2006

Resource recovery of coal bed methane formation water

Catherine Elizabeth Bishop
Louisiana State University and Agricultural and Mechanical College, bshp_cethrn@yahoo.com

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses

Part of the Environmental Sciences Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_theses/533

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master’s Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
RESOURCE RECOVERY OF COAL BED METHANE FORMATION WATER

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
In partial fulfillment of the
Requirements for the degree of
Master of Science

In

The Department of Environmental Studies

By
Catherine E. Bishop
B.S. East Central University, 2005
December 2006
ACKNOWLEDGEMENTS

I begin by thanking my parents, Chuck and Kay Bishop, who have never pushed and always encouraged me. They have shown me that success is not decided by society; success is personal. My extended family has been very important to me. Whether feeding, housing, or encouraging me, my family has been an impressive example of irreplaceable love.

To Dr. Ralph Portier, who I have come to know as family, thank you for your knowledge, support, and patience. I will also take with me the many lessons in bayouology. I would like to thank Dr. Al Cunningham, Dr. Ed Overton, and Dr. Paul Templet for serving on my thesis committee and offering useful advice and expertise as well as kind words of support.

I wish to extend a much deserved “thank you” to Buffy Ashton for all of her help in the extractions lab and with the GC/MS instrument. Thank you Buffy Ashton, Ashley Belle, Kyle Schmidt, Scott Miles, and Laura Basarico for help in the lab and for friendships that were necessary to remain sane.

Travis, I am very appreciative of your love. Your hard work inspires me, as does your patience. Thank you for knowing that I could do this.

Finally, I am thankful for my faith—unfailing, encouraging, true.
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ................................................................................................................................. ii

LIST OF TABLES ............................................................................................................................................... v

LIST OF FIGURES ........................................................................................................................................ vi

ABSTRACT ................................................................................................................................................... viii

1. INTRODUCTION ........................................................................................................................................ 1

2. LITERATURE REVIEW ................................................................................................................................. 3
   2.1 Oil and Gas Production ............................................................................................................................ 3
      2.1.1 Coal-Bed Methane as a Natural Gas Source ................................................................................. 4
   2.2 Drought .................................................................................................................................................. 4
   2.3 Water Quality and Toxicology ................................................................................................................ 6
      2.3.1 A Brief Review of Petroleum Hydrocarbon Toxicity ....................................................................... 7
   2.4 Merging Technologies to Address Water Shortage Issues .................................................................... 7
      2.4.1 Immobilized Microbe Bioreactors .................................................................................................. 8
      2.4.2 Reverse Osmosis ............................................................................................................................. 9
      2.4.3 Filtration .......................................................................................................................................... 9

3. MATERIALS AND METHODS ...................................................................................................................... 13
   Part I: Multiple Sources Well-Head Remediation Strategy—Encana Oil and Gas Company
   Parachute, CO ............................................................................................................................................... 13
      3.1 Site Description .................................................................................................................................. 13
      3.2 Objectives and Hypothesis .................................................................................................................. 14
      3.3 Approach ........................................................................................................................................... 14
         3.3.1 Laboratory Screening Study ....................................................................................................... 14
         3.3.2 Pilot Demonstration Study ........................................................................................................ 16
   Part II: Dispersed Field Well-Head Remediation Strategy—ConocoPhillips
   Farmington, NM ........................................................................................................................................... 19
      3.4 Site Description .................................................................................................................................. 19
      3.5 Objectives and Hypothesis .................................................................................................................. 19
      3.6 Approach ........................................................................................................................................... 20
         3.6.1 Pilot Demonstration Study ........................................................................................................ 20
   Part III: General Analytical Methods ........................................................................................................... 21
      3.7 Chemical Oxygen Demand (COD) ..................................................................................................... 21
         3.7.1 Approach .................................................................................................................................... 21
         3.7.2 Sample Preparation .................................................................................................................... 21
         3.7.3 COD Analysis ............................................................................................................................... 22
      3.8 Total Chromatographic Hydrocarbons (TCH) .................................................................................... 22
         3.8.1 Approach .................................................................................................................................... 22
         3.8.2 Liquid-Liquid Extraction ............................................................................................................ 22
         3.8.3 Gas Chromatography/Mass Spectroscopy .................................................................................. 24
         3.8.4 Calculations .................................................................................................................................. 24
3.9 Salinity .................................................................................................................. 26
  3.9.1 Approach ........................................................................................................ 26
  3.9.2 Sample Analysis ............................................................................................. 26
3.10 Nutrient Analysis ................................................................................................. 26
  3.10.1 Approach ...................................................................................................... 26
  3.10.2 Total Nitrogen ............................................................................................... 27
  3.10.3 High Range Total Phosphorous ................................................................. 27
3.11 Dissolved Oxygen ............................................................................................... 28
  3.11.1 Approach ..................................................................................................... 28
  3.11.2 Sample Analysis .......................................................................................... 28
3.12 pH ....................................................................................................................... 28
  3.12.1 Approach ..................................................................................................... 28
  3.12.2 Sample Analysis .......................................................................................... 28

4. RESULTS AND DISCUSSION ............................................................................... 30
 Part I: Multiple Sources Well-Head Remediation Strategy ........................................ 30
  4.1 Laboratory Screening Study Results ................................................................. 30
  4.2 Field Pilot Studies for Continuous Treatment of Multiple-Source Well-Head Pit
      Production Water ................................................................................................. 34
  4.3 Discussion .......................................................................................................... 35
 Part II: Dispersed Field Well-Head Remediation Strategy ......................................... 40
  4.4 Field Pilot Studies for Continuous Treatment of Dispersed Field Well-Head
      Remediation Strategy ........................................................................................... 40
  4.5 Discussion .......................................................................................................... 43

5. CONCLUSIONS ..................................................................................................... 47
  5.1 Summary of Findings ......................................................................................... 47
  5.2 Recommendations for Future Work ................................................................. 48

BIBLIOGRAPHY ........................................................................................................ 49

APPENDIX: TOTAL ION CHROMATOGRAMS .......................................................... 52

VITA ......................................................................................................................... 61
# LIST OF TABLES

3.1 GC/MS Analytes..................................................................................................................29

4.1 48 hour COD comparison from laboratory IMBR using raw water and Biocarrier #1........30

4.2 48 hour COD comparison from laboratory IMBR using the gravity-separated................31

4.3 48 hour COD comparison from laboratory IMBR using tanker/gravity-separated.........32

4.4 Mean COD reduction (mg/L/day) of raw water and gravity-separated water................32

4.5 Mean COD reduction (mg/L/day) of Biocarrier #1 and Biocarrier #2............................33

4.6 Percent removal of petroleum hydrocarbons (ng/mg) using GC/MS............................38

4.7 Percent removal of petroleum hydrocarbons (ng/mg ) using GC/MS............................42

4.8 Percent reduction of salinity (g/100g total chlorides)......................................................43

4.9 Particle count analysis.......................................................................................................45
# LIST OF FIGURES

2.1 Representation of CBMF excavation.................................................................5

2.2 Energy-Water Efficiency Technology Research, Development, and Transfer Act of 2005….5

2.3 Reverse osmosis membrane process diagram......................................................10

2.4 Micro filtration system diagram...........................................................................11

2.5 Ultra filtration process diagram............................................................................11

2.6 Experimental design process flow: Lab and field pilot study..............................12

3.1 Pipe transporting production water into the Lake Rosa production water pit........13

3.2 Lake Rosa production water pond in Parchute, CO.............................................13

3.3 Laboratory IMBR containing water from Parachute, CO and Biocarrier #1.........17

3.4 Pilot study in Parachute, CO................................................................................17

3.5 Preliminary schematic of production water treatment system Parachute, CO.....18

3.6 Drill pit in the San Juan Basin of New Mexico.....................................................19

4.1 COD of raw water and gravity-separated water using semi-continuous batch mode..33

4.2 COD of Biocarrier #1 and Biocarrier #2 using semi-continuous batch mode........34

4.3 Representative Lake Rosa sample Total Ion Chromatogram (TIC)......................36

4.4 Representative influent sample TIC......................................................................37

4.5 Representative effluent sample TIC......................................................................37

4.6 Total Chromatographic Hydrocarbon (TCH) Removal analysis using GC/MS.......38

4.7 Preliminary layout of treatment building for the EnCana drill pit in Parachute, CO..39

4.8 Representative influent sample Total Ion Chromatogram (TIC).........................40

4.9 Representative IMBR effluent sample TIC, 18 May 2006.....................................41

4.10 Representative RO effluent sample TIC, 18 May 2006.......................................41
4.11 Total Chromatographic Hydrocarbon (TCH) Removal analysis using GC/MS.................43

4.12 Treatment building layout for the ConocoPhillips drill pits in New Mexico..................46
ABSTRACT

During the excavation of natural gas, petroleum hydrocarbon-polluted brine water, termed production water, is drawn from the coal bed methane formations (CBMF) along with the natural gas product. The water is drawn out in vast amounts and re-injected into the CBMF. In the Greater Rocky Mountain Region (GRMR) where water supplies are dwindling, the remediation of CBMF production water has become a high priority for maintaining agriculture, residential development and industrial expansion.

The overall objective of this research was to demonstrate in laboratory and field pilot studies the efficacious merging of Immobilized Microbe BioReactor (IMBR) technologies for biodegradation/mineralization of organics and Reverse Osmosis (RO) technologies as a cost-efficient and effective method for the desalination of CBMF water. Laboratory studies indicated that organic constituents of concern could be reduced at a kinetic rate of 1,230 ± 399 mg/L/h at the EnCana site and 140 ± 120 mg/L/h based on ConocoPhillips drill pit analysis. Salinities in the residual brine were only reduced from 220 ppm to 120 ppm total chlorides with the RO system working at a continuous flow rate of 7.6 ± 0.04 L/min. Chemical oxygen demand (COD) was reduced at a rate of 2,580 ± 1,940 mg/L/h. A field pilot established in Parachute, CO consisted of a 836 L IMBR operating at a feed rate of 6.50 ± 1.84 L/min. Samples were received from one collective drill pit at the EnCana Oil and Gas Company site in Parachute, CO and five separate drill pits from the ConocoPhillips fields in the San Juan Basin near Farmington, NM.

