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STUDENT FALL INTERNSHIP TECHNICAL REPORT

For September 13, 2008 to December 20, 2008

Coal-Bed Methane Produce Water Treatment

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ABSTRACT

Natural gas produced from coal beds (coal-bed methane or CBM) accounts for about 7.5 percent of the total natural gas production in the United States. Along with this gas, water is also brought to the surface. The amount of water produced from most CBM wells is relatively high compared to conventional natural gas wells since coal beds contain many fractures and pores that can contain and transmit large volumes of water. The contribution of CBM to total natural gas production in the United States is expected to increase in the future [1]. As the number of CBM wells increases, the amount of water produced will also increase. Produced water must be treated before reuse and/or disposal.

This work aims to improve treatment of produced water by maximizing oxidation of organic compounds present in produced water via ozonation. It is part of a larger project focused on coal-bed methane produced water treatment by means of ozonation, magnetic seeded filtration, and electrosorption. Ozone is a very powerful oxidizing agent used in modern water treatment operations. A treatment process based upon ozonation during a single-pass operation through a gas-liquid reactor was studied. An experimental apparatus consisting of an ozone generator, a counter-flow gas-liquid reactor, and a spectrophotometer was used to monitor the concentration of ozone. Produced water was obtained from coal-bed methane wells in Idaho.

The samples were collected after a two-hour interval of treatment. The treated sample showed a significant change in clarity. Then, the treated sample and untreated samples were analyzed for organics content, chloride ion content, and carbonate/bicarbonate content, using a gas chromatograph, an ion selective electrode and a Metrohm Titrino respectively. The results revealed a reduction of one third of the organics, a reduction from 14% to 5% of the chloride ions, and complete elimination of the carbonate/bicarbonate ions.

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1. INTRODUCTION

Water contained in coal seams must be removed in order to release the methane that is trapped by the groundwater pressure. A series of 1 to 9 production wells are drilled into the coal so that the groundwater can be pumped to the surface to reduce the hydrostatic pressure in the coal seam. The water production from coal-bed methane (CBM) wells typically starts at a high volume but generally falls dramatically over time as the coal seam becomes depressurized in the producing area. Once the fluid pressure is lowered in the coal seam, the methane is released and available for production through the wells. The water produced from CBM wells can vary in quality from very high quality (meeting state and federal drinking water standards) to having very high total dissolved solids (TDS) concentrations (up to 180,000 parts per million TDS) which is not suitable for reuse. As a matter of fact, CBM produced water can contain high levels of TDS including bicarbonate/carbonate ions, sodium ions, chloride ions, and organics.

Currently, the management of CBM produced water is conducted using various water management practices depending on the quality of the produced water. In areas where the produced water is relatively fresh, the produced water is handled by a wide range of activities including direct discharge, storage in impoundments, livestock watering, irrigation, and dust control. In areas where the water quality is not suitable for direct use, some operators are using treatment prior to discharge. At ORNL, ozonation is being tested as one of those treatments prior to discharge. Ozone is an extremely powerful oxidant that can attack organic materials and convert them to nonhazardous products. It is sparingly soluble in water. The main limitation comes from the low mass transfer rate of ozone from the gas phase to the liquid phase. By use of a glass frit, the effectiveness of ozone as an oxidant can be increased by creating a higher surface area to volume ratio for the contact of ozone with the solution through the generation of smaller bubbles. Smaller bubbles have higher residence times in contactors leading to higher gas volume fractions. This experiment will determine the effectiveness of ozone treatment of CBM produced water.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE/FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the fall semester of 2008, a FIU intern spent 14 weeks doing a fall internship at ORNL's Nuclear Science and Technology Division under the supervision and guidance of Dr. Costas Tsouris and Dr. Joanna McFarlane. This internship was organized and directed by the Higher Education Research Experience (HERE) and the Oak Ridge Institute for Science and Education (ORISE).

The intern's project was initiated on September 15, 2008, and continued through December 20, 2008, with the objective of treating coal-bed methane produced water using an Ozonation system. The process of Ozonation is the first step of a three step process including magnetic seeded filtration and electrosorption, designed to treat produced water to meet Idaho's water discharge criteria.

The treatment of this water could alleviate the issue of wastewater storage and perhaps the treated water could be reused in very dry areas of the country where it is desperately needed.

3. PROJECT OBJECTIVE

The objective of this project is to demonstrate that treatment of coal-bed methane (CBM) produced water to discharge criteria via ozonation, magnetic seeded filtration, and electrosorption is possible. The reuse of produced water could alleviate issues of storing the waste water as well as providing clean water in dry areas of the country where it is desperately needed.

4. WATER OZONATION

During the ozonation process, a system designed and assembled by Dr. Costas Tsouris at ORNL was used. As can be seen in Figure 1, the system consists of a pressurized air cylinder connected to a Labazone model L-110 ozone generator from Ozonology, Inc. It is connected to a gas-water reactor. This gas-water reactor is a glass column consisting of four openings, the first opening on the bottom contains a glass frit tube through which the ozone gas is fed; the second opening on the bottom is an outlet for treated produced water; the third opening on the top is an outlet for the ozone gas which is attached to a flowmeter, and finally, the fourth opening located on the top is an outlet for ozone gas to go the atmosphere or to the spectrophotometer for analysis. A Hewlett Packard Model 4852A spectrophotometer was used to show the effectiveness of ozone as an oxidant for treating the CBM produced water.

