.

Electrocoagulation chemically alters the aqueous stream by causing oxidation-reduction reactions and further reactions of modified anions and cations to form solids. These reactions are facilitated by the release of anodic material into the solution when a sacrificial anode such as iron or aluminum is used. Iron and aluminum are considered sacrificial because they release oxidized metal ions into the solution. If an inert anode such as titanium or platinum is used, oxygen is produced at the anode and may oxidize other oxidizable substances. The solids produced by this process can potentially precipitate. The floc formed by the precipitate may again entrap and/or adsorb suspended colloidal particles and other soluble species in the solution, thereby further purifying the solution.

Reverse Osmosis

Reverse osmosis (RO) and membrane filtration are common terms used for a broad range of separation processes from filtration and ultrafiltration to actual reverse osmosis (Eckenfelder 1989). Reverse osmosis employs a semipermeable membrane that will allow pure water to flow through the membrane. Dissolved and suspended solids are rejected by the membrane and will concentrate on the high pressure side of the RO unit. Because of diffusion, water tends to flow from a solution of low salinity to a solution of higher salinity. The diffusion force that drives the water through the membrane from the low salinity side to the high salinity side is known as the osmotic pressure. Pressure created by the RO unit overcomes this osmotic pressure, thus the term, reverse

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osmosis. Ultrafiltration refers to systems where microscopic holes or pores exist in the filter media. These pores will allow molecules and ions to pass through the filter media if the molecule or particle is smaller than the pore opening.

Reverse osmosis and membrane filtration require a pressure gradient across the membrane or filter media. This pressure will overcome the osmotic pressure, and/or resistance of the filter, and will drive water through the media. The rejected dissolved and suspended solids are thus concentrated on the high pressure side of the RO unit, and the purified water or permeate can be put to its intended use or be safely discharged.

There are a multitude of membrane materials available commercially. Choosing an appropriate membrane for the given application depends on the membrane's reaction to the feedwater, the required percent rejection of salts, the operating pressure of the RO unit, the temperature and pH of the feedwater, plus any other parameters that may affect the performance of the specific membrane. The four most commonly used membrane materials are cellulose acetate (CA), cellulose triacetate (CTA), aromatic polyamide (PA), and polysulfone (PS). Some general properties of these membrane materials are shown in Figure 1.

Flux   Smaller   PA ---- CTA ---- CA ------ PS   Larger

Salt Rejection   Larger   PS ---- PA ----- CTA ---- CA   Smaller

Sensitivity to
   Biological Attack   Lower   PS ---- PA ------ CTA ---- CA   Greater