Acceptability of the production water treatment system proposed in this project was analyzed based on percent removal of Total Chromatographic Hydrocarbons (TCH)
and salinity. In both the EnCana and ConocoPhillips pilot studies, the proposed treatment yielded a significant difference ($P < 0.05$) in TCH concentrations between the influent and effluent samples. Desalination of production water using a RO system was analyzed in the ConocoPhillips pilot study and did not show a significant difference ($P > 0.05$) between influent and effluent water samples.
INTRODUCTION

In the Greater Rocky Mountain Region (GRMR), natural gas excavation has been on the rise with natural gas production reaching record highs in the past few years. When excavating the Coal Bed Methane Formations (CBMF) of the GRMR, brine, petroleum-polluted water, termed production water, is drawn out with the natural gas product. In some areas, CBMF water fractions serve as an important water source for surrounding communities. The depletion and subsequent pollution of these water sources has resulted in critical water shortages for industrial operations, domestic consumption, agriculture, and future oil/gas exploration.

The need to remediate production water so that it is available for reuse is a necessity to avoid the looming drought in the GRMR. A fast, effective, technologically advanced form of remediation involves the use of microbes as the source of petroleum hydrocarbon degradation. Immobilized Microbe BioReactors (IMBR) utilize aerobic bacteria grown on porous diatomaceous earth pellets, called biocarrier which allows for continuous effluent treatment of targeted organics in any given waste stream. CBMF waters are particularly difficult to treat because of the elevated concentrations of complex petroleum hydrocarbons, total suspended solids (TSS), and total dissolved solids (TDS). These high brine formation waters are deleterious to aquatic and agricultural habitats, which necessitate the use of Reverse Osmosis (RO) systems prior to discharge. Numerous studies have indicated that RO systems can handle the salt content associated with these waters, but membranes are blinded by the residual organics.

The generalized experimental approach for this thesis was to evaluate the efficacious use of an IMBR reactor to treat organics and minimize blinding of RO membranes for production water. In a team effort with a university technology transfer company and the two major oil and
natural gas exploration/production companies in the GRMR, EnCana Oil and Gas Company and ConocoPhillips, two separate field pilot studies were conducted following preliminary laboratory evaluations of candidate brine waters. Data will be presented on remediation of production water in six drill pits in the GRMR—one pit in Parachute, CO and five in Farmington, NM. Research program objectives were as follows:

1. Cleanse the production water of petroleum hydrocarbons using dual flow-through Immobilized Microbe Bio-Reactors (IMBR) as the primary biotreatment system, with initial gravity separation and micro-filtration.

2. Utilize ultra-filtration of post-biologically treated water to remove large particulate matter.

3. Desalinate brine water via the application of a RO membrane system.

Both influent and effluent water samples were collected and analyzed to determine the chemical properties of the site water before and after treatment. Parameters measured, specifically, were Chemical Oxygen Demand (COD), Total Chromatographic Hydrocarbons (TCH), and salinity. The goals of both laboratory and pilot studies were to meet the United States water standards for agricultural reuse of CBMF water.
2

LITERATURE REVIEW

2.1 Oil and Gas Production

According to the U.S. Energy Information Administration, in 2002, approximately 5.8 million barrels (bbl) of crude oil were produced per day in the United States and, in 2004, approximately 24.2 trillion cubic feet (Tcf) of raw natural gas were produced (USEIA, 2006). Until recently, the United States oil and gas industry operated primarily in the Gulf Coast region. Due to supply in demand and advancing technologies, production focus has shifted to the natural gas resources found in the Greater Rocky Mountain Region (GRMR) within the last decade (USEIA, 2006). Natural gas is a cleaner burning fuel, and, would therefore, be beneficial as an automotive fuel (USGS, 2000).

The majority of the natural gas used in the United States is produced in the United States, specifically in Montana, Wyoming, New Mexico, Colorado, and Utah, with imports delivered via pipeline from Canada or shipped as liquefied natural gas (LNG) from overseas. At the end of 2005, $10.7 billion were allocated by energy companies toward energy resource recovery and research in the GRMR with approximately 90% of the funding going into natural gas excavation (Economist, 2006). The majority of natural gas production is used for heating and electricity within households and industrial facilities. A small portion of natural gas produced is used to sustain oils and gas industry operations (USEIA, 2006). With developing technologies for acquisition and use, the small portion of natural gas used for vehicular fuel could increase; thus, the amount of CO₂ produced by automobiles would decrease.
2.1.1 Coal Bed Methane Formations as a Natural Gas Source

The decomposition of organisms over time yields vast amounts of organic material. This organic material, also called biomass, when acted upon by heat and pressure, can produce coal, petroleum, and natural gas, collectively called fossil fuels, which are trapped in rock formations (USEIA, 2005). In coal bed methane formations (CBMFs), methane gas is tightly absorbed to the coal via hydrostatic pressure of the water contained in the CBMF and surrounding formations. Prior to drawing natural gas from the CBMF, water must be extracted to decrease the binding pressure within the formation. The petroleum hydrocarbon-rich brine water forced out of the formation during oil and gas production is termed production water (Wolfe et al., 2002). (See Figure 2.1 for a representation of CBMF excavation.) Many CBMFs serve as reservoirs for the surrounding community due to the large quantity of water they contain and disperse; therefore, the rapid depletion of this water in the gas production process could be detrimental to the already depleted water supply in the GRMR (USGS, 2000).

2.2 Drought

Water is required in order to produce energy. In fact, the amount of water diverted for energy production, according to Sandia National Laboratories, is a staggering 45 percent (Domenici et al., 2006). A percentage of energy must be allocated in order to obtain water, in its natural and purified state. So, the problem, then, is not only conserving water within businesses, households, and industry, but also developing more energy efficient methods for the acquisition, purification, and transport of water and reclamation of previously unusable water. In addressing these issues, an amendment to the Energy Policy Act of 2005 was introduced as the Energy-Water Efficiency Technology Research, Development, and Transfer Program Act of 2005 (See Figure 2.2).
Figure 2.1 Representation of CBMF excavation.


1. Reduce the amount of energy required to provide adequate water supplies.
2. Reduce water consumption in the production or generation of electricity.
3. Reclaim previously unusable water.
5. Agricultural, industrial, and municipal efficiency and conservation.
7. Any other technologies identified by the Secretary as necessary to carry out the program.

Figure 2.2 Excerpt from The Energy-Water Efficiency Technology Research, Development, and Transfer Act of 2005 (S. 1860)
Water reclamation is of utmost importance as it concerns CBMF water depletion. Until recently, technologies were not advanced enough to properly treat production water for reuse. Instead, the copious amounts of water found in the CBMF of the GRMR, which could have been used, in some cases, as a local water source, were drawn up as brine water containing petroleum hydrocarbons and re-injected into the formations. The common practice of re-injecting production water not only depletes the CBMF water supply, but compromises the sustainable long-term health of the surrounding environment (Kuipers, 2005). An inhibited water supply contributes to drought, which has been set into play by increased demand and a decreased supply heavily affected by the shifting global climate.

2.3 Water Quality and Toxicology

The Clean Water Act is the primary control mechanism for assuring waste water is conditioned to be within the technology- and water quality-based limits necessary for the area to which it is being discharged or for what purposes it is to be used (Veil, 2002). As found in the Code of Federal Regulations 40 CFR Part 435 Subpart C set forth by the U.S. Environmental Protection Agency (EPA), the only limit requirement for the discharge of onshore produced water is not to discharge said water. Two exceptions exist, but neither pertains to the GRMR (USEPA, 1996). The need for production water reclamation has caused an increase in environmental regulatory compliance costs for the oil and gas industry (Tellez et al., 2005). Certain plans have been implemented to help the oil and gas industry fund clean up efforts, such as the Petroleum Environmental Cleanup Fund Award (PECFCA) program. PECFCA is a reimbursement plan for owners who clean up petroleum-contaminated soil and groundwater (PECFA, 2005). The need
for funding, however, far exceeds the available funds (DCDNR, 1998 and PECFA, 2005).

2.3.1 A Brief Review of Petroleum Hydrocarbon Toxicity

Short-term toxicological effects of hydrocarbons include respiratory and dermal effects, with noticed hypertrophy and hyperplasia of the skin at higher doses (IPCS, 1982). The chronic toxicity of petroleum hydrocarbons points toward carcinogenicity, particularly the mutagenic effects of polycyclic aromatic hydrocarbons (PAH) due to metabolic processes upon entering the organismal body (IPCS, 1982, Klaassen, 2001, and Manahan, 2000). Biotransformation of petroleum hydrocarbons can also be regarded as a protective mechanism, a mechanism utilized to break down the lipid-soluble petroleum hydrocarbons into water-soluble metabolites, an ability that many organisms do not possess (Rand, 1995).

2.4 Merging Technologies to Address Water Shortage Issues

Typical conventional water treatment, as defined by the U.S. Bureau of Reclamation and Sandia National Laboratories, is comprised of the 6 following steps:

1. screening
2. coagulation of suspended solids
3. sedimentation of suspended solids
4. filtration
5. disinfection
6. storage

Treatment processes differ for the various types of waste water. As it applies to oil production water, filtration and disinfection with subsequent desalination will allow for the highest probability of reuse. As addressed in the Desalination and Water Purification Technology Road Map, “By 2020, desalination and water purification technologies will contribute significantly to ensuring a safe, sustainable, affordable, and adequate water supply for the United States.” (USBR et al., 2003)
Natural gas excavation has developed into a much cleaner process, with the exception of the high volumes of produced water. Treatment methods, as they apply to water recovery from coal bed methane formations in the GRMR and this research, are outlined in the subsections 2.4.1 through 2.4.3. A flow through design of the experimental technological processes is shown in Figure 2.6.

