PERFORMANCE OF IRON ELECTROLYSIS FOR TRANSFORMATION OF TRICHLOROETHYLENE IN GROUNDWATER

A Dissertation Presented

By

Ali Ciblak

to

The Department of Civil and Environmental Engineering

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in the field of

Environmental Engineering

Northeastern University
Boston, Massachusetts

December 2015
ACKNOWLEDGMENTS

First of all, I would like to thank my advisor, Professor Akram N. Alshawabkeh, for providing me guidance, encouragement, and financial support during my graduate career. His endless knowledge and kind attitude were invaluable during my study.

I thank the dissertation committee members: Professor Thomas C. Sheahan, Professor Phillip Larese-Casanova and Professor Loretta Fernandez for their valuable contribution in this dissertation.

I would like to thank all my colleagues in the PROTECT Research Team. Special thanks to PROTECT Training Core, Professor Thomas Sheahan, Kristin Hinks, and Melanie Smith for providing opportunities to develop my career and for making PROTECT feel like a family. Special thanks to my colleagues Dr. Xuhui Mao and Dr. Kitae Baek, for their help in improving my electrochemistry knowledge. They have been helpful in every aspect of my research.

I would also like to thank the faculty and staff at the Department of Civil and Environmental Engineering for contributing to my knowledge and career. Special thanks to laboratory technicians Kurt Braun and Michael MacNeil for their technical support to fabricate the experimental setups for this study.
I would like to express my love and appreciation for my family: my mom Gullu, my dad Hasan, and my sister Seher for their unconditional love, encouragement, and support. Their existence has given me the extra push during the difficult time of this study, and I cannot express how lucky I am to have them in my life. Also, I would like to acknowledge my girlfriend Sarah Whitley for her support and patience during this study.

The work described in this dissertation is supported by Award Number P42ES017198 from the National Institute of Environmental Health Sciences. The content is solely the responsibility of the author and does not necessarily represent the official views of the National Institute of Environmental Health Sciences or the National Institutes of Health.
TABLE OF CONTENTS

Acknowledgments ........................................................................................................................................ ii

Table of Contents ....................................................................................................................................... iv

List of Tables .............................................................................................................................................. vii

List of Figures ............................................................................................................................................ ix

Abstract ......................................................................................................................................................... xiii

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

1.1 Overview ................................................................................................................................................. 1

1.2 Objectives of Research .......................................................................................................................... 8

1.3 Scope ....................................................................................................................................................... 9

1.4 Organization .......................................................................................................................................... 10

2 BACKGROUND ......................................................................................................................................... 11

2.1 Introduction .......................................................................................................................................... 11

2.2 Environmental Fate and Transport of Chlorinated Solvents .............................................................. 11
   2.2.1 Basic Physical and Chemical Properties of Chlorinated Solvents ............................................. 11
   2.2.2 Environmental Fate of Chlorinated Solvents .............................................................................. 14

2.3 Remediation of Chlorinated Solvents ................................................................................................. 16
   2.3.1 In Situ Bioremediation ..................................................................................................................... 16
   2.3.2 Monitored Natural Attenuation (MNA) ......................................................................................... 18
   2.3.3 In situ Chemical Oxidation ........................................................................................................... 19
   2.3.4 Permeable Reactive Barriers .......................................................................................................... 21

2.4 Electrochemical Remediation Methods ............................................................................................... 27
2.4.1 Fundamental Concepts of Electrochemical Remediation Methods.................27
2.4.2 Electrochemical Remediation Processes.........................................................32
  2.4.2.1 Electrochemical Oxidation or Anodic Oxidation ...........................................32
  2.4.2.2 Electrochemical Reductive Dechlorination or Cathodic Reduction ............38

3 MATERIALS AND METHODS ........................................................................... 47

3.1 Introduction....................................................................................................... 47

3.2 Batch Experiments.......................................................................................... 49
  3.2.1 Batch Experiment for Temporal Chemical Changes .....................................49
    3.2.1.1 Materials ................................................................................................... 49
    3.2.1.2 Experimental Methods and Procedures .................................................... 49
  3.2.2 Batch Experiment for the Evaluation of Electrode Effects on Electrochemical
       TCE Dechlorination ...........................................................................................53
    3.2.2.1 Materials ................................................................................................... 53
    3.2.2.2 Experimental Methods and Procedures .................................................... 55