Sensitivity to
   Hydrolysis   Lower   PS ---- PA ------ CTA ---- CA   Greater

Resistance to Oxidants   Greater   PS ---- CTA ---- CA ------ PA   Lower

Figure 1. Properties of Membrane Materials

MATERIALS AND METHODS

Electrocoagulation

The electrocoagulation unit used in the study was modeled after the Liggett design with incorporation of the Herbst/Renk patent modification (Patent Application 1987). This design incorporates an inner and outer piping system with a helical wrapping to promote turbulent flow and minimize the build-up of a stationary layer of ionic particles on the charged surface (Figure 2). The feedwater enters the unit in the inner pipe, travels the length of the inner pipe until the inner pipe ends, and opens up into the outer pipe. Here the water flow reverses
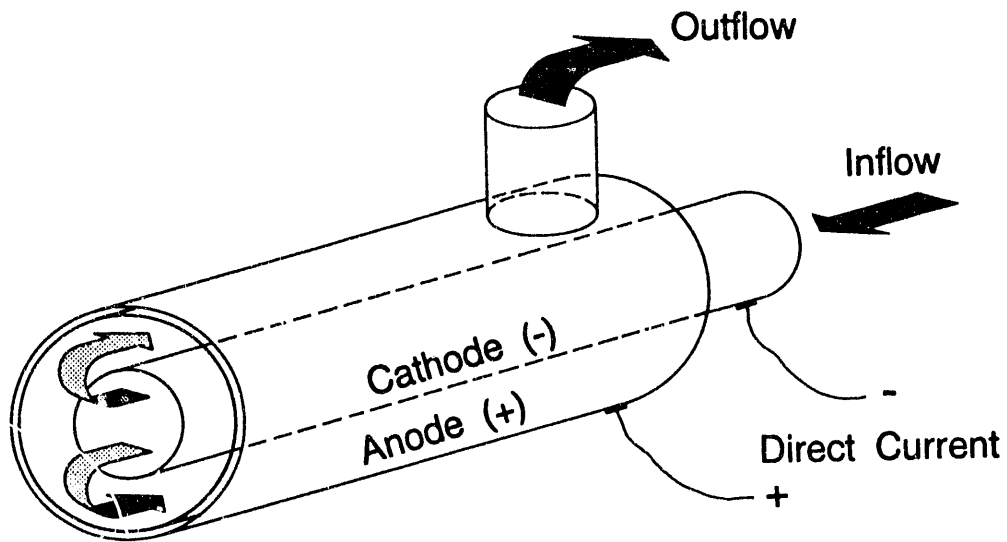
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Figure 2(a). Wastewater Flow Through Electrocoagulation Unit and Polarity of the Inner and Outer Piping System
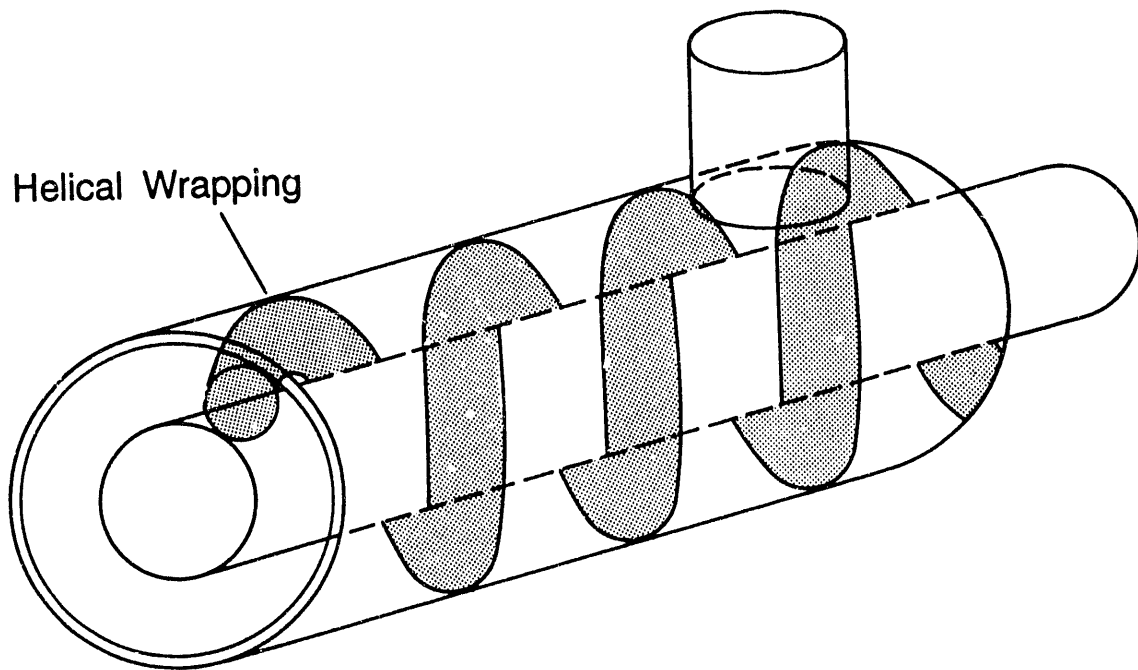

Figure 2(b). Helical Wrapping Between Inner and Outer Pipe

Figure 2. Electrocoagulation Unit

direction and flows between the inner and outer pipe, back to an outlet at the front of the unit where the treated water exits the unit. In the electrocoagulation unit the inner pipe acts as the cathode and the outer pipe acts as the anode. The outer pipe had a 1 1/4-inch inside diameter and the inner pipe had a 1/2-inch inside diameter. Each pipe was approximately 24 inches long.