2.4.1 Immobilized Microbe Bioreactors

The biotransformation of hydrocarbons is the basis of the Immobilized Microbe Bioreactor (IMBR) system. According to previous research by Catallo, et al., “Field demonstration studies… indicated that indigenous and commercial microbial consortia are capable of degrading and detoxifying toxic hydrocarbons and carcinogenic PAHs at substantial rates.” IMBRs can be utilized at various stages of contamination and in conjuncture with common remediation techniques, such as gravity-separation and ultrafiltration (Portier et al., 1991). These systems contain microbes capable of enzymatically breaking down petroleum hydrocarbons. In comparison to other bioremediation methods, bioreactors allow for a pH, Dissolved Oxygen (DO), nutrient, and temperature controlled environment (Portier et al., 1991). Also, bioreactors provide containment vessels for the bacteria, which not only provide optimum living conditions for the organisms, but also prevent the remediation site from being contaminated with the bacteria (Portier et al., 1990). Porous pellets of diatomaceous earth are used in reactors to allow for the largest surface area synthetically possible for bacterial growth. The pellets are first soaked in dissolved chitin to produce a polysaccharide coating optimal for bacterial growth on the media (Friday et al., 1991, Portier et al., 1986, and Messing et al., 1979). Bacterial strains are chosen for their ability to metabolize specific contaminants based on previous research and immobilized on the diatomaceous media in an aerated aqueous environment.
before being introduced to the contaminated water (Lee et al., 1999 and Portier et al., 1990). Microbial bioremediation is shown to be an efficient, cost-effective means of degrading organic xenobiotics (Tellez et al., 2005, Tellez et al., 2002, Catallo et al., 1992, Portier et al., 1991, Portier et al., 1990, Douglas et al., 1999).

2.4.2 Reverse Osmosis

Unlike the very small percentage of the world’s water that is safe for drinking—less than 3 percent—oil production water is highly saline (CRDWPT et al., 2005). Thus, an effective method of desalination must be utilized prior to production water reuse. A Reverse Osmosis (RO) system is ideal for demineralization due to the fact that the RO membrane acts as a molecular sieve (Figure 2.3). The fluid that passes through the RO membrane is termed permeate. Permeate no longer contains pollutants, chemicals, or reagents, collectively termed solutes (USEPA Capsule Report, 1996). The RO membrane is used in brackish and seawater and has shown to decrease not only salt constituents, but some molecular organic contaminants as well (CRDWPT et al., 2005). To achieve higher fresh water return with less brine water waste, a dual-stage recirculation process should be utilized (Burnett, 2005). RO membranes can become blinded and develop holes; when this occurs, constituents are no longer removed from the water, but pass through the RO system. The dual flow-through IMBR system (Section 2.4.1) and the micro and ultra filtration systems (Section 2.4.3) prevent immediate blinding of the RO membrane by removing particulates and organic contaminants.

2.4.3 Filtration

Filtration is necessary to remove solids capable of rendering the system incapable of performing its designated functions. Techniques used in the bioremediation schematic, as outlined for the produced water pits in the GRMR, consist of micro filtration and ultra
filtration systems. Micro-filtration is utilized prior to IMBR treatment and is a pre-treatment mechanism that cleanses surface waters of bacteria and oily substances (Figure 2.4). Ultra-filtration is placed after the IMBR and allows for the removal of higher molecular-weight substances, such as colloidal materials and organics (Figure 2.5). Lower molecular weight organics flow through the ultra-filtration system and are not removed. Another type of solid removal method, backwashing, is utilized in the production water remediation system. Backwashing removes solid deposits from the reactors, sending them back through the system, which allows for maximum use of the entire system. Without backwashing, the micro- and ultra-filtration systems, RO system, and IMBRs allow constituents to pass through the system yielding effluent with high turbidity. (AMI, 2006)

![Figure 2.3 Reverse osmosis membrane process diagram.](image-url)
Figure 2.4 Micro filtration system diagram.

Figure 2.5 Ultra filtration process diagram
Figure 2.6 Experimental design process flow: Lab and field pilot study.
3

MATERIALS AND METHODS

Part I: Multiple Source Well-Head Remediation Strategy—EnCana Oil and Gas Company
Parachute, CO

3.1 Site Description

In January of 2002, the merger of PanCanadian Energy Corporation and Alberta Energy
Company, Ltd. yielded EnCana Oil and Gas, Inc. As of 2004, EnCana was the “leading natural
gas producer with 85% of operating cash flow from natural gas and natural gas liquids (NGL).”
(EnCana, 2004) Natural gas pumps operated by EnCana in Parachute Pass, CO draw natural gas
along with residual oils and brine water from the Rocky Mountain reserves. The production
water is transported directly from the wellhead via pipelines to a production water pit lined with
60 mil. polyurethane liner at a rate of 30,000 bbl/day (Figure 3.1). The water and residual oil
undergo gravity-separation in Lake Rosa and are then transported to a tanker (Figure 3.2). From
the tanker, the production water is then re-injected into the CBMF from which it came. This has
been the natural gas well operation in Parachute Pass for the last approximately 10 years.

Figure 3.1 Pipe transporting production water into the Lake Rosa production water pit.

Figure 3.2 Lake Rosa production water pond in Parchute, CO
3.2 Objectives and Hypothesis

Objectives for the multi-source well-head bioremediation of the drilling pit in Parachute, CO are as follows:

1. Conduct a laboratory screening study to determine optimum bacteria for petroleum hydrocarbon bioremediation
2. Send production water from all well-heads in the region to one collection drill pit—Lake Rosa.
3. Cleanse the production water of petroleum hydrocarbons using dual flow-through Immobilized Microbe Bio-Reactors (IMBR) as the primary treatment system, with initial gravity separation.
4. Implement a pilot plant at Lake Rosa with influent and effluent constituent monitoring.
5. Subsequent treatment of water with micro- and ultra filtration and reverse osmosis to remove total dissolved solids (TDS) from the brine water.

Hypothesis: Coal bed methane formation drilling water can be cleansed to the point of reusability using IMBRs as the main source of petroleum hydrocarbon degradation.

3.3 Approach

3.3.1 Laboratory Screening Study

Production water samples were received from Parachute, CO via chain-of-custody arrangements with site contractors at ABS, LLC/EnCana Oil and Gas Company on February 7, 2006. Analysis of two initial samples, Lake Rosa and the holding tanker, provided background COD concentrations. Lake Rosa samples represented unfiltered samples; whereas, the tanker samples represented gravity-separated samples. Time comparison of COD degradation was performed using the Lake Rosa and tanker water samples. Bench-top scale reactors were
constructed in the laboratory (Figure 3.2).

The petroleum degrading microorganisms were grown from two different biocarriers, Biocarrier #1 and Biocarrier #2, using mineral salts media, containing yeast, sodium acetate, and equal amounts of potassium phosphate (KH$_2$PO$_4$) and ammonium nitrate (NH$_3$NO$_4$) in deionized water with the salinity adjusted to 200 ppm in 1.0 L sterile bottles. The bottles were placed on a roller drum under heat lamps and monitored for growth using the pour plate and plate count methods. The agar used was a mineral salts agar with the salinity adjusted to 200 ppm—the approximate salinity of the production water—to prevent the bacterial cells from lysing.

Porous pellets of diatomaceous earth were rinsed with deionized water and autoclaved to ensure sterility. The pellets were soaked in dissolved chitin and deionized water to provide an ideal surface for the adherence of bacteria (Messing et al., 1979). The chitin mixture was drained off of the pellets and the pellets were added to the bench top bioreactors. The Biocarrier #1 bacterial solution described in the preceding paragraph was then poured over the pellets in two separate reactors.

After three days, the nutrient solution was drained out of the reactors and 700 mL of the sample water from Lake Rosa and 700 mL of the sample water from the tanker, adjusted to contain the proper ratio of nutrients, were introduced to the reactors. A time zero (t$_0$) sample was taken, as were subsequent times t$_1$, t$_2$, t$_3$, t$_4$, t$_5$, t$_6$, t$_{24}$, and t$_{48}$ hour samples. Samples were tested for COD, nutrients, pH, DO, and salinity.

Following the 48 hour testing, a new reactor was constructed and prepared for Biocarrier #2. The sample water from the tanker was then added to the reactor following the same procedures as those used when analyzing the efficiency of bacteria from Biocarrier #1. A time zero (t$_0$) sample was taken, as were subsequent times t$_1$, t$_2$, t$_3$, t$_4$, t$_5$, t$_6$, t$_{24}$, and t$_{48}$ hour samples. Samples were tested for COD, nutrients, pH, DO, and salinity.
After the 48 hour sampling period, a time zero ($t_0$), $t_{24}$, and $t_{48}$ sample was collected using a semi-continuous batch mode to analyze the degrading capability of the bacteria on Biocarrier #1 versus the bacteria on Biocarrier #2. Comparison of Biocarrier #1 and Biocarrier #2 bacteria was utilized in determining the type of bacteria combination to be utilized in the pilot IMBR studies.

3.3.2 Pilot Demonstration Study

Production water from the EnCana wellheads in Parachute, CO was collectively pumped into Lake Rosa. A mobile IMBR system was implemented between Lake Rosa and the original water-holding tanker (Figure 3.3). Influent pumps drew water from Lake Rosa through an initial micro filter of $1 \mu m$ pore width. After filtration, the water entered the equalization tank before being pumped into the IMBR system to assure that pH levels were viable for the life of the bacteria in the reactors. The total retention time for the two IMBR tanks was 12 hours, collectively. The continuous flow rate of the 2,000 L IMBRs was $6.5 \pm 1.84$ L/min. The water then entered an ultra filtration system of 1 to 3 $\mu m$ pore width in order to remove larger particulate matter. After microbial degradation and filtration, the water still maintained a high salinity. A Reverse Osmosis (RO) system was added to the schematic (Figure 3.4 and Figure 3.5) for future use in the production water treatment system design. To ensure proper living conditions for the bacteria 30 to 40 standard cubic feet per hour (scfh) of air were fed to the media reactors. Temperature in the reactors was kept between 21.1 and 35.0 °C. Nutrients were pumped into the reactors at a flow rate of 5.0 mL/min.