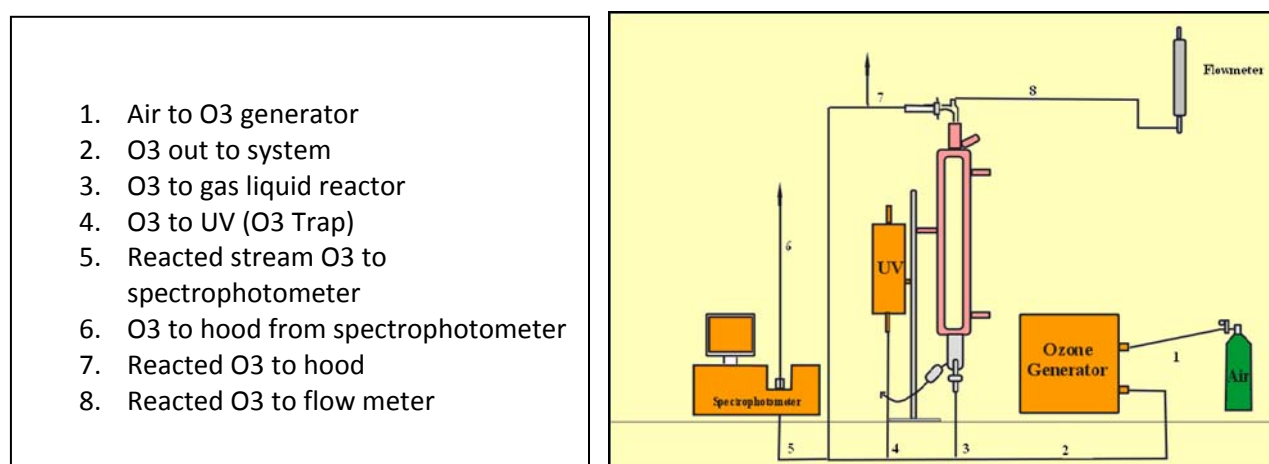


Figure 1. Schematic of the experimental set up for the ozonation experiment in the laboratory.

The ozonation experiment started by preparing a calibration curve, using pure water instead of produced water, to measure O_3 depletion during the reaction. It was done using the spectrophotometer to measure O_3 absorbance seven times using different flow rates (Table 1).

Table 1. Flow and Absorbance for Calibration Curve

Flow Rate (standard cubic feet per hour or SCFH)	Absorbance (Au)
1	1.9844
1.5	1.8845
2	1.7701
2.5	1.6395
3	1.5177
3.5	1.3969
4	1.2926

Spectrophotometry is based on light absorbance by the sample being tested. Therefore, by using Beer's Law, measurements of concentration can be obtained.

$$C = \frac{\text{Absorbance}}{E \times L}$$

Where:

C = ozone concentration in moles/liter

E = molar absorptivity at standard temperature and pressure, $3000 \pm 30 / [(M)(cm)]$

L = path length of the cuvette

For the results previously shown, the values for ozone concentration are provided in Table 2.

X	Y1	Y2
Flow Rate (SCFH)	Concentration (M)	Absorbance (Au)
1	0.0006615	1.9844
1.5	0.0006282	1.8845
2	0.0005900	1.7701
2.5	0.0005465	1.6395
3	0.0005059	1.5177
3.5	0.0004656	1.3969
4	0.0004309	1.2926

By plotting the results against the flow rate, we can obtain the calibration curve in Figure 2.

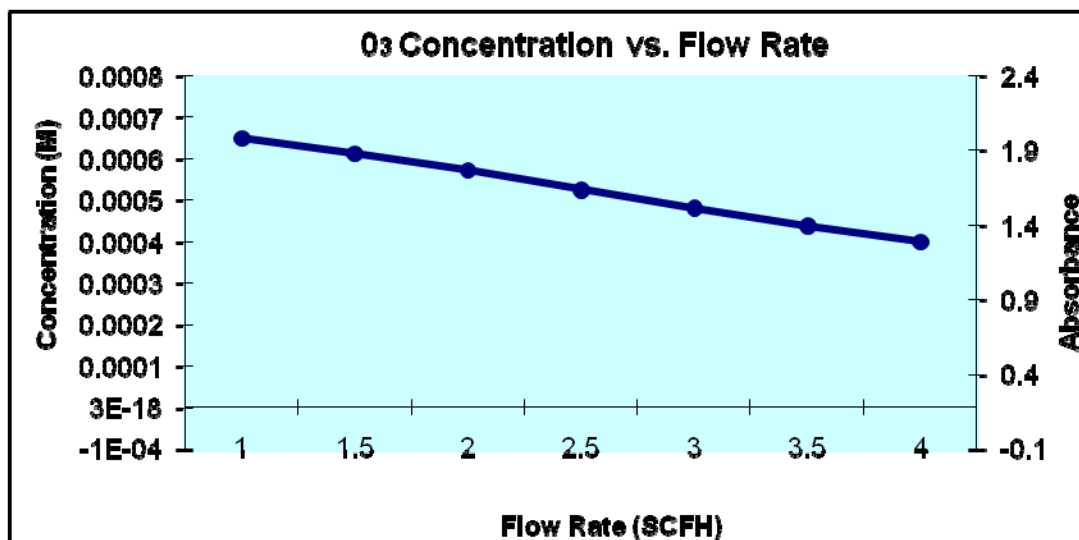


Figure 2. Calibration curve for ozonation.