A Masterflex veristatic pump was connected to the electrocoagulation unit to supply the solution flow. The DC power supply was delivered by a Powerstat 100 volt voltage supply unit. Each electrocoagulation tube was cleaned with acetone before testing was conducted. Distilled water was run through the electrocoagulation unit after each run for a period of 5 minutes to clean the unit. Samples were collected in acid-washed glass containers and the overnight settling procedure was conducted in a refrigerated storage area. The energy input that the electrocoagulation unit delivered to the water was dependent on the electrolytic characteristics of the water and the type of cathode material. A constant current of 20 amps through the unit was maintained allowing voltage to vary. Energy input was not optimized in this study. See Table 2 for the electrocoagulation operating conditions.

A sample of the produced water with the highest radium 226 concentration was filtered through standard filter paper and analyzed for radium 226 to establish whether the radium 226 was associated with the soluble or insoluble fraction of the total solids. The results from the filtered sample would also indicate whether the electrocoagulation process was physically and chemically altering the produced water stream.

Reverse Osmosis

The RO unit used in this study was the laboratory scale Sepa CF-HP Membrane cell model, manufactured by Osmonics. A Jaeco piston pump, model 106-115-S2T2, 1/3 hp, was used as the high pressure pumping source. The Sepa CF-HP membrane cell and the Jaeco pump were designed for pressures up to 1000 and 1300 psig, respectively. A damping system was employed to dampen the pressure variation over the pump stroke of the piston pump. The damping system consisted of three gas-filled containers positioned along the pressure line from the pump to the RO unit. The pressurized feedwater flowed into the containers, thereby compressing the gas, and the feedwater exited the container somewhat dampened. With this damping system the pressure variation over the pump stroke could be reduced to approximately 50 psig.

The three membranes used in the study were all obtained from Osmonics. The selection of membranes was limited to those that could withstand the chemical composition of the produced waters and the high pressures required for treatment of high salinity waters, without being damaged or physically altered. The three membranes used were the Sepa SR10, the Sepa ST10, and the Sepa MS10. The SR10 and ST10 membranes are cellulose acetate membranes and the MS10 is a polyamide membrane.

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Table 2. Operating Conditions for Electrocoagulation Treatment

Produced Water	Tube Type	Current (amps)	Voltage (volts)	Volume of Sample (mL)	Retention Time (min)	Temp In °C	Temp Out °C	pH In	pH Out	Color of Floc
LRO	Fe one-pass	18-20	25	4000	2:24	7.3	16.4	7.7	7.8	Grey
LRO	Fe two-pass	18-20	25	4000	4:50	10.6	23.9	7.7	7.7	Tan
LRO	Al one-pass	8-18	120	4000	2:50	15.3	34.2	7.7	7.7	White
LRO	Al two-pass	12-15	116	4000	4:50	12.2	44.7	7.7	7.4	White
LRO	Ti one-pass	20-15	85	4000	2:50	15.3	37.8	7.7	7.4	White
LRO	Ti two-pass	19-15	120	4000	5:10	15.3	50	7.7	7.2	White
CBM	Ti one-pass	20	40-35	4000	2:52	6	20.3	9.0	8.8	White
CBM	Ti two-pass	20	40-30	4000	5:30	5.6	25.6	9.1	8.9	White
CBM	Al one-pass	20	55-85	4000	2:50	5.6	28.8	9.1	8.8	Tan
CBM	Al two-pass	20	65-90	4000	5:32	6	48	9.0	8.7	Grey
CBM	Fe one-pass	20	10	4000	2:45	7.2	13.4	9.0	9.0	None
CBM	Fe two-pass	20	10-12	4000	5:30	7.2	16.8	9.0	8.9	None
HRO	Al two-pass	15-20	110	4000	4:30	6	44.1	6.5	6.4	Blk & Wht
HRO	Ti one-pass	20	120	4000	2:20	6	27	6.5	6.4	Blk & Wht
HRO	Ti two-pass	20	100	4000	4:30	6	40.5	6.5	6.4	Green fluff

For each RO run, the concentrate or reject was recycled back to the feedwater container until the whole system reached equilibrium and no more permeate was produced. This method simulates a large RO production unit that would utilize a series of spirally wound membrane elements (Parekh 1988).