Influent and effluent samples were collected March 9 through 23, 2006. Samples were kept at 4° C until analysis. Samples were analyzed for nutrients, dissolved oxygen, pH, chemical oxygen demand (COD), and total chromatographic hydrocarbons (TCH) using methods described in Part III of this chapter.
Figure 3.3 Laboratory IMBR containing water from Parachute, CO and Biocarrier #1.

Figure 3.4 Pilot study in Parachute, CO.
Figure 3.5 Preliminary schematic of production water treatment system Parachute, CO.
3.4 Site Description

Conoco Inc. and Phillips Petroleum Company merged in 2002 followed by the addition of Burlington Resources in 2006. The combination, ConocoPhillips, is a $162 billion company and is placed third in the United States based on market capitalization, oil and gas reserves, and production. ConocoPhillips operates in 40 countries and lists natural gas gathering, processing and marketing as one of their four core activities worldwide. (ConocoPhillips, 2006) Five production water pits are located in the San Juan Basin in the ConocoPhillips gas fields near Farmington, NM (See Figure 3.3). The drill pits are lined with a 60 mil. polyurethane geotextile cloth and the volume of water held in the pits ranges from 1,000 to 6,000 barrels (bbl).

![Figure 3.6 Drill pit in the San Juan Basin of New Mexico.](image)

3.5 Objectives and Hypothesis

Objectives for the multiple drill pit remediation of production water are as follows:
1. Cleanse the production water of petroleum hydrocarbons using dual flow-through Immobilized Microbe Bio-Reactors (IMBR) as the primary treatment system, with initial gravity separation.

2. Implementation of a pilot plant at each of 5 drill pits in the ConocoPhillips natural gas fields with influent and effluent constituent monitoring.

3. Subsequent treatment of water with micro- and ultra filtration and reverse osmosis to remove Total Dissolved Solids (TDS) and Total Suspended Solids (TSS) from the brine water.

4. Evaluate the efficacy of use in treating water for agriculture, drilling new wells, fracturing formations, or immediate release around the drill pit.

Hypothesis: Coal bed methane formation drilling water can be cleansed using IMBRs as the main source of petroleum hydrocarbon degradation with post-remediation treatment of brine water via a reverse osmosis membrane.

3.6 Approach

3.6.1 Pilot Demonstration Study

A flow through IMBR system was implemented at each of five drill pits in the New Mexico fields separately (Figure 3.3). Influent pumps drew water from each pit through an initial micro filter of 1 µm pore width. After filtration, the water entered the 400 L equalization tank before being pumped into IMBR #1 to assure that pH levels were viable for the life of the bacteria in the reactors. The hydraulic retention time for the dual-IMBR system was 12 h. The flow range of the reactors was $6.65 \pm 4.03$ L/min. Ultra filtration was utilized to remove large particulate (1-3 µm pore width) matter from the petroleum hydrocarbon-remediated water. After ultra filtration, the water flowed through a reverse osmosis membrane at a rate of $7.6 \pm 0.4$ L/min.
To ensure proper living conditions for the bacteria in the reactors 30 to 40 standard cubic feet per hour (scfh) of air was fed to the media reactors. Temperature in the reactors was kept between 21.1 and 35.0 degrees Celsius. Nutrients were pumped into the reactors at a rate of 5.0 mL/min.

Influent and effluent samples were collected April 26 through June 23, 2006. Samples were kept at 4° C until analysis. Samples were analyzed for phosphorous, nitrogen, dissolved oxygen, pH, COD, and TCH using methods described in Part III of this chapter.

**Part III: General Analytical Methods**

**3.7 Chemical Oxygen Demand (COD)**

**3.7.1 Approach**

The quantity of oxidant consumed by chemical constituents in a sample is known as COD (Clesceri, 1998). COD was analyzed using the Hach colorimetric kit for COD (mg/L) Method 8000 for water, wastewater, and seawater and the Hach DR/2000 spectrophotometer. Samples were analyzed in triplicate to assure read out accuracy. Tests were performed in LSU’s Aquatic and Toxicology Laboratory.

**3.7.2 Sample Preparation**

Water samples were homogenized for 2 minutes to ensure the distribution of solids and improve reproducibility. Dilutions of 10:1 and 50:50 were prepared with sample water and deionized (DI) water to improve accuracy. A vial containing the water sample with no dilution was also prepared. Two mL of sample water was added to the COD Digestion Reagent Vial provided by Hach. A blank was prepared by adding 2 mL of DI water to a COD Digestion Reagent Vial. The vials were re-capped and inverted gently several times to mix the contents. The vials were placed in the COD Reactor, preheated to 150° C, for 2 hours to allow for complete digestion. After the two hours had passed, the vials were inverted several times while
warm and allowed to cool to room temperature before being analyzed.

3.7.3 COD Analysis

The COD program number 435 was entered into the DR/2000 Spectrophotometer and the wavelength was adjusted to 620 nm. The COD vial containing the blank sample was wiped clean of fingerprints and other marks and then placed into the COD Vial Adapter and into the spectrophotometer in order to tare the instrument. The sample vials were placed in the spectrophotometer and the reading appeared in the display screen if the COD was between 0 and 1,500 mg/l.

3.8 Total Chromatographic Hydrocarbons (TCH)

3.8.1 Approach

Samples were placed in 200 mL sterile bottles and kept at 4°C until liquid-liquid extraction was performed according to EPA Method 3510C. A Modified EPA Method SW846-8270 was used to determine the concentration of Polycyclic Aromatic Hydrocarbons (PAH) and nC_{10}-nC_{35} alkanes using a gas chromatograph containing the separation column specific for the compounds in the petrol-sample and proper temperature settings (USEPA Method 8270C, 1996). The mass spectrometer, which utilizes the charge-to-mass ratio and ions produced by an electrical discharge or chemical process to compute a chromatograph, was operated in a Selected Ion Monitoring mode (SIM) (Manahan, 2000). Concentrations of 72 analytes, including surrogate and internal standards, are analyzed using the modified Method SW846-8270 (Table 3.1). Tests were performed in LSU’s Extractions and Analytical Laboratories.

3.8.2 Liquid-Liquid Extraction

Samples were prepared using Separatory Funnel Liquid-Liquid Extraction, EPA Method 3510C. The method was performed under the supervision of a trained analyst, Buffy M. Ashton, Response and Chemical Assessment Team, Department of Environmental Studies, LSU.
Surrogates were chosen based on Subchapter J of the Code of Federal Regulations—Superfund, Emergency Planning, and Community Right-to-Know Program, Part 300—National Oil and Hazardous Substances Pollution Contingency Plan—Appendix C (USEPA, 2000).

The full 200 mL of stored sample were placed in a 500 mL separatory funnel. Dichloromethane (DCM) was used to extract the organic constituents from the sample water. DCM was added to the separatory funnel containing the water sample at a volume of 20 ml. Before shaking the sample, 1 mL of surrogate is added containing 100 µg/mL Phenanthrene-d10 and 100 µg/mL 5-alpha Androstane. The sample was then gently mixed to combine all constituents. Initial venting was done immediately after shaking the separatory funnel due to the excessive pressure rapidly produced by DCM. The mix rested in the separatory funnel until separation occured between the organic and water layers. The organic, or bottom layer, is slowly released from the separatory funnel and flows through a .45 µm filter containing anhydrous sodium sulfate, which acts as a drying agent, allowing only the DCM and organic compounds from the sample to pass into the 250 mL round bottom collecting flask. The process of adding 20 mL of DCM, shaking, and filtration is repeated twice more for each sample. To assure safety, the aforementioned process should be performed under a fume hood due to the extreme volatility of DCM.

The round bottom flask containing the organic compounds was attached to a rotovap with the water temperature adjusted to 45° C, the boiling point of DCM. When all but approximately 1 mL of sample had evaporated into the DCM collecting flask attached to the rotovap, the round bottom glass containing the remaining 1 mL of sample was removed from the rotovap. The remaining portion, or organic portion, of the sample was pipetted into 1.5 mL glass vials with polytetrafluorethylene (PTFE)-lined crimp tops. Ten µL of internal standard containing 1000 µg/mL each of Naphthalene-d8, Acenaphthen-d10, Chrysene-d12, and Perylene-23
d12 was added to the sample vials, which were then capped. The samples were then ready for GC/MS analysis.

### 3.8.3 Gas Chromatography/Mass Spectroscopy

The gas chromatograph (GC), Model 5890 Hewlett Packard and the 5972 Series Hewlett Packard Mass Selective Detector (MSD) were calibrated using a 5-point calibration system in accordance with Modified EPA Method SW846-8270 Subsection 5.5 (USEPA GC/MS, 1996). Prior to beginning the calibration, the oven temperature was adjusted to 200° C to tune the MS. Also, the appropriate method was loaded onto the computer attached to the MS before calibration began. Samples were loaded onto the automatic sampler and were then injected into the GC, which has a 30m x 0.25 mm ID 0.25 µm film thickness silicone-coated fused-silica capillary column. On this particular instrument, the column is a Rtx-5. Sample run time was 88 minutes per sample. The oven temperature programming for the entire processed dropped from the 200° C tuning temperature to 55° C and held for 3min. The temperature then increased to 300° C at 0.50° C/min. The injector and MS interface temperature for both GC/MS methods was set at 250 and 280° C respectively.

The ChemStation Data Analysis Program was utilized to integrate and quantitate the target analysis to ensure accuracy. Analytes were identified using retention times and mass spectral data. Integration of each analyte of interest was manually checked for each sample and re-integrated.

### 3.8.4 Calculations and Quality Assurance/Quality Control (QA/QC)

The surrogate and internal standards used were composed of hydrocarbons not typical to the aquatic environment being tested so as not to interfere with sample analysis. Sample findings were acceptable if surrogate concentration fell within a 60-120% recovery range. A DCM blank
was utilized before and after each set of extracted samples to insure that there was no contamination.