The second phase of this experiment was to actually run the system using CBM produced water. Prior to treating the produced water via ozonation, the water was centrifuged using a Beckmans G6 centrifuge. Then, 100 ml of produced water, and 5 psig of ozone were fed into the gas-water

reactor. An electric pump was connected to circulate the water in a loop. This was done for a period of 120 minutes. The photograph in Figure 3 was taken during the ozonation process. The main observation during the experiment was a foam-like gas-water interface, which moved up through the top opening to the atmosphere.



Figure 3. Laboratory set-up of the ozonation experiment.

After the two-hour period, the treated produced water sample was ready to be analyzed for contaminants content. Figure 4 is a photograph taken to visually compare the treated and untreated water samples.

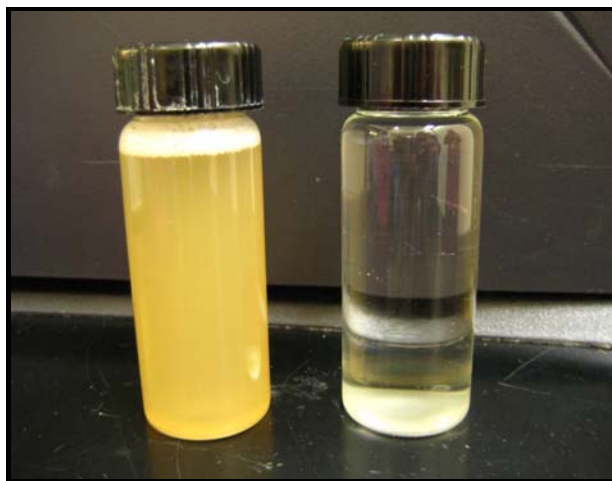


Figure 4. Samples before and after ozonation.

5. POST-TREATMENT ANALYSIS

Based on the major contaminants of produced water previously mentioned, three chemical tests were performed on samples of treated and untreated produced water to compare CBM produced water before and after ozonation treatment.

5.1 Chloride (Cl⁻) Ion Analysis

This analysis was done to measure the salinity of both samples. By using an ionic selective electrode (ISE), the ionic activity of chloride in the produced water was measured. An ISE is a transducer which converts the activity of Cl⁻ dissolved in a solution into an electrical potential which can be measured by a voltmeter. The sensing part of the electrode is usually made of an ion-specific membrane, in this case an Orion chloride electrode along with a reference electrode (Figure 5).

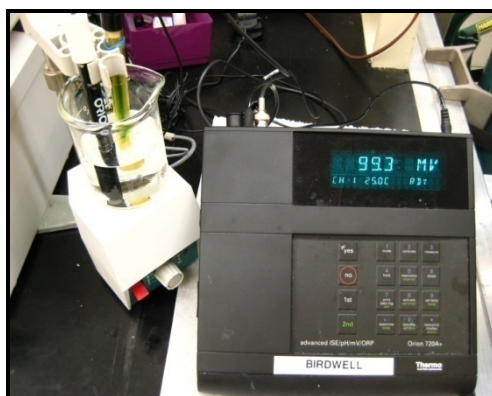


Figure 5. Ion selective electrode.

Since the ISE shows results in μV , a calibration curve was created. This calibration curve was established with six samples of sodium chloride (NaCl) with known concentrations. Then, the electrical conductivity was measured and the calibration curve was established (Table 3 and Figure 6). In order to obtain a concentration value for an unknown sample, its ISE signal is converted to the log of concentration which is then converted to concentration values.

Table 3. Cl⁻ Concentration and ISE Results

NaCl Concentration (ppm)	Log of NaCl Concentration	ISE Results (mV)
40	1.60206	167
70	1.845098	156.8
100	2	148.8
400	2.60206	115.7
700	2.845098	102.1
1000	3	94

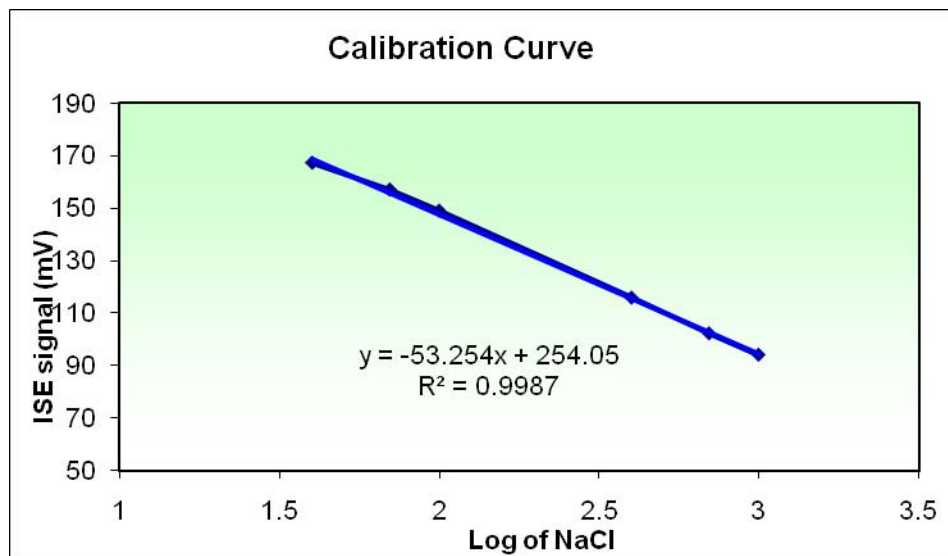


Figure 6. Calibration curve for ISE results.