3.3 Recirculation Experiments for the Optimization of Electrochemical Operating
Variables ...................................................................................................................... 59
  3.3.1 Materials .......................................................................................................59
  3.3.2 Experimental Methods and Procedures ....................................................... 60

3.4 Flow-Through Column Experiments ................................................................ 65
  3.4.1 Sand-Packed Flow-Through Experiments for Chemical Changes ...............65
    3.4.1.1 Materials ................................................................................................... 65
    3.4.1.2 Experimental Methods and Procedures .................................................... 65
  3.4.2 Experiments for the Assessment of Hydraulic Conductivity Change ..........69
    3.4.2.1 Experimental Procedures .......................................................................... 69
  3.4.3 Limestone Gravel-Packed Flow-Through Column Experiment for the
       Regulation of Chemical Properties in the Effluent and the Evaluation of TCE
       Transformation Under Flow ..................................................................................72
    3.4.3.1 Materials ................................................................................................... 72
    3.4.3.2 Experimental Methods and Procedures .................................................... 73

4 RESULTS AND DISCUSSION ........................................................................... 78

4.1 Introduction....................................................................................................... 78

4.2 Batch Experiments for the Evaluation of the TCE Dechlorination Effectiveness
and Chemical Changes Due to Iron Electrolysis..................................................... 79
  4.2.1 Batch Experiment for Temporal Chemical Changes in pH and ORP ..........79
4.2.1.1 Effect of Electrode Types ........................................................................ 79
4.2.1.2 Effect of Background Electrolyte on Iron Electrolysis ................................ 84
4.2.1.3 Effect of Different Current Densities on Iron Electrolysis ....................... 89
4.2.1.4 Polarity Reversal with Iron Electrolysis ................................................... 91
4.2.1.5 Identification of the Iron Precipitates ....................................................... 93

4.2.2 Batch Experiments for the Evaluation of Electrochemical TCE Dechlorination ................................................................................................................ 99
4.2.2.1 Effect of Anode Type ................................................................................ 99
4.2.2.2 Effect of Cathode Type ........................................................................... 106
4.2.2.3 Effect of Current and Initial TCE Concentration .................................... 112
4.2.2.4 Effect of Electrolyte Type and Electrolyte Concentration ....................... 119

4.3 Optimization of Operating Variables for Electrochemical Dechlorination of TCE ................................................................................................................................ 122
4.3.1 Regression Model and Assessment of the Main Factors ................................ 122
4.3.1.1 Na2SO4 Concentration ............................................................................ 130
4.3.1.2 Current Intensity ..................................................................................... 131
4.3.1.3 Thickness of Foam Electrode .................................................................. 132
4.3.1.4 Initial TCE Concentration ....................................................................... 132

4.4 Flow-Through Column Experiments .................................................................. 133
4.4.1 Sand-Packed Flow-Through Column Experiment for Chemical Changes .... 133
4.4.1.1 Effect of Electrode Type ......................................................................... 133
4.4.1.2 Effect of Current Density ........................................................................ 137
4.4.1.3 Effect of Flow Rate ................................................................................. 140
4.4.1.4 Effect of Electrolyte Composition .......................................................... 143
4.4.2 The Assessment of Hydraulic Conductivity Change During Iron Electrolysis ......................................................................................................................... 146
4.4.3 Regulation of the Effluent ORP and pH Under Flow ...................................... 155
4.4.4 Transformation of TCE Under Flow .............................................................. 160

5 SUMMARY AND CONCLUSIONS ................................................................. 170

5.1 Summary .................................................................................................... 170

5.2 Conclusions .............................................................................................. 171

5.3 Recommended Future Research ................................................................. 176

6 REFERENCES ............................................................................................. 178
LIST OF TABLES