Chromatographs must be translated from response factors into concentration based units, such as ng/mg or ng/mL. An excel spreadsheet had been formatted prior to GC/MS analysis utilizing the following equations:

**Calculation of Relative Response Factor**

\[
RRF = \frac{A_x \times C_{is}}{A_{is} \times C_x}
\]

Where:
- \(A_x\) = area of analyte in calibration standard
- \(C_{is}\) = concentration of the internal standard (ng)
- \(A_{is}\) = area of the internal standard
- \(C_x\) = concentration of calibration standard (ng)

**Calculation of Concentrations of Analytes in Sample**

\[
[C] \ (\text{ng/mg or ng/mL}) = \frac{A_x \times I_x \times V_{\text{fin}} \times 1000 \times \text{DF}}{A_{is} \times \text{RRF} \times V_i \times M \ or \ V_{\text{ini}}}
\]

Where:
- \([C]\) = concentration
- \(A_x\) = area/target response of analyte
- \(I_x\) = amount of internal standard injected (ng)
- \(V_{\text{fin}}\) = final volume of the total extract (mL)
- 1000 = conversion factor (1000 ng in a µl)
- \(\text{DF}\) = dilution factor
- \(A_{is}\) = area/target response of internal standard
- \(\text{RRF}\) = average relative response of internal standard
- \(V_i\) = volume of sample injected (µL)
Calculation of Surrogate Standard Recovery

\[ [C]_{\text{SS}} \text{ (ng/mg or ng/mL)} = \frac{V_{\text{SS}} \times C_{\text{SS}}}{M \text{ or } V_{\text{ini}} \times 1000} \]

Where:

- \([C]_{\text{SS}}\) = concentration of surrogate standard
- \(V_{\text{SS}}\) = volume of surrogate standard added to sample (mL)
- \(C_{\text{SS}}\) = concentration of surrogate standard (µg/mL)
- \(M\) = mass of sample (mg)
- \(V_{\text{ini}}\) = initial volume of sample (mL)
- 1000 = conversion factor

3.9 Salinity

3.9.1 Approach

Salinity of the production water before and after treatment was analyzed in order to determine the adequacy of the Reverse Osmosis (RO) system in decreasing the ionic content of the water.

3.9.2 Sample Analysis

Salinity was assessed in grams per one-hundred grams (g/00) using an Atago Hand Refractometer Model No. S-28E. The S-28E measures salt concentration as sodium chloride from 0-28.0 %. A sterile TenSette® Pipet was used to place three drops of the sample water on the plate of the refractometer. Samples were read through the view finder and recorded as g/00 NaCl.

3.10 Nutrient Analysis

3.10.1 Approach
To assure optimal living conditions for the bacteria, nutrients were added to the bioreactors. Nutrients were analyzed using the Hach colorimetric test kits and DR/2000 spectrophotometer. Total nitrogen was measured as mg/L NO₃⁻N using the Nitrate, High Range Test ‘N Tube™ Method 10020 for water and wastewater. Total Phosphorous was measured as mg/L PO₄³⁻ using the Phosphorous, HR, Test ‘N Tube™ Method 10127 for water and wastewater.

3.10.2 Total Nitrogen

One mL of samples was added to a Nitra Ver X Reagent A Test’N Tube. The contents of one NitriVer X Reagent B foil packet were added to the vial. The cap was replaced on the test vial and inverted 10 times to mix. After a 5 minute reaction the presence of nitrogen produced a yellow color in the test vials. A blank was prepared by adding 2 mL of DI water to a Nitra Ver X Reagent A Test ‘N Tube and following the same steps as those used in preparing the sample vial.

The Nitrate, High Range Test ‘N Tube program number 344 was entered into the DR/2000 Spectrophotometer and the wavelength was adjusted to 410 nm. The NitraVer X Reagent vial containing the blank sample was wiped clean of fingerprints and other marks and then placed into the COD Vial Adapter and into the spectrophotometer in order to tare the instrument. The sample vials were placed in the spectrophotometer and the reading appeared in the display screen as 0 to 30 mg/L NO₃⁻-N.

3.10.3 High Range Total Phosphorous

A TenSette® Pipet was used to add 5 mL of sample to a Total Phosphorus Test ‘N Tube vial. An entire Potassium Persulfate foil packet was added to the vial and shaken to dissolve. The vials were placed in a COD reactor at 150° C for 30 minutes. Once the reaction period was complete, the vials were placed in a test tube rack until they cool to room temperature (18-25° C). A TenSette® Pipet was used to add 2 mL of 1.54 N sodium hydroxide to each vial. A
polyethylene dropper was used to add 0.5 mL of Molybdoanadate Reagent to each vial. The vial was re-capped and inverted to mix. A seven minute reaction was allowed to take place.

The Phosphorous, HR, Test ‘N Tube program number 541 was entered into the DR/2000 Spectrophotometer and the wavelength was adjusted to 420 nm. The Total Phosphorous Test ‘N Tube vial containing the blank sample was wiped clean of fingerprints and other marks and then placed into the COD Vial Adapter and into the spectrophotometer in order to tare the instrument. The sample vials were placed in the spectrophotometer and the reading appeared in the display screen as 0 to 100 mg/L PO$_4^{3-}$.

**3.11 Dissolved Oxygen (DO)**

**3.11.1 Approach**

Dissolved oxygen (DO) was analyzed for the bench top laboratory screening study only, due to the nature of test parameters. DO is the measure of gaseous oxygen dissolved in an aqueous solution. To obtain an adequate reading, DO must be measured immediately after the sample has been collected.

**3.11.2 Sample Analysis**

A sample was collected from the bench top reactors and analyzed on a Yellow Springs Instrument’s Dissolved Oxygen Meter, Model No. 55. Results were documented to assure proper DO levels for bacterial survival.

**3.12 pH**

**3.12.1 Approach**

The measure of hydrogen ion activity in a sample is termed pH. A drastic spike or decline is problematic for organisms within the environment being sampled. Optimal pH conditions for bacterial survival in the IMBRs are between 6 and 8.

**3.12.2 Sample Analysis**
The Orion pH meter Model No. 210A was used for determining pH. An autocalibration using two buffers was performed using pH buffers of 4 and 7 and a temperature setting of 24° C. Sample water was poured into a 50 mL beaker using at a volume of 40 mL. The Orion pH meter probe was suspended in the sample water. The pH reading was recorded when “ready was displayed (Orion, 1993).

Table 3.1 GC/MS Analytes.

<table>
<thead>
<tr>
<th>Alkane Analytes</th>
<th>Aromatic Analytes</th>
<th>Internal Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>nC-10 Decane</td>
<td>Naphthalene</td>
<td>Naphthalene-d8 IS #1</td>
</tr>
<tr>
<td>nC-11 Undecane</td>
<td>C1-C4 Naphthalene</td>
<td>Acenaphthene-d10 IS #2</td>
</tr>
<tr>
<td>nC-12 Dodecane</td>
<td>Fluorene</td>
<td>Chrysene-d12 IS #3</td>
</tr>
<tr>
<td>nC-13 Tridecane</td>
<td>C1-C3 Fluorene</td>
<td></td>
</tr>
<tr>
<td>nC-14 Tetradecane</td>
<td>Dibenzothiophene</td>
<td>Surrogates</td>
</tr>
<tr>
<td>nC-15 Pentadecane</td>
<td>C1-C3 Dibenzothiophene</td>
<td>Phenanthrene-d10 SS #1</td>
</tr>
<tr>
<td>nC-16 Hexadecane</td>
<td>Phenanthrene</td>
<td></td>
</tr>
<tr>
<td>nC-17 Heptadecane</td>
<td>C1-C4 Phenanthrene</td>
<td>Phenanthrene-d10 SS #1</td>
</tr>
<tr>
<td>Pristane</td>
<td>Anthracene</td>
<td>Phenanthrene-d10 SS #2</td>
</tr>
<tr>
<td>nC-18 Octadecane</td>
<td>Fluoranthene</td>
<td></td>
</tr>
<tr>
<td>Phytane</td>
<td>Pyrene</td>
<td></td>
</tr>
<tr>
<td>nC-19 Nonadecane</td>
<td>C1-C4 Pyrene</td>
<td></td>
</tr>
<tr>
<td>nC-20 Eicosane</td>
<td>Benzo (a) Anthracene</td>
<td></td>
</tr>
<tr>
<td>nC-21 Heneicosane</td>
<td>Chrysene</td>
<td></td>
</tr>
<tr>
<td>nC-22 Docosane</td>
<td>C1-C4 Chrysene</td>
<td></td>
</tr>
<tr>
<td>nC-23 Tricosane</td>
<td>Benzo (b) Fluoranthene</td>
<td></td>
</tr>
<tr>
<td>nC-24 Tetracosane</td>
<td>Benzo (k) Fluoranthene</td>
<td></td>
</tr>
<tr>
<td>nC-25 Pentacosane</td>
<td>Benzo (e) Pyrene</td>
<td></td>
</tr>
<tr>
<td>nC-26 Hexacosane</td>
<td>Benzo (a) Pyrene</td>
<td></td>
</tr>
<tr>
<td>nC-27 Heptacosane</td>
<td>Perylene</td>
<td></td>
</tr>
<tr>
<td>nC-28 Octacosane</td>
<td>Indeno (1,2,3 - cd) Pyrene</td>
<td></td>
</tr>
<tr>
<td>nC-29 Nonacosane</td>
<td>Dibenzo (a,h) anthracene</td>
<td></td>
</tr>
<tr>
<td>nC-30 Triacontane</td>
<td>Benzo (g,h,i) perylene</td>
<td></td>
</tr>
<tr>
<td>nC-31 Hentriacontane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nC-32 Dotriacontane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nC-33 Tritriacontane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nC-34 Tetratriacontane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nC-35 Pentatriacontane</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Part I: Multiple Sources Well-Head Remediation Strategy

4.1 Laboratory Screening Study Results

Samples (40 mL) were collected aseptically directly from the laboratory reactors and diluted at 10:1 volume to volume ratio to remain on the linear range of Beer’s law following an initial analysis of a time zero sample from Lake Rosa in Parachute, CO. The COD method proved to be disappointing. COD is a traditional waste water analytical tool for assessing contaminant loading in industrial waste streams. However, production waste water posts 3 additional challenges: 1) high salinity; 2) 1-3 µm diameter suspended solids; and 3) unique to this process, bleeding microbial biomass exiting the IMBRs.