The pump was set to deliver a flow volume of 4 mL/s. This low flow rate was chosen to minimize the pressure variations over the pump stroke. The feedwater was allowed to reach room temperature (20 °C) before each run. Three liters of feedwater was used in each run. Each of the three membranes was run at two different concentrate outlet pressures, and the pressure applied to the membrane cell plates was maintained at 1000 psig to minimize any movement of the plates due to pressure variations.

After each run the unit was cleaned with hot tap water and then distilled water, and a new cell membrane was installed. The RO unit was then run with distilled water for a period of approximately 10 minutes to allow the membrane to wet and to clean the system further. The feedwater and permeate containers were glass vessels that had been acid washed to minimize contamination of the sample. The reject or concentrate stream was recycled back to the feedwater container, and both containers were capped with a paraffin film to minimize evaporation during the run. Times were recorded for specific volumes of permeate until the test was concluded. Once the test was concluded, the permeate was stirred and transferred to the appropriate containers for the specific analyses to be performed.

RESULTS AND DISCUSSION

The characterization of the raw produced waters indicated an array of chemical species and concentrations of those species (Table 3). All three produced waters contained substantial amounts of radium 226, total solids, and oil and grease; thus the project objectives that were initially identified could be achieved.

Electrocoagulation

Removal of Radium 226

Percent removals of radium 226 by the electrocoagulation treatment process ranged from 24 to near 100% for all the waters tested. The best removal efficiencies were obtained with the titanium tube, which had a non-sacrificial titanium anode. Electrocoagulation treatment with the titanium tube reduced the radium 226 concentration from 29.2 pc/L to 0.8 pc/L for the low radium oil (LRO) produced water, which corresponded to 97.3% removal. Treatment with the titanium tube reduced the radium 226 concentration in the high radium oil (HRO) produced water from 116 pc/L to 18.9 pc/L, which corresponded to 83.7% removal. Treatment with the titanium tube reduced the radium 226 concentration in the coal bed methane (CBM) produced water from 12.4 pc/L to 0.0 pc/L, which corresponded to a 100% removal. These removals were obtained with the

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Table 3. Characterization of Untreated Produced Waters (mg/L except as noted)

Parameter	Low Radium Oil Produced Water	High Radium Oil Produced Water	Coal Bed Methane Produced Water
Radium 226 (pc/L)	29.2	116	12.4
Oil & Grease	39	29.2	2
Alkalinity	1085	310	13,525
Suspended Solids	180	20	100
Dissolved Solids	3540	3160	23,980
Sulfide	42	>100	<1
Fluoride	No Test	4.61	No Test
Chloride	510	160	5,960
Nitrite as N	<0.004	<0.01	<0.004
Bromide	2.41	<0.01	3.63
Nitrate as N	<0.004	<0.01	0.37
Phosphate as P	<0.01	<0.01	<0.01
Sulfate	1300	1620	13.5
Mineral Carbon	72	260	2800
TOC	No Test	<10	No Test
Silver	<0.007	<0.04	<0.
Aluminum	<0.05	<0.23	<0.50
Arsenic	<0.10	<0.5	<1.0
Boron	1.6	2.6	3.5
Barium	0.05	0.06	1.9
Beryllium	<0.002	<0.01	<0.02
Bismuth	<0.10	<0.5	<1.0
Calcium	460	420	9.1
Cadmium	<0.01	<0.05	<0.1
Cobalt	<0.007	<0.04	<0.07
Chromium	<0.008	0.04	0.08
Copper	<0.006	<0.03	<0.06
Iron	<0.006		0.38
Mercury	<0.50		<5.0
Potassium	89	68	240
Lithium	1.5	0.79	5.3
Magnesium	77	79	20
Manganese	<0.003	<0.02	<0.03
Molybdenum	<0.01	<0.05	<0.10
Sodium	450	510	9000
Nickel	<0.02	<0.1	<0.2
Phosphorus	<1.0	<5	<10
Lead	0.05	<0.3	<0.5
Antimony	<0.10	<0.5	<1.0
Selenium	<0.10	<0.5	<1.0
Silicon	15		<1.0
Strontium	7.1		<1.0
Thorium	<0.05	<0.3	<0.5
Vanadium	<0.008	<0.04	<0.08
Zinc	0.01	<0.02	<0.03

Note: Different detection limits for the same parameter result from dilution of samples required in analysis procedure.