Once this calibration curve was established, four samples of treated produced water were analyzed for salinity (Table 4 and Figure 7). These samples were prepared and treated by a previous intern and who did not have the time to analyze them for chloride ion content.

Table 4. Results of Salinity from Previous Samples

Sample Name	ISE Results (mV)	log of [NaCl]	[NaCl]	Cl ⁻	Cl ⁻ in samples (ppm)
air	163.2	1.54697169	35.23479	21.4932	3009.05
50 min	160	1.61364252	41.08114	25.0595	3508.33
65 min	159.3	1.62822676	42.48413	25.9153	3628.14
80 min	158.1	1.65322833	45.00164	27.451	3843.14

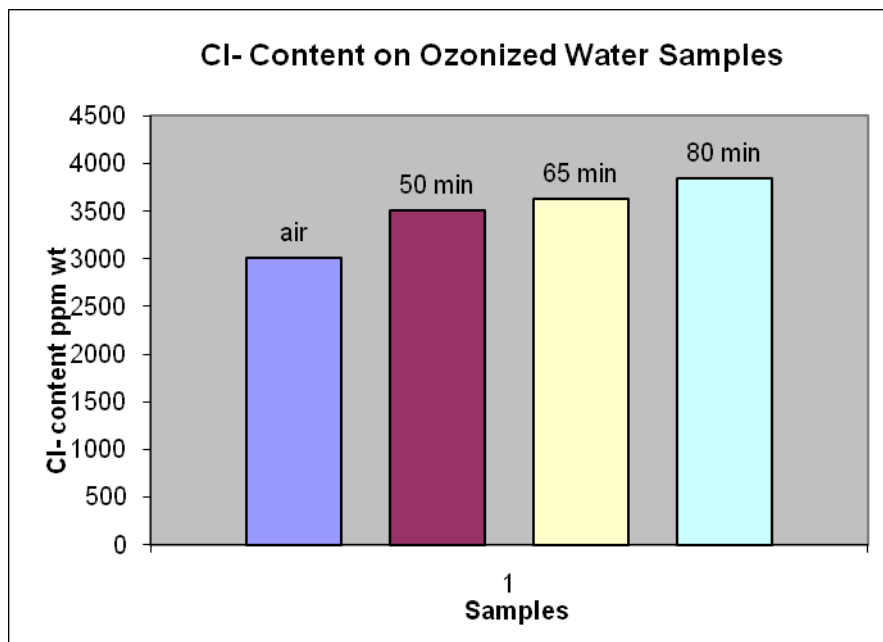


Figure 7. Results of salinity from previous samples.

In order to achieve reproducibility, chloride ion analysis on this sample was repeated a total of four times. However, during the last experiment, there was not exactly the amount of sample used in the other three experiments. Therefore the Cl^- concentration in the last sample is less and the results were not included in the calculated average results (Table 5 and Figure 8).

Table 5: Results of Salinity from Previous Samples, Four Trials

Sample Name	ISE Results (mV)	log of [NaCl]	[NaCl]	[Cl ⁻]	Cl ⁻ in samples (ppm)	Average Cl ⁻ in sample (ppm)
air	106.1	2.7366293	545.292	332.62	7761.32720	7799.909779
	106.4	2.7303789	537.500	327.87	7650.42571	
	105.5	2.7491301	561.216	342.34	7987.97642	
	118.4	2.4803633	302.24	184.37	4301.99574	
50 min	106.4	2.7303789	537.500	327.87	7650.42571	7669.161859
	107.4	2.7095443	512.323	312.51	7292.07231	
	105.3	2.7532970	566.626	345.64	8064.98755	
	121.4	2.4178594	261.733	159.65	3725.34132	
65 min	105.5	2.7491301	561.216	342.34	7987.97642	7988.527951
	105.8	2.7428797	553.196	337.45	7873.83634	
	105.2	2.7553805	569.351	347.30	8103.77109	
	113.8	2.5762026	376.879	229.89	5364.25357	
80 min	104.4	2.7720482	591.627	360.89	8420.82948	8407.395839
	104.5	2.7699647	588.795	359.16	8380.52854	
	104.4	2.7720482	591.627	360.89	8420.82948	
	112.3	2.6074546	404.999	247.05	5764.49481	