As shown in Table 4.1 COD treatment of production water from Lake Rosa was initiated using Biocarrier #1. Water was taken directly from the IMBR into 40 mL sample vials and stored at 4° C prior to COD analysis (See procedures described in Section 3.7). Concentrations shown in Table 4.1 represent an average taken from the COD performed in triplicate for each sample. The results show a reduction in COD concentration of 31.5 mg/L/h over a 48 hour period.

Table 4.1 48 hour COD comparison from laboratory IMBR using raw water and Biocarrier #1.

<table>
<thead>
<tr>
<th>Chemical Oxygen Demand (COD)*</th>
<th>Raw Water Sample - Biocarrier #1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (h)</td>
<td>0</td>
</tr>
<tr>
<td>10:1 Dilution</td>
<td></td>
</tr>
<tr>
<td>204</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td></td>
</tr>
<tr>
<td>168</td>
<td></td>
</tr>
<tr>
<td>172</td>
<td></td>
</tr>
<tr>
<td>164</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
</tr>
<tr>
<td>183</td>
<td></td>
</tr>
<tr>
<td>146</td>
<td></td>
</tr>
<tr>
<td>163</td>
<td></td>
</tr>
<tr>
<td>181</td>
<td></td>
</tr>
<tr>
<td>166</td>
<td></td>
</tr>
<tr>
<td>169</td>
<td></td>
</tr>
<tr>
<td>173</td>
<td></td>
</tr>
<tr>
<td>164</td>
<td></td>
</tr>
<tr>
<td>202</td>
<td></td>
</tr>
<tr>
<td>188</td>
<td></td>
</tr>
<tr>
<td>147</td>
<td></td>
</tr>
<tr>
<td>162</td>
<td></td>
</tr>
<tr>
<td>328</td>
<td></td>
</tr>
<tr>
<td>178</td>
<td></td>
</tr>
<tr>
<td>174</td>
<td></td>
</tr>
<tr>
<td>173</td>
<td></td>
</tr>
<tr>
<td>167</td>
<td></td>
</tr>
<tr>
<td>202</td>
<td></td>
</tr>
<tr>
<td>189</td>
<td></td>
</tr>
<tr>
<td>147</td>
<td></td>
</tr>
<tr>
<td>162</td>
<td></td>
</tr>
<tr>
<td>COD mg/L</td>
<td>2,380</td>
</tr>
</tbody>
</table>

*Data represents mean of triplicate aliquots.
Table 4.2 shows the COD of the bench top IMBR containing water from the collection tanker in Parachute, CO, which had undergone gravity separation. The water was collected at the holding tanker at the EnCana site in Parachute, CO. Again Biocarrier #1 was used as the bacterial inocula source. Water was taken directly from the IMBR into 40 mL sample vials and stored at 4° C prior to COD analysis.

The COD concentrations shown in Table 4.2 represent an average taken from the COD performed in triplicate for each sample. Gravity-separated water showed a significant improvement in COD reduction as compared to raw water. The reduction rate of COD was 83.6 mg/L/h for 48 hours.

Table 4.2 48 hour COD comparison from laboratory IMBR using the gravity-separated production water and Biocarrier #1.

<table>
<thead>
<tr>
<th>Chemical Oxygen Demand (COD)*</th>
<th>Gravity-Separated Water Sample - Biocarrier #1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (h)</td>
<td>0</td>
</tr>
<tr>
<td>10:1 Dilution</td>
<td>250</td>
</tr>
<tr>
<td>10:1 Dilution</td>
<td>226</td>
</tr>
<tr>
<td>10:1 Dilution</td>
<td>237</td>
</tr>
<tr>
<td>COD mg/L</td>
<td>2,380</td>
</tr>
</tbody>
</table>

*Data represents the mean of triplicate aliquots.

Table 4.3 shows the COD of the bench top IMBR containing water from the collection tanker in Parachute, CO. Biocarrier #2 was used as the bacterial inocula source. Water was taken directly from the IMBR into 40 mL sample vials and stored at 4° C prior to COD analysis. The COD concentrations shown in Table 4.3 represent an average taken from the COD performed in triplicate for each sample. Biocarrier #2 showed a slight improvement in COD reduction as compared to Biocarrier #1. The reduction rate of COD was 85.1 mg/L/h for 48 hours.
**Table 4.3** 48 hour COD comparison from laboratory IMBR using tanker/gravity-separated production water and Biocarrier #2

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>24</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:1 Dilution</td>
<td>246</td>
<td>229</td>
<td>131</td>
<td>139</td>
<td>123</td>
<td>115</td>
<td>115</td>
<td>60.1</td>
<td>42.1</td>
</tr>
<tr>
<td></td>
<td>253</td>
<td>229</td>
<td>131</td>
<td>136</td>
<td>123</td>
<td>116</td>
<td>118</td>
<td>62.0</td>
<td>42.0</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>230</td>
<td>131</td>
<td>140</td>
<td>123</td>
<td>116</td>
<td>112</td>
<td>62.5</td>
<td>42.2</td>
</tr>
</tbody>
</table>

COD mg/L | 2,460 | 2,290 | 1,310 | 1,380 | 1,230 | 1,160 | 1,150 | 615  | 421  |

*Data represents the mean of triplicate aliquots.

The pre-treated production water showed a much higher decrease in COD as compared to water pulled directly from Lake Rosa. Using semi-continuous batch mode (See Table 4.4), the net COD reduction rates were $947 \pm 1,340$ mg/L/day for raw water and $1,820 \pm 598$ mg/L/day for gravity-separated water. The differences between remediation rates are shown in Figure 4.1. Visual observations indicated that there were fewer solids in the gravity-separated water than the raw water. So therefore, in subsequent field pilot studies in-line filtration systems were used to protect the biocarrier from solids build-up.

**Table 4.4** Mean COD reduction (mg/L/day) of raw water and gravity-separated water: Semi-continuous batch mode.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Raw Water Sample (mg/L COD)</th>
<th>Gravity-Separated Sample (mg/L COD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>3,780 ± 1,200</td>
<td>4,830 ± 2,860</td>
</tr>
<tr>
<td>24h</td>
<td>3,990 ± 1,770</td>
<td>3,430 ± 2,310</td>
</tr>
<tr>
<td>48h</td>
<td>1,890 ± 382</td>
<td>1,190 ± 1,160</td>
</tr>
</tbody>
</table>

Net mg/L COD reduction per day | 947 ± 1,340 | 1,820 ± 598
Figure 4.1 COD of raw water and gravity-separated water using semi-continuous batch mode.

Biocarrier #2 showed a slightly higher decrease in COD as compared to Biocarrier #2.

Using semi-continuous batch mode (See Table 4.5), the net COD reduction rates were 1,820 ± 598 mg/L/day for Biocarrier #1 and 2,360 ± 307 mg/L/day for Biocarrier #2. The differences between remediation rates are shown in Figure 4.2.

Table 4.5 Mean COD reduction (mg/L/day) of Biocarrier #1 and Biocarrier #2: Semi-batch mode for gravity-separated.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Biocarrier #1 (mg/L COD)</th>
<th>Biocarrier #2 (mg/L COD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>4,830 ± 2,860</td>
<td>5,660 ± 2,730</td>
</tr>
<tr>
<td>24h</td>
<td>3,430 ± 2,310</td>
<td>3,080 ± 2,310</td>
</tr>
<tr>
<td>48h</td>
<td>1,190 ± 1,160</td>
<td>940 ± 735</td>
</tr>
<tr>
<td>Net mg/L COD reduction per day</td>
<td>1,820 ± 598</td>
<td>2,360 ± 307</td>
</tr>
</tbody>
</table>
COD Semi-Continuous Batch Comparison of Raw Water and Gravity Separated Water
Hach DR/2000
Hach colorimetric kit for COD (mg/L) Method 8000 for water, wastewater, and seawater

![Graph showing COD comparison](image)

**Figure 4.2** COD of Biocarrier #1 and Biocarrier #2 using semi-continuous batch mode.

### 4.2 Field Pilot Studies for Continuous Treatment of Multiple-Source Well-Head Pit Production Water

EnCana Oil and Gas Company is obligated under the state of Colorado legal statutes to report treated production water using GC/MS methods (See Section 3.8). Multiple samples were aseptically collected and shipped to LSU March 3 through 23, 2006 from the field pilot plant in Parachute, CO (See Part I of Chapter 3). Figure 4.3 shows the Total Ion Chromatogram (TIC) of the Lake Rosa production water (See Table 3.1 for a complete list of analytes, internal standards, and surrogate standards). Total Chromatographic Hydrocarbons (TCH) was calculated for each sample by adding the number of nC\text{10} through nC\text{35} alkanes to the number of aromatics found in the sample; thus, a typical raw water TCH concentration was found to be 32,700 ng/mL.
Influent and effluent samples were analyzed in the same manner as the Lake Rosa sample. Figures 4.4 and 4.5 are representative of influent and biotreated effluent TICs. The TCH concentration for the influent sample was 45,800 ng/mL; the IMBR effluent sample showed a TCH concentration to 4,210 ng/mL. A percent removal of 95.2% was realized for a continuous flow rate of 6.50 ± 1.80 L/min. (See Part I of the appendix for complete additional TCH data of influent and effluent treatment.)

The influent concentrations in Table 4.6 represent the mean of samples collected prior to remediation. The total concentration of nC_{10} through nC_{35} alkanes, C_{al}, in the influent sample was 29,900 ± 8,980 ng/mL. The concentration of total aromatics, C_{ar}, in the influent sample was 276 ± 152 ng/mL; thus, influent TCH was 30,200 ± 9,060 ng/mL. The effluent concentrations represent the mean of samples collected from the end of the IMBR system. The C_{al} in the effluent sample was 1,450 ± 1,850 ng/mL and the C_{ar} totaled 11.5 ± 8.30 ng/mL yielding a TCH of 1,460 ± 1,850 ng/mL. Following biological treatment, a 95.2% reduction occurred over the 20d sampling period; Figure 4.3 is representative of this reduction.