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"two-pass" treatment method, which effectively doubled the retention time in the tubes to 5:30 minutes for the LRO and CBM waters and 4:30 minutes for the HRO. The one-pass treatment with the titanium tube reduced the radium 226 concentration from 29.2 pc/L to 8.6 pc/L (70.5% removal) for the LRO, from 12.4 pc/L to 5.6 pc/L (54.8% removal) for the CBM produced water and from 116 pc/L to 38.9 pc/L (66.4% removal) for the HRO with retention times of 2:50 minutes, 2:52 minutes, and 2:15 minutes, respectively.

The average radium 226 removals for all three waters with the two-pass treatment were 93.7% removal for the titanium tube, 83.3% removal for the aluminum tube, and 42.1% removal for the iron tube. However, the one-pass treatment showed 63.9% radium 226 removal for the titanium tube, 83.4% radium 226 removal for the aluminum tube, and 99.3% radium 226 removal for the one analysis on the iron tube. A complete analysis on the variations in treatment removals for radium 226 with the given electrocoagulation tube and retention time is difficult without a more comprehensive study of all the produced waters under all the given treatment conditions. Replicated runs should also be performed and analyzed to establish any inherent variability in the process.

The results showed that electrocoagulation treatment effectively removed radium 226. The higher removals of radium 226 by the titanium tube may have been in part due to the chemical reactions associated with an inert anode. The free oxygen radicals that may have been formed at the inert anode of the titanium tube may cause radium 226 particles to form complexes with other particles in solution or become adsorbed onto newly formed complexes and settle out with the precipitates. The oxygen or hydroxide radicals produced at the inert anode may also cause oxidation of organics. The oxidized and un-oxidized organics can also react with ozone and hydrogen peroxide, possibly created at the anode, to produce carbon dioxide and water. This reaction would release any radium 226 adsorbed onto the organics in solution and allow the radium 226 particles to react with other components in solution or be adsorbed onto the precipitate formed and subsequently settle out with the floc.

A thick floc was created when the aluminum tube was used for treatment. Possibly, the radium 226 was adsorbed onto the floc or the particles that they were associated with could have become entrapped in the settling floc and would thus have been removed from the solution. Suspended solids were effectively removed by treatment with the aluminum tube, and the radium 226 species associated with the suspended solids would also be removed. Treatment with the aluminum tube created a similar amount of floc for both the one-pass and two-pass retention times. The corresponding removal of radium 226 for both retention times is nearly the same. The two-pass treatment achieved only 5% more removal for both treatment runs.

The results for the radium 226 removal with the iron tube were inconclusive. Further testing should be done to determine if the one-pass treatment is as effective in removing radium 226 as the 99.3% removal (29.2 pc/L to 0.2 pc/L) achieved on the LRO sample indicates.

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Without information from replicate runs and duplicate analysis, this one result did not provide enough information to draw a reasonable conclusion. Tables 4, 5, and 6 summarize the performance achieved using electrocoagulation on the three produced waters.

The radium 226 analysis on the filtered sample of the HRO water is shown in Table 6. The radium 226 concentration in the filtered sample and the raw HRO sample were 123 pc/L and 116 pc/L, respectively. The difference in these two values is negligible considering the experimental error inherent in the analysis. The two values do indicate that the amount of radium 226 that was associated with the suspended solids in the sample was small, and that the electrocoagulation process must have altered the produced water's dissolved solids physically and chemically.

Oil and Grease Removal

Electrocoagulation effectively removed oil and grease when the process was operated to create a reasonable amount of floc. The concentration of oil and grease in the LRO was reduced from 39 mg/L to <3.0 mg/L by all three electrocoagulation tubes with the one-pass and two-pass retention times. The concentration of oil and grease in the HRO was reduced from 29.2 mg/L to 2 mg/L with the aluminum tube, two-pass retention time. However, higher concentrations of oil and grease after treatment for this water indicate that the initial measured concentration was questionable and the removal was probably greater than indicated (see below). Treatment of the HRO with the titanium tube resulted in no reduction of oil and grease. The post-treatment concentrations of 38.9 mg/L and 31.0 mg/L for the one-pass and two-pass treatment with the titanium tube indicate that the oil and grease analysis on the raw HRO was probably not accurate and that the concentration of oil and grease in the raw HRO was higher than 29.2 mg/L. Duplicate samples and duplicate analysis would be required to establish the initial concentration more accurately.