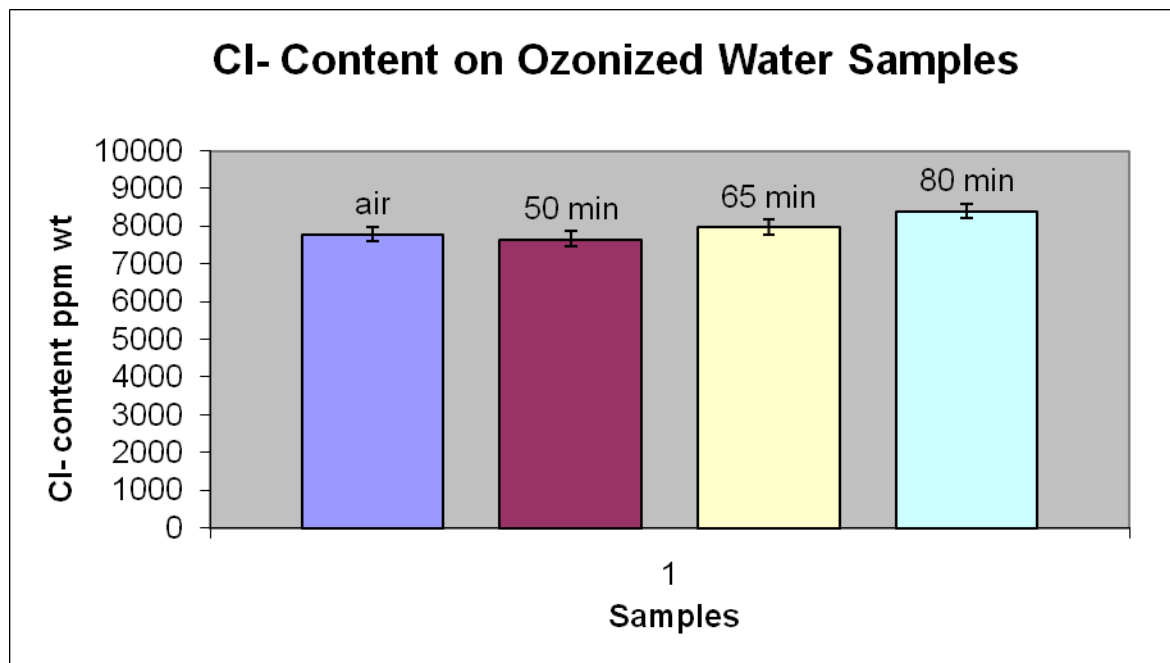


Figure 8. Results of salinity from previous samples, four trials.

Once my samples were ozonized, I performed the same procedure using the treated and untreated produced water samples and ran 2 trials (Tables 6 and 7, Figures 9 and 10).

Table 6. Results for Salinity, Trial 1

Sample Name	ISE Results (mV)	log of [NaCl]	[NaCl]	[Cl-]	Cl- in samples
Treated Produced Water	112.2	2.681573247	480.3671	293.0239	4883.73209
Untreated Produced Water	86.6	3.13987003	1379.971	841.7824	14029.70743

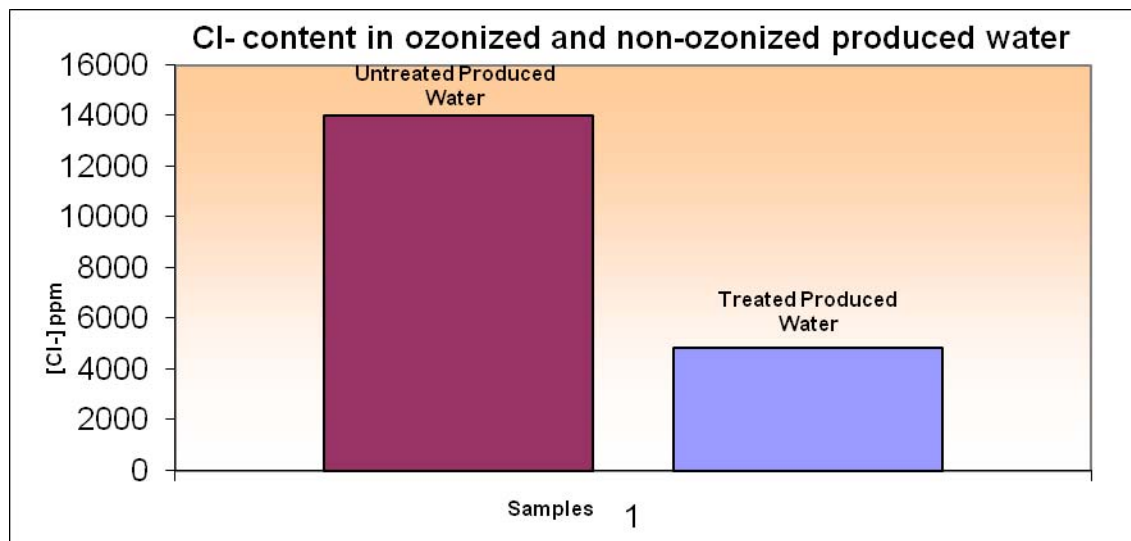


Figure 9. Salinity results for produced water samples, trial 1.