4.3 Discussion

The experiment was designed to determine if the proposed IMBR system described in Part I of Chapter 3 would be beneficial for the remediation of production water at the EnCana Site—Lake Rosa—in Parachute, CO. Analysis was based on the hypothesis below:

\[ H_0: \mu_I = \mu_E \]
\[ H_E: \mu_I \neq \mu_E \]

Where:

\( \mu_I \) = Influent, or pre-treatment, samples

\( \mu_E \) = Effluent, or remediated, samples

\( H_E \) = Experimental hypothesis
The data indicated that there was a significant difference between the TCH concentration in the influent and effluent samples collected from the EnCana site (P < 0.05). Rejection of $H_0$ indicated that influent samples were not equal ($\mu_I \neq \mu_E$), meaning that the microbial treatment system adequately removed contaminants from the petroleum hydrocarbon-polluted water. The percent removal of TCH was consistently $\geq 90.0\%$ for all samples over the 20d sampling period yielding an average removal percentage of 95.2%. (See appendix for Quality Assurance/Quality Control.) Laboratory studies indicated that organic constituents of concern could be reduced at a kinetic rate of $1,230 \pm 398\ mg/L/h$ at the EnCana site. The proposal for a permanent production water remediation facility at the EnCana site is shown in Figure 4.7. The proposed system contains both micro- and ultra-filtration units, three Immobilized Microbe BioReactors, an equalization tank, backwash system, and Reverse Osmosis system to assure environmental quality parameters are met by the effluent water for reuse in agricultural irrigation systems.

Figure 4.3 Representative Lake Rosa sample Total Ion Chromatogram (TIC). The red arrows point toward extraction surrogates and internal standards (See Table 3.1 for a complete list).
**Figure 4.4** Representative influent sample TIC. The red arrows point toward extraction surrogates and internal standards.

**Figure 4.5** Representative effluent sample TIC. The red arrows point toward extraction surrogates and internal standards.
Table 4.6 Percent removal of petroleum hydrocarbons (ng/mg) using GC/MS Modified Method EPA 8270C for analysis of water samples taken from the EnCana site in Parachute, CO.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Influent (ng/mg)</th>
<th>Effluent (ng/mg)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>nC_{10}-nC_{35} Alkanes</td>
<td>29,900 ± 8,980</td>
<td>1,450 ± 1,850</td>
<td>95.2</td>
</tr>
<tr>
<td>Total Aromatics</td>
<td>276 ± 152</td>
<td>11.5 ± 8.30</td>
<td>95.8</td>
</tr>
<tr>
<td>Total Chromatographic Hydrocarbons</td>
<td>30,200 ± 9,060</td>
<td>1,460 ± 1,850</td>
<td>95.2</td>
</tr>
</tbody>
</table>

Figure 4.6 Total Chromatographic Hydrocarbon (TCH) Removal analysis using GC/MS Modified Method EPA 8270C.
Figure 4.7 Preliminary layout of treatment building for the EnCana drill pit in Parachute, CO.
Part II: Dispersed Field Well-Head Remediation Strategy

4.4 Field Pilot Studies for Continuous Treatment of Dispersed Field Well-Head Remediation Strategy

ConocoPhillips is obligated under the state of New Mexico legal statutes to report treated production water using GC/MS (See Section 3.8). Multiple samples were aseptically collected April 26-June 23, 2006 from the field pilot. Figure 4.8 shows the TIC of influent water (See Table 3.1 for a complete list of analytes, internal standards, and surrogate standards). TCH was calculated by adding the number of nC_{10} through nC_{35} alkanes to the number of aromatics found in the sample; thus, a typical influent TCH concentration was found to be 254 ng/mL. Biotreated effluent and RO effluent samples were also analyzed. Figures 4.9 and 4.10 are representative of IMBR and RO effluent. The TCH concentration for the IMBR effluent sample was 75 ng/mL; TCH for the RO effluent was 30 ng/mL. A percent removal of 37.3% was realized for a continuous flow rate of 6.5 ± 1.8 L/min. (See Part II of the appendix for additional TICs).

Figure 4.8 Representative influent sample Total Ion Chromatogram (TIC). The red arrows point toward extraction surrogates and internal standards (See Table 3.1 for a complete list).
**Figure 4.9** Representative IMBR effluent sample TIC, 18 May 2006. The red arrows point toward extraction surrogates and internal standards.

**Figure 4.10** Representative RO effluent sample TIC, 18 May 2006. The red arrows point toward extraction surrogates and internal standards.
The influent concentrations in Table 4.7 represent the mean of samples collected prior to remediation. The total concentration of nC_{10} through nC_{35} alkanes, C_{al}, in the influent sample was 141 ± 93.0 ng/mL. The concentration of total aromatics, C_{ar}, in the influent sample was 35.1 ± 24.4 ng/mL; thus, the TCH in the influent sample from the ConocoPhillips drill pits, collectively, was 214 ± 117 ng/mL. The IMBR Effluent concentrations represent the mean of samples collected from the end of the IMBR system. The C_{al} in the IMBR effluent sample was 78.8 ± 35.5 ng/mL and the C_{ar} totaled 22.2 ± 8.20 ng/mL yielding a TCH concentration of 101 ± 37.3 ng/mL. The RO Effluent sample represents the mean of samples collected from the end of the RO system. The C_{al} in the RO effluent sample was 44.0 ± 42.4 ng/mL and the C_{ar} totaled 15.0 ± 1.40 ng/mL yielding a TCH concentration of 59.0 ± 41.0 ng/mL. Following biological treatment coupled with the RO membrane desalination system a 72.5% reduction occurred.

Analysis of field samples post-RO system treatment revealed a decrease in salinity of approximately 2.08 mg/L/h at the continuous flow rate of 7.60 ± 0.04 L/min. Percent removal revealed a 25.0% decrease in salinity concentrations for the permeate collected from the pilot study at the ConocoPhillips drill pits in the San Juan basin of New Mexico. Table 4.2 shows the mean salinity concentration for all samples received and analyzed using procedures described in Section 3.9.

Table 4.7 Percent removal of petroleum hydrocarbons (ng/mg) using GC/MS Modified Method EPA 8270C for analysis of water samples taken from the ConocoPhillips site in Farmington, NM.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Influent</th>
<th>Effluent</th>
<th>% Removal</th>
<th>RO Effluent</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>nC_{10}-nC_{35} Alkanes</td>
<td>141 ± 93.0</td>
<td>78.8 ± 35.5</td>
<td>44.4</td>
<td>44.0 ± 42.4</td>
<td>69.0</td>
</tr>
<tr>
<td>Total Aromatics</td>
<td>35.1 ± 24.4</td>
<td>22.2 ± 8.20</td>
<td>36.9</td>
<td>15.0 ± 1.40</td>
<td>57.3</td>
</tr>
<tr>
<td>Total Chromatographic Hydrocarbons</td>
<td>214 ± 117</td>
<td>101 ± 37.3</td>
<td>52.9</td>
<td>59.0 ± 41.0</td>
<td>72.5</td>
</tr>
</tbody>
</table>
**Figure 4.11** Total Chromatographic Hydrocarbon (TCH) Removal analysis using GC/MS Modified EPA Method EPA 8270C.

**Table 4.8** Percent reduction of salinity (g/100g total chlorides) using the Asago Hand Refractometer.

<table>
<thead>
<tr>
<th></th>
<th>Influent Mean Value</th>
<th>RO Effluent Mean Value</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity (g/100g)</td>
<td>1.70 ± 0.26</td>
<td>1.20 ± 0.04</td>
<td>25.0 ± 0.04</td>
</tr>
</tbody>
</table>

4.5 Discussion

The experiment was designed to determine if the proposed IMBR system described in Part II of Chapter 3 would be beneficial for the remediation of production water at the ConocoPhillips Sites in the San Juan Basin of New Mexico. Analysis was based on the hypothesis below:

\[ H_0: \mu_I = \mu_E \]
\[ H_E: \mu_I \neq \mu_E \]
Where:

\[ \mu_I = \text{Influent, or pre-treatment, samples} \]

\[ \mu_E = \text{RO Effluent, or microbial remediated and desalinated, samples} \]

\[ H_E = \text{Experimental hypothesis} \]

The data indicated that there was a significant difference between the TCH concentration in the Influent and RO Effluent samples collected from the EnCana site (\( P < 0.05 \)). Rejection of \( H_0 \) indicated that the microbial treatment system adequately removed contaminants from the petroleum hydrocarbon-polluted water. The average TCH removal percentage for all of the drill pits was 72.5\%. Laboratory studies indicated that organic constituents of concern could be reduced at a kinetic rate of 140 ± 120 mg/L/h based on ConocoPhillips drill pit analysis. A lower percent removal was noted at the ConocoPhillips site, as compared to the EnCana site, due to the shorter remediation time allotted at each separate drill pit in New Mexico. (See Part III of the appendix for Quality Assurance/Quality Control.) Although salinity had decreased by 25.0\%, no significant difference was observed (\( P > 0.05 \)) between the influent and RO effluent field pilot samples. The pilot RO system was unable to desalinate the production water to the full potential of the system due to membrane blinding by 0.50 to 50.3 \( \mu \)m particulates (Table 4.9). Particles with a diameter of < 1.00 \( \mu \)m made up 97.9\% of the particulates found in the treated water. In order to address membrane blinding, an ultra filtration system will be utilized in the permanent facilities. The proposal for a permanent production water remediation facility at the ConocoPhillips sites is shown in Figure 4.12. The proposed system contains micro- and ultra-filtration units, two Immobilized Microbe BioReactors, an equalization tank, backwash system, and Reverse Osmosis system to assure environmental quality parameters are met by the effluent water for reuse in agricultural irrigation systems.
Table 4.9 Particle count analysis.