Table 1-1 Activities that can cause groundwater contamination .............................................2
Table 2-1 Physical and chemical properties of chlorinated solvents .....................................13
Table 2-2 The standard reduction potentials at standard state (25 °C, pH 7 and 1 M) ............24
Table 2-3 Potential for oxygen evolution of different anode materials ..................................33
Table 3-1 The experiment list for investigation of temporal chemical changes in batch setup ...................................................................................................................................52
Table 3-2 The experiment list for the evaluation of operating variables on TCE dechlorination kinetics .................................................................................................................57
Table 3-3 The range of variation of the parameters used in the experiment design ...............63
Table 3-4 List of experiments and operating parameters used for each experiment ............64
Table 3-5 The experiment list with sand-packed flow-through column setup ..................67
Table 3-6 Experiment list for the investigation of hydraulic conductivity change during iron electrolysis .................................................................................................................72
Table 3-7 List of experiments for the evaluation of two- and three-electrode system for pH and ORP changes in effluent and TCE degradation efficacy .....................................77
Table 4-1 The equilibrium constants of the ferrous and ferric complexes with sulfate, chloride and bicarbonate anions .................................................................................................................................86
Table 4-2 Iron speciation in sulfate, chloride and bicarbonate solutions at different times, 112.5 mA L⁻¹ current density, mixed-electrolyte (total volume 400 mL), and cast iron electrodes ............................................................................................................................................87
Table 4-3 The list of pseudo-first order rate constants and final dechlorination efficiencies for different anode and cathode materials ..............................................................................111
Table 4-4 The list of pseudo-first order rate constants and final dechlorination efficiencies with different current densities and initial TCE concentration ......................................................................................113
Table 4-5 The range of variation of the parameters used in the experiment design

Table 4-6 Summary of the variables and results of the experiment design

Table 4-7 Summary of initial (k_{initial}) and final (k_{final}) hydraulic conductivity values with different flow rates, electrical current and electrolysis duration

Table 4-8 Summary of TCE transformation under flow experiments with different electrode arrangement (4 mL min^{-1}, 90 mA current, Reactor B, 1.27 cm thick foam cathode)
LIST OF FIGURES

Figure 1-1 Schematic DNAPL distribution in the subsurface.................................................................4

Figure 2-1 The proposed pathways by Matheson and Tratynek for reductive dehalogenation.........................................................................................................................................................25

Figure 2-2 Schemes for direct (a) and indirect EO of targeted contaminant. Indirect EO can be done both with (b) reversibly and (c) irreversibly electrogenerated reagents. R is the targeted contaminant, C is the reagent and O is the oxidation byproduct. ........................................34

Figure 3-1 Flow chart of research phases within this study........................................................................48

Figure 3-2 Divided glass electrochemical cell: 1) cathode side; 2) anode side; 3) electrolyte; 4) gas release port to the syringe; 5) magnetic stirrer; 6) membrane connection; 7) sampling port. ..................................................................................................................53

Figure 3-3 The anode materials from left to right: lead dioxide, cast iron, and MMO. ........55

Figure 3-4 The cathode materials from left to right: vitreous carbon foam, iron foam, copper foam, nickel foam, pure iron plate, and copper plate..................................................................................................55

Figure 3-5 A schematic of the electrochemical cell 1) cathode; 2) anode; 3) sampling port; 4) to expandable syringe; 5) stir bar; 6) gas-tight adapter; 7) electrolyte (115 mL); 8) headspace of cell (67 mL).................................................................58

Figure 3-6 a) Schematic of the experiment setup b) electrical connections .................................62

Figure 3-7 Schematic of sand-packed flow-through column.................................................................68

Figure 3-8 MMO and iron electrode for flow-through column experiment.........................69

Figure 3-9 The experimental setup for permeability experiments.................................................71

Figure 3-10 Reactor A, Reactor B and schematic of electrical connection .................................76

Figure 4-1 pH and ORP profiles in divided-electrolyte and mixed-electrolyte, 0.02 M Na$_2$SO$_4$ background electrolyte, 112.5 mA L$^{-1}$ current density (a) MMO electrodes (b) Iron electrodes.................................................................................................................................83
Figure 4-2 pH and ORP profiles (a) in different electrolyte compositions using iron electrodes, 112.5 mA L$^{-1}$ current density, mixed-electrolyte; (b) with different current densities (mA L$^{-1}$), using iron electrodes, in 0.02 M Na$_2$SO$_4$ mixed-electrolyte. 88