All the electrocoagulation runs that produced a moderate to large amount of floc also greatly reduced the concentration of oil and grease. The two electrocoagulation runs on the HRO with the titanium tube created very little floc and the corresponding removal of oil and grease was minimal to none. All the electrocoagulation runs on the LRO, and the two-pass run with the aluminum tube on the HRO, produced a moderate to large amount of floc. The dissolved oil particles probably adsorbed onto the settling floc and were thus removed from the solution. The emulsified oil (free oil) may have been coagulated if the charged particles released into the solution by the electrocoagulation process reduced the charge density in the emulsion and thus allowed colloidal oil particles to coagulate and settle out of solution. However, the amount of free oil was small in all the samples. Adsorption of dissolved oil particles onto a settling floc and de-emulsification of colloidal free oil has been well studied with chemical and polyelectrolyte coagulation. Studies show that dissolved oil will adsorb to some extent onto floc particles, and the electrically charged particles (positive and negative) in the floc will facilitate the coagulation of emulsified oil particles.

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Table 4. Results of Electrocoagulation Treatment on Low Radium Oil Produced Water (mg/L except as noted)

Parameter	Untreated Wastewater	Fe One-Pass	Fe Two-Pass	Al One-Pass	Al Two-Pass	Ti One-Pass	Ti Two-Pass
Radium 226 (pc/L)	29.2	0.2	11.7	7.8	6.4	8.6	0.8
Oil & Grease	39	<3	<3	<3	<3	<3	<3
Alkalinity	1085	815	672	735	687	715	570
Suspended Solids	180	70	90	0	20	10	20
Dissolved Solids	3540	3350	3060	3090	2930	3150	2740
Silver	<0.007	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Aluminum	<0.05	<0.23	<0.23	0.24	1	<0.23	<0.23
Arsenic	<0.10	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Boron	1.6	1.7	1.7	1.8	2	1.6	1.7
Barium	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Beryllium	<0.002	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bismuth	<0.10	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Calcium	460	530	450	450	390	450	360
Cadmium	<0.01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cobalt	<0.007	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Chromium	<0.008	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Copper	<0.006	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Iron	<0.006	0.27	0.39	<0.03	<0.03	<0.03	<0.03
Mercury	<0.50	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
Potassium	89	180	160	170	160	170	170
Lithium	1.5	1.7	1.6	1.5	1.6	1.6	1.5
Magnesium	77	93	91	87	89	89	88
Manganese	<0.003	<0.02	0.03	<0.02	<0.02	<0.02	<0.02
Moly' denum	<0.01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sodium	450	500	490	460	480	480	470
Nickel	<0.02	<0.10	<0.01	<0.01	<0.01	<0.01	<0.01
Phosphorus	<1.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Lead	0.05	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Antimony	<0.10	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Selenium	<0.10	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Silicon	15	18	17	9.9	7	17	14
Strontium	7.1	7.2	6.5	6.1	5.6	6.5	5.4
Thorium	<0.05	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Vanadium	<0.008	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Zinc	0.01	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Note: Different detection limits for the same parameter result from dilution of samples required in analysis procedure.

Table 5. Results of Electrocoagulation Treatment on Coal Bed Methane Produced Water (mg/L except as noted)