<table>
<thead>
<tr>
<th>Particle Diameter (microns)</th>
<th>Particles/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>15,600,000</td>
</tr>
<tr>
<td>0.75</td>
<td>1,630,000</td>
</tr>
<tr>
<td>0.80</td>
<td>1,110,000</td>
</tr>
<tr>
<td>0.90</td>
<td>516,000</td>
</tr>
<tr>
<td>0.99</td>
<td>346,000</td>
</tr>
<tr>
<td>1.10</td>
<td>263,000</td>
</tr>
<tr>
<td>2.00</td>
<td>106,000</td>
</tr>
<tr>
<td>4.98</td>
<td>30,900</td>
</tr>
<tr>
<td>10.0</td>
<td>8,800</td>
</tr>
<tr>
<td>15.0</td>
<td>2,810</td>
</tr>
<tr>
<td>20.0</td>
<td>1,150</td>
</tr>
<tr>
<td>25.0</td>
<td>546</td>
</tr>
<tr>
<td>50.2</td>
<td>101</td>
</tr>
<tr>
<td>75.0</td>
<td>0.00</td>
</tr>
<tr>
<td>100</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Figure 4.12 Treatment building layout for the ConocoPhillips drill pits in New Mexico.
CONCLUSIONS

5.1 Summary of Findings

The hypothesis for both the EnCana and ConocoPhillip projects was that coal bed methane formation drilling water can be subjected to a biological treatment process so as to be acceptable for agricultural reuse using Immobilized Microbe BioReactors (IMBR). The ConocoPhillips project also included post-remediation treatment of brine water using a Reverse Osmosis (RO) membrane. Application of the pilot system at the drill pits was developed based on laboratory screening studies, which showed an 85.1 mg/L/hour decrease in Chemical Oxygen Demand based on a gravity-separated water sample and Biocarrier #2 bacteria.

Performance of the pilot system was measured by percent removal of Total Chromatographic Hydrocarbons (TCH). The EnCana site contained more asphaltic compounds because both crude oil and natural gas are drawn from the CBMFs in Parachute, CO. Due to the rejection of the null hypothesis (H₀) based on the Student-T test, a significant difference was recorded between the influent and effluent samples for the EnCana and ConocoPhillips sites. The resulting percent removal of TCH for the EnCana project was 96.0%. The average percent removal of TCH at the New Mexico drill pits was 63.3%. Reduction of TCH was 1,231.0 ± 398.6 mg/L/hour for the EnCana project and 139.5 ± 119.5 mg/L/hour for the ConocoPhillips project. Based on water quality standards found under Evaluation/Corrective Action Program (RECAP), Total Petroleum Hydrocarbons (TPH) concentrations in remediated water to be utilized in soil should be ≤ 65 ppm (DEQ, 2003). The water from the EnCana site was remediated to an effluent mean of 1,456 ± 1,852 ppm, which does not show reusability; however, the proposal for the EnCana facility includes larger bed reactors, which, in turn, will produce water with constituent concentrations ≤ 65 ppm. The ConocoPhillips drill pits, which were
smaller and held lower TCH concentrations initially, showed a mean effluent concentration of 59
± 41 ppm, which was in accordance with reusability standards in soil set forth by the Department
of Environmental Quality (DEQ). Salinity was reduced by 2 mg/kg/h total chlorides with an
effluent salinity concentration of 120 ppm. A total chloride concentration ≤ 70 ppm is generally
safe for all plants; as total chlorides increase, the less stable crops tend to be effect with severe
problems noticed at ≥ 350 ppm (Bauder et al., 2006). Before reuse, a salinity concentration of ≤
70 ppm would be preferred to prevent plasma lysing in plants and salinization in such arid
regions.

The results indicated that the proposed water remediation systems shown in Figure 4.7
and 4.12 would be an efficacious method for remediating production water drill pits associated
with natural gas excavation of petroleum hydrocarbons. Although salinity did not show a
significant decrease, continued analysis of desalinated production water using RO membranes
should be considered before rejecting the use of a RO system as the desalination technology for
the proposed production water remediation system. For subsequent testing associated with
agricultural reuse, see Section 5.2.

5.2 Recommendations for Future Work

Areas of future work include:

1. Obtaining proper permits for installation of permanent water remediation
facilities at natural gas drilling pits throughout the Greater Rocky Mountain
Region (GRMR)

2. Consistent monitoring of both influent and effluent water at the permanent
facilities to ensure adequate systems operation and bacterial metabolism.

3. Toxicity testing of vegetation, possibly a freshwater algal species, to determine
reusability of water for agricultural use.
BIBLIOGRAPHY


Committee to Review the Desalination and Water Purification Technology Road Map (CRDWPT), Water Science and Technology Board (WSTB), and Division on Earth and Life Studies (DELS). 2005. Review of the Desalination and Water Purification Technology Road Map. National Research Council of the National Academies (NRCNA) and the National Academy of Science (NAS). ISB No. 0-309-53043-1 (PDF).


APPENDIX: TOTAL ION CHROMATOGRAMS

Part I: EnCana Oil and Gas Co. Site—Parachute, CO

**Figure A.1** March 21, 2006 influent sample Total Ion Chromatogram (TIC).

**Figure A.2** March 21, 2006 effluent sample TIC.

Note: Red arrows point toward extraction surrogates and internal standards.
Figure A.3 March 22, 2006 influent sample TIC.

Figure A.4 March 22, 2006 effluent sample TIC.
Figure A.5 March 23, 2006 influent sample TIC.

ABUNDANCE 0-200,000
TCH = 29,300 ng/ml

Figure A.6 March 23, 2006 effluent sample TIC.

ABUNDANCE 0-200,000
TCH = 239 ng/ml
Part II: New Mexico Sites

Figure A.7 April 26, 2006 influent sample from Farmington, NM TIC.

Figure A.8 April 26, 2006 effluent sample from Farmington, NM TIC.

Note: Red arrows point toward extraction surrogates and internal standards.
Figure A.9 May 19, 2006 influent sample from North Aztec, NM TIC.

Figure A.10 May 19, 2006 effluent sample from North Aztec, NM TIC.
Figure A.11 June 22, 2006 influent sample from Sample Pit 260-S, NM TIC.

Figure A.12 June 22, 2006 effluent sample from Sample Pit 260-S, NM TIC.
Figure A.13 June 23, 2006 influent sample from Sample Pit 260-S, NM TIC.

Figure A.14 June 23, 2006 IMBR effluent sample from Sample Pit 260-S, NM TIC.
**Figure A.15** June 23, 2006 RO system effluent sample from Sample Pit 260-S, NM TIC.
Part III: Quality Assurance/Quality Control for GC/MS Data

Below is a list of samples and the percent recovery of extraction surrogates Phenanthrene d-10 and 5-alpha Androstane. In order for data to be acceptable, surrogate recovery must be between 70 and 120% (See Section 3.8). Low percent recovery was frequently recorded in the EnCana and ConocoPhillips samples due to high emulsion and large amounts of particulate matter (See Table 4.9).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phenanthrene-d10 SS #1 (% Recovery)</th>
<th>5-alpha Androstane SS #2 (% Recovery)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Rosa (Figure 4.3)</td>
<td>7.90</td>
<td>7.70</td>
</tr>
<tr>
<td>03-09-06 Influent (Figure 4.4)</td>
<td>109</td>
<td>97.0</td>
</tr>
<tr>
<td>03-09-06 Effluent (Figure 4.5)</td>
<td>92.0</td>
<td>87.0</td>
</tr>
<tr>
<td>05-18-06 Influent (Figure 4.8)</td>
<td>73.0</td>
<td>70.0</td>
</tr>
<tr>
<td>05-18-06 IMBR Effluent (Figure 4.9)</td>
<td>37.0</td>
<td>44.0</td>
</tr>
<tr>
<td>05-18-06 RO Effluent (Figure 4.10)</td>
<td>50.0</td>
<td>43.0</td>
</tr>
<tr>
<td>03-21-06 Influent (Figure A.1)</td>
<td>56.0</td>
<td>50.0</td>
</tr>
<tr>
<td>03-21-06 Effluent (Figure A.2)</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>03-22-06 Influent (Figure A.3)</td>
<td>73.0</td>
<td>71.0</td>
</tr>
<tr>
<td>03-22-06 Effluent (Figure A.4)</td>
<td>119</td>
<td>116</td>
</tr>
<tr>
<td>03-23-06 Influent (Figure A.5)</td>
<td>85.0</td>
<td>80.0</td>
</tr>
<tr>
<td>03-23-06 Effluent (Figure A.6)</td>
<td>42.0</td>
<td>41.0</td>
</tr>
<tr>
<td>04-26-06 Influent (Figure A.7)</td>
<td>103</td>
<td>98.7</td>
</tr>
<tr>
<td>04-26-06 Effluent (Figure A.8)</td>
<td>86.0</td>
<td>74.0</td>
</tr>
<tr>
<td>05-19-06 Influent (Figure A.9)</td>
<td>42.0</td>
<td>40.0</td>
</tr>
<tr>
<td>05-19-06 Effluent (Figure A.10)</td>
<td>47.0</td>
<td>39.0</td>
</tr>
<tr>
<td>06-22-06 Influent (Figure A.11)</td>
<td>59.4</td>
<td>49.7</td>
</tr>
<tr>
<td>06-22-06 Effluent (Figure A.12)</td>
<td>59.5</td>
<td>50.0</td>
</tr>
<tr>
<td>06-23-06 Influent (Figure A.13)</td>
<td>37.4</td>
<td>30.8</td>
</tr>
<tr>
<td>06-23-06 IMBR Effluent (Figure A.14)</td>
<td>39.2</td>
<td>33.2</td>
</tr>
<tr>
<td>06-23-06 Effluent RO (Figure A.15)</td>
<td>32.7</td>
<td>26.0</td>
</tr>
</tbody>
</table>
VITA

Catherine Elizabeth Bishop—Cat—was born on August 3, 1983, in Ada, Oklahoma. She is the only child of Mr. Charles E. and Mrs. Mary Kay Bishop. Cat is soon to be married to Travis A. Isom. She earned a Bachelor of Science degree in biology from East Central University in 2001 and, having begun undergraduate research at the Robert S. Kerr Environmental Research Center, and Environmental Protection Agency Lab in Ada, Oklahoma, was appointed to a GS-7 position with the EPA for the summer of 2001. Cat is a candidate for the degree of Master of Science in environmental sciences, with a concentration in environmental toxicology, from Louisiana State University for the fall of 2006. After graduation she plans to pursue a career path that allows her to primarily work with water reclamation and other arenas that are beneficial to the health of the biosphere.