Table 7. Results for Salinity, Trial 2

Sample Name	ISE Results (mV)	log of [NaCl]	[NaCl]	[Cl ⁻]	Cl ⁻ in samples (ppm)
Treated Produced Water	109.3	2.718105682	522.5233	318.7392	5312.320476
Untreated Produced Water	87.3	3.13122019	1352.758	825.1825	13753.04217

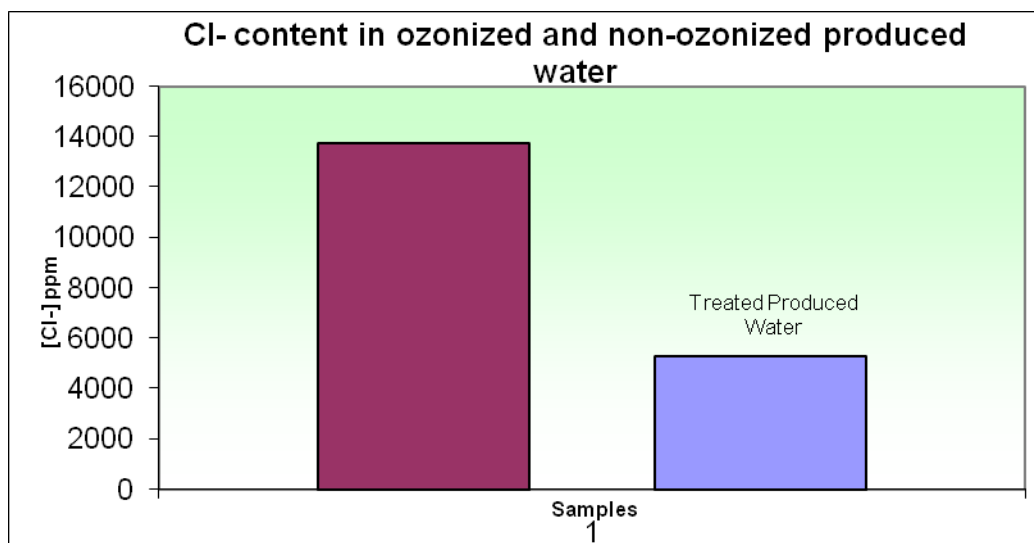


Figure 10. Salinity results for produced water samples, trial 2.

The average results of the two trials is shown in Figure 11.

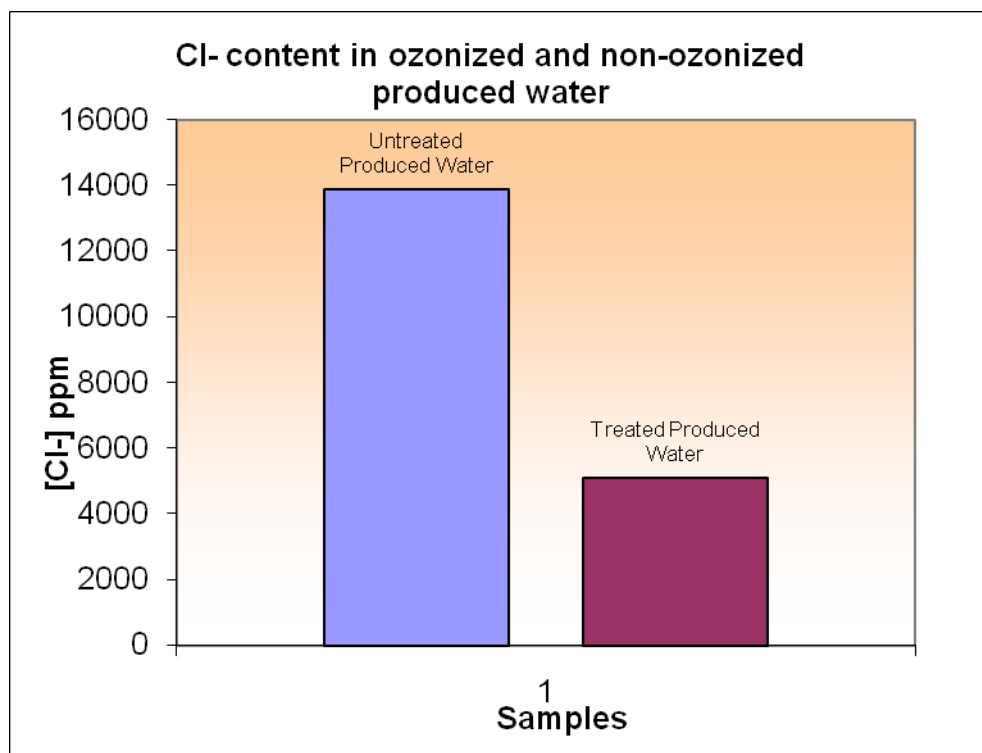


Figure 11. Salinity results for produced water samples, average of trials 1 and 2.

5.2 Carbonate/Bicarbonate Ion Analysis

Carbonate/bicarbonate ion analysis was performed by titration. Titration is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of a known reactant. A reagent, called the *titrant*, of known concentration (a standard solution) and volume is used to react with a solution of the analyte or *titrand*, whose concentration is not known. In this case, I used a Metrohm Titrino, which is an electronic titrator (Figure 12). The procedure “Measurements for Carbonate and Bicarbonate in Produced Water” (Appendix) was followed during this experiment. Basically, two solutions were prepared: 0.01N NaOH and 0.01N HCl. The HCl solution was then used as the titrand and the NaOH as the titrant, for 3 trials, to check the Titrino. Table 8 summarizes the end pHs and volumes of these three runs.