Parameter	Untreated Wastewater	Fe One-Pass	Fe Two-Pass	Al One-Pass	Al Two-Pass	Ti One-Pass	Ti Two-Pass
Radium 226 (pc/L)	12.4	NT[a]	9.4	0.8	0.2	5.6	0
Oil & Grease	2	NT	NT	NT	NT	NT	NT
Alkalinity	13,500	13,750	13,850	13,150	13,250	13,700	13,675
Suspended Solids	90	0	90	50	60	80	75
Dissolved Solids	23,975	24,030	23,920	24,300	23,930	24,200	24,000
Silver	<0.07	0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Aluminum	<0.50	<0.23	<0.23	0.24	1	<0.23	<0.23
Arsenic	<1.0	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Boron	3.5	3.1	3	3	3.1	3.3	3.2
Barium	1.9	1.6	1.5	0.21	0.17	0.21	0.08
Beryllium	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bismuth	<1.0	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Calcium	9.1	9.3	9.5	2.7	3	7.2	5.1
Cadmium	<0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cobalt	<0.07	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Chromium	0.08	<0.04	0.05	<0.04	<0.04	<0.04	<0.04
Copper	<0.06	0.06	0.09	0.07	0.09	0.06	0.06
Iron	0.38	1.9	3.2	1.5	2.8	<0.03	<0.03
Mercury	<5.0	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
Potassium	240	150	160	160	160	180	190
Lithium	5.3	5.4	5.3	5.3	5	5.7	5.7
Magnesium	20	17	17	15	13	17	16
Manganese	<0.03	0.04	0.05	0.03	0.03	<0.02	<0.02
Molybdenum	<0.10	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sodium	9000	8600	8600	8600	8300	9000	9300
Nickel	<0.2	<0.10	<0.01	<0.01	<0.01	<0.01	<0.01
Phosphorus	<10	<5.0	<5.0	<5.0	<5.0	7.6	<5.0
Lead	<0.5	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Antimony	<1.0	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Selenium	<1.0	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Silicon	<1.0	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Strontium	<1.0	0.12	0.12	0.03	0.04	0.07	0.03
Thorium	<0.5	<0.25	0.26	0.29	0.27	0.31	0.26
Vanadium	<0.08	<0.04	0.05	0.06	0.07	0.07	0.05
Zinc	<0.03	0.06	0.04	<0.02	<0.02	<0.02	<0.02

[a] NT = not tested

Note: Different detection limits for the same parameter result from dilution of samples required in analysis procedure.

Table 6. Results of Electrocoagulation Treatment on High Radium Oil Produced Water (mg/L except as noted)

	Untreated Wastewater	Ti One-Pass	Ti Two-pass	Al Two-pass	Filtered
Radium 226 (pc/L)	116	38.9	18.9	30.7	123
Oil & Grease	29.2	38	31	2	
Alkalinity	310	260	180	210	
Suspended Solids	20	0	0	0	
Dissolved Solids	3160	2900	2920	2560	
Silver	<0.04		<0.04	<0.04	
Aluminum	<0.23		<0.23	0.34	
Arsenic	<0.50		<0.50	<0.50	
Boron	2.6		2.5	2.6	
Barium	0.06		0.06	0.06	
Beryllium	<0.01		<0.01	<0.01	
Bismuth	<0.5		<0.5	<0.5	
Calcium	420		380	300	
Cadmium	<0.05		<0.05	<0.05	
Cobalt	<0.04		<0.04	<0.04	
Chromium	<0.04		<0.04	<0.04	
Copper	<0.03		<0.03	<0.03	
Iron	NT[a]		NT	NT	
Mercury	NT		NT	NT	
Potassium	68		64	68	
Lithium	0.79		0.77	0.82	
Magnesium	79		75	77	
Manganese	<0.02		<0.02	<0.02	
Molybdenum	<0.05		<0.05	<0.05	
Sodium	510		480	540	
Nickel	<0.1		<0.1	<0.1	
Phosphorus	<5		<5	<5	
Lead	<0.3		<0.3	<0.3	
Antimony	<0.5		<0.5	<0.5	
Selenium	<0.5		<0.5	<0.5	
Silicon	NT		NT	NT	
Strontium	NT		NT	NT	
Thorium	<0.3		<0.3	<0.3	
Vanadium	<0.04		<0.04	<0.04	
Zinc	<0.02		<0.02	<0.02	
Sulfide	>100	190	170	230	
TOC	<10	<10	<10	<10	
Fluoride	4.61	4.93	5.02	4.15	
Chloride	160	145	145	127	
Nitrate as N	<0.01	<0.01	<0.01	<0.01	
Bromide	<0.01	<0.01	<0.01	<0.01	
Nitrate as N	<0.01	<0.01	<0.01	<0.01	
Phosphate as P	<0.01	<0.01	<0.01	<0.01	
Sulfate	1620	1610	1650	1290	
Mineral Carbon	72	57	48	44	

[a] NT = not tested

The amount of floc produced by electrocoagulation is probably dependent on many factors: the amount and type of dissolved solids in the solution, the type of electrocoagulation tube, the retention time, and the temperature of the solution. More experimentation would be required to establish what type of floc removed oil and grease more efficiently.