Table 8. Titration Results for HCl , 3 Trials

Trial	Start pH	End pH	Average End pH	End Volume (ml)	Average End Volume (ml)
1	2.02	7.27	7.233333333	26.729	26.254
2	2.08	7.21		27.342	
3	2.03	7.22		24.691	

Then, by using the formula $V_1 \times N_1 = V_2 \times N_2$, the experimental normality of HCl can be calculated:

$$N_{HCl} = \frac{V_{NaOH} \times N_{NaOH}}{V_{HCl}} \quad N_{HCl} = \frac{0.009375 \times 26.254}{20} = 0.012307N$$

Once the Titrino was checked, the treated and untreated produced water samples were titrated. The results were used to calculate the carbonate/ bicarbonate concentration (Tables 9 and 10), using the following formulas:

$$HCO_3^- = \frac{(V_{final} - 2V_{initial}) \times N_{HCl} \times 61.0171}{Sample Volume} \quad CO_3^{2-} = K_a \times \frac{HCO_3^-}{H}$$

Table 9. Titration Results for Produced Water

Sample Name	Start pH	End pH	average end pH	End Volume (ml)	Average End Volume (ml)
Untreated-produced water sample	6.28	3.7	3.7	107.418	106.686
Treated-produced water sample	6.29	3.7		105.954	

Table 10. Calculations Results for both treated and untreated produced water samples

Sample	[HCO ₃ ⁻] ppm	[CO ₃ ²⁻] ppm
Treated PH ₂ O	0.018998717	3.153002278
Untreated PH ₂ O	2.512486519	1585.271822



Figure 12. Metrohm Titrino.

5.3 Organic Content Measurement

To perform this experiment, a HP 5890 II series gas chromatograph (GC) was used (Figure 13). Gas chromatography is a chemical analysis instrument for separating chemicals in a complex sample. This gas chromatograph uses a flow-through column, through which different chemical constituents of a sample pass in a helium stream at different rates depending on their various chemical and physical properties and their interaction with the polymer column filling. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time).

Prior to placing the sample in the GC, the sample needed to be prepared so the GC can effectively read its components. First, both treated and untreated samples of produced water were acidified to pH 2 using a 1N HCl solution (Table 11). This was performed by using a glass pipette and a pH meter. The organic materials were extracted; by placing 10 ml of methylene chloride in a separatory funnel then each sample (treated and untreated produced water) was added to the funnel one at the time, then shaken. Finally the organics were extracted by taking out the denser layer of the mixture. Then, to this layer, 2,4,6 –tribromophenol, was added to spike the organics. Figure 14 shows the GC results.

Table 11. Sample pHs Before and After Acidification

Sample Name	Starting pH	Ending pH
Treated Sample	6.25	2
Untreated Sample	5.92	2

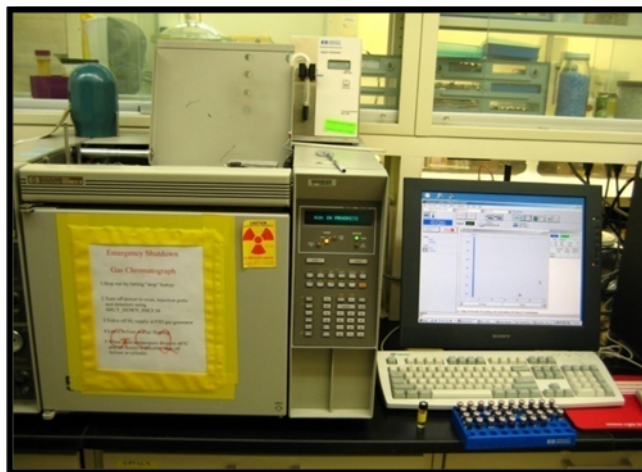


Figure 13. HP 5890 II series gas chromatograph.

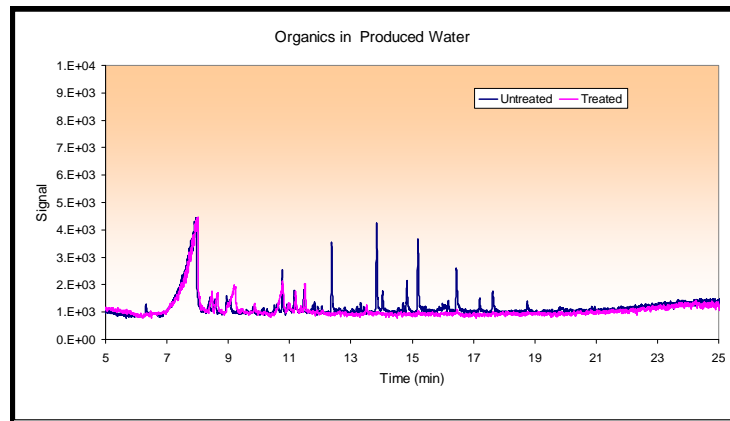


Figure 14. GC results for produced water samples.

6. DISCUSSION OF RESULTS

The objective of the experiments was to determine the affect of ozonation on decreasing the major contaminants of CBM produced water: chloride ions, carbonate/bicarbonate ions and organics. The first test measured ionic interaction using an ion selective electrode. The results of ISE are shown in Figures 9 and 10. The concentration of chloride ions in the samples was reduced from 14,000 ppm in the untreated produced water sample to 5,000 ppm in the treated produced water sample. This represents a decrease from 14% salinity to 5%. According to the practical salinity scale (PSS) the salinity of the samples went from saline water, which is equivalent to sea water, to brackish water, which has a higher salinity than fresh water but a lower salinity than saline water.

The second test, carbonate/bicarbonate ion analysis, reflected a decrease in these ions to about 0%. Ozonation results in the breaking of double bonds in compounds so most likely, the ozonation treatment of the produced water broke the double bonds of the carbonate/bicarbonate ions.