Reverse Osmosis

Removal of Total Dissolved Solids

Reverse osmosis removed dissolved and suspended solids from the CBM produced water. The total dissolved solids concentration in the CBM produced water was reduced from 24,000 mg/L to between 3,100 and 7,560 mg/L during treatment with three different membranes, and at various outlet pressures (Table 7). All suspended solids (SS) were removed. A more complete discussion of removal efficiencies achieved with reverse osmosis with different membranes and at various outlet pressures would be appropriate; however, the treatment performances were more dependent on the problems resulting from the piston pump and the corresponding damage to the membranes.

Table 7. **Results of Reverse Osmosis Treatment on Coal Bed Methane Produced Water**

Type of Membrane	Outlet pressure (psig)	Permeate TDS (mg/L)	Percent TDS Removal	Percent SS Removal
Sepa CF ST10	400	21,010	12.5	100
Sepa CF ST10	500	3,100	87.1	100
Sepa CF ST10	600	5,900	75.4	100
Sepa CF SR10	400	4,760	80.2	100
Sepa CF SR10	700	7,560	68.5	100
Sepa CF MS10	500	6,140	74.4	100

Radium 226 Removal

Reverse osmosis removed radium 226. The initial radium 226 concentration in the CBM-produced water was 12.4 pc/L. This concentration was lowered to 5.1 pc/L by the ST10 membrane at 600 psig outlet pressure, to 0.6 pc/L by the ST10 membrane at 500 psig outlet pressure, to 3.0 pc/L by the SR10 membrane at 400 psig outlet pressure, to 1.0 pc/L by the SR10 membrane at 700 psig outlet pressure, and to 1.2 pc/L by the MS10 membrane at 500 psig outlet pressure. Radium 226 particles that were associated with colloidal particles or dissolved solids in the solution were probably rejected by the membrane because of the size of the particles.

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There were several problems with the RO equipment that made the results questionable. The problems were created by the piston pump. The pump would cause a pressure surge and drop in the RO unit for each pump stroke. The dampening system that was used did not completely dampen out the pressure variations. Since the pressure across the membrane was not constant, the permeate flow was a function of a pressure range and not one specific pressure. Another problem created by the pump was that the plates that held the RO membrane in place would move slightly with each pressure variation, thus causing the membrane to wear at the site of contact with the rubber O-ring. The worn areas of the membrane could then allow preferential flow through to the permeate stream. The worn areas of the membrane would not reject dissolved solids as effectively as the intact membrane surface and a higher percentage of solids would flow through to the permeate outlet as a result.

However, the results do show that the CBM produced water could be treated effectively with RO to reduce dissolved and suspended solids concentrations, thus concurrently lowering the concentrations of components such as radium 226. Reverse osmosis would be a treatment alternative for this water depending on its intended use, but the cost of using the RO process at pressures above 500 psig would have to be taken into consideration. The disposal of the brine created in the RO process may also be an economic consideration.

CONCLUSIONS

1. The best treatment with electrocoagulation reduced the radium 226 concentration from 29.2 pc/L to 0.2 pc/L and the oil and grease concentration from 39 mg/L to less than 3 mg/L in the oil produced water.

2. The best removal of radium 226 was achieved with the titanium electrocoagulation tube, while the best removal of oil and grease was achieved with the aluminum electrocoagulation tube.

3. Radium 226 and oil and grease concentrations were lowered in the two oil produced waters to below the current WDEQ discharge standards.

4. Treatment with reverse osmosis reduced the total dissolved solids concentration in the coal bed methane produced water from 24,000 mg/L to 3,100 mg/L along with all suspended solids.

5. Treatment of the coal bed methane produced water with reverse osmosis reduced the radium 226 concentration from 12.4 pc/L to 0.6 pc/L using an ST10 membrane at 500 psig.

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ACKNOWLEDGMENTS

DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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