Lastly, the organic content results reflected a reduction or elimination of one third of the organic content. This portion encompasses the longer-chain aliphatic hydrocarbons, and the n-alkanes (C_{12} to C_{19}).

The visual results indicated a significant change in color as shown in Figure 5. Prior to ozonation, the CBM produced water looked dark and dense. After ozonation, the treated CBM produced water had a clear appearance.

7. CONCLUSION AND FUTURE WORK

The results of this experiment were very successful. Contaminants in the CBM produced water were eliminated to a great extent. Ozonation is an excellent approach to the treatment of CBM produced water to eliminate the major contaminants: carbonate/bicarbonate ions, chloride ions, and various organics. Rates of elimination of these contaminants were very satisfactory.

The samples need further analyses by inductively coupled plasma mass spectrometry (ICP-MS) to detect the presence of other minerals. In addition, the samples cannot be considered for reuse yet as they still need to undergo additional treatment via electrosorption and magnetic seeded filtration, in addition to post treatment analysis.

8. CONTRIBUTION TO OTHER PROJECTS

During this internship, I also had the opportunity to collaborate in other two projects. The first project focused in the analysis of biodiesel production kinetics for a biodiesel production company, NuEnergy, located in the tri-cities area of Tennessee. The main objective of this project was to find the residence time for biodiesel production. I had the opportunity to participate in several biodiesel production mimicking runs where twelve samples were obtained. After these samples were obtained, they were prepared for the gas chromatograph. I also had the opportunity to visit NuEnergy, see biodiesel production on a large scale, and witness the functioning of such a plant.

The second project was related to the study of surface interactions of radioactive particles and their transport and deposition. In order to perform this study, an atomic force microscope (AFM) was used. The AFM, or scanning force microscope (SFM), is a very high-resolution type of scanning probe microscope, with demonstrated resolution of fractions of a nanometer. The AFM is one of the foremost tools for imaging, measuring and manipulating matter at the nano scale. The information is gathered with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on command enable the very precise scanning.

9. REFERENCES

- [1] ALL Consulting, Handbook on Coal Bed Methane Produced Water: Management and Beneficial Use Alternatives. Tulsa, Oklahoma. 2003.
- [2] American Public Health Association, American Water Works Association, Water Pollution Control Federation. STANDARD METHODS :For the Examination of Water and Wastewater. Washington ,DC: APHA, AWWA, WPCF, 1985.

APPENDIX

Measurements for Carbonate and Bicarbonate in Produced Water

A Metrohm 717 DMS Titrino automatic titrator is used to determine the pH and the hydroxide/bicarbonate/carbonate content of produced water samples (Franson 1992).

Use 60 mL sample (3x20 aliquots) of produced water

Standard solutions: Use degassed DI (boil for 15 minutes and then cool, pH>6)
standardization of NaOH (0.01 N)

dissolve 0.4 g NaOH in 1 L degassed DI

Prepare $\text{KHC}_8\text{H}_4\text{O}_4$ (potassium hydrogen phthalate, CAS 877-24-7) solution by crushing 15-20 g $\text{KHC}_8\text{H}_4\text{O}_4$ and dry at 120 °C for 2 h. Let cool in a dessicator.

Weigh 1g $\text{KHC}_8\text{H}_4\text{O}_4$ and make up in 1 L volumetric flask to ~0.005N.

Titrate 40 mL $\text{KHC}_8\text{H}_4\text{O}_4$ solution using NaOH. Inflection point should be around pH 8.7 – repeat 3 times for statistics

Prepare HCl (0.01 N) by diluting 5 N HCl (2 mL stock in 1 L solution)

Titrate 40 mL HCl with standardized 0.01 N NaOH prepared in step 1. Repeat three times for statistics.

The instrument is calibrated with two NIST-traceable buffer solutions (pH 7 and pH 10, respectively). The temperature of the solution is entered digitally before the pH of the sample is measured. The OH^- , CO_3^{2-} , and HCO_3^- concentrations are determined by titrating 20 mL of produced water with standard 0.01 N HCl. End points are measured at pH 8.3 (i.e., volume end point A) and 3.7 (i.e., volume end point B), which are then entered into the following calculations:

Calculations

If $2A > B$, the solution contains OH^- and CO_3^{2-} ,

$$(2A - B) \times \text{normality of HCl} \times 17.0073 / (\text{sample volume}) = \text{ppm OH}^-$$

$$2(B - A) \times \text{normality of HCl} \times 30.0046 / (\text{sample volume, mL}) = \text{ppm CO}_3^{2-}$$

If $B > 2A$, the solution contains CO_3^{2-} and HCO_3^- ,

$$2A \times \text{normality of HCl} \times 30.0046 / (\text{sample volume, mL}) = \text{ppm CO}_3^{2-}$$

$$(B - 2A) \times \text{normality of HCl} \times 61.0171 / (\text{sample volume, mL}) = \text{ppm HCO}_3^-$$

Total alkalinity is determined from the total volume of acid required to achieve a pH of 3.7. It is calculated as:

$$\frac{(A + B) \times \text{normality of HCl} \times 1000}{\text{sample volume, mL}} = \text{Alkalinity to pH 3.7, mg CaCO}_3/\text{L}$$