Figure 4-3 Iron speciation at different current densities (37.5, 75, 112.5, 150 mA L$^{-1}$). The asterisk (*) means under detection limit. 90

Figure 4-4 pH and ORP profiles under polarity reversal using iron electrodes, 112.5 mA L$^{-1}$ current density and 0.02 M Na$_2$SO$_4$ background electrolyte: (a) first 5 hours served as anolyte then polarity reversed and then served as catholyte from 5 hours to 10 hours (b) first 5 hours served as catholyte then polarity reversed served as anolyte from 5 hours to 10 hours. 92

Figure 4-5 X-Ray diffraction patterns of produced precipitates during iron electrolysis in a) 0.02 M Na$_2$SO$_4$ electrolyte; b) 0.02 M NaCl electrolyte; c) 0.02 M NaHCO$_3$ electrolyte. 5 hours of electrolysis, 90 mA current, iron anode and MMO cathode, final pH $\approx$ 10 for Na$_2$SO$_4$ and NaCl, $\approx$ 9 for NaHCO$_3$. 96

Figure 4-6 X-Ray diffraction patterns of produced precipitates during iron electrolysis in pre-purged (oxygen free) 0.02 M Na$_2$SO$_4$ electrolyte. 5 hours of electrolysis, 90 mA current, iron anode and MMO cathode, final pH $\approx$ 10. 97

Figure 4-7 Transmission Electron Microscopy (TEM) images of precipitates formed by iron electrolysis in: a) 0.02 M Na$_2$SO$_4$; b) 0.02 M NaCl; c) 0.02 M NaHCO$_3$ electrolyte. 5 h of electrolysis, 90 mA current, iron anode and MMO cathode. 98

Figure 4-8 a) Aqueous TCE (Ca) electroreductive dechlorination profile; b) ORP profile with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, initial TCE concentration 39 mg L$^{-1}$, 90 mA current, 0.01 M NaHCO$_3$ electrolyte. The control experiment was conducted without an electrical current. 101

Figure 4-9 The concentrations of hydrocarbon gases after 0.5 hour with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, 90 mA current, 0.01 M NaHCO$_3$ electrolyte. 102

Figure 4-10 Aqueous TCE decay and main by-products with copper foam cathode and a) PbO$_2$ anode; b) MMO anode; and c) iron anode; initial TCE concentration 298 µmol L$^{-1}$ (39 mg L$^{-1}$), 90 mA current, 0.01 M NaHCO$_3$ electrolyte. 104

Figure 4-11 Molar ratio of ethene to ethane at time 0.5 h with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, 90 mA current, 0.01 M NaHCO$_3$ electrolyte. 106

Figure 4-12 a) Electro-reductive dechlorination profile of aqueous TCE (Ca) with variable cathode types and cast iron anode b) Pseudo-first order TCE degradation kinetics with variable cathode materials and cast iron anode, the initial TCE concentration 39 mg L$^{-1}$, 90 mA current, 0.01 M NaHCO$_3$ electrolyte. 109
Figure 4-13 Time profiles of average current efficiency (ACE) of TCE electroreductive dechlorination with variable applied current values, cast iron anode and copper foam as electrodes, the initial TCE concentration 39 mg L\(^{-1}\), 0.01 M NaHCO\(_3\) electrolyte. .......115

Figure 4-14 (a) ORP profile, (b) final pH values with variable applied current values, cast iron anode and copper foam as electrodes, the initial TCE concentration 39 mg L\(^{-1}\), 0.01 M NaHCO\(_3\) electrolyte..........................................................118

Figure 4-15 Normalized aqueous TCE concentration profile with variable background electrolyte type, a) MMO anode coupled with copper plate cathode; b) Cast iron anode with copper plate cathode, initial TCE concentration ≈66 mg L\(^{-1}\), 30 mA current. .......121

Figure 4-16 a) Normalized aqueous TCE concentration profile with variable background electrolyte concentration, cast iron and copper foam cathode, initial TCE concentration ≈66 mg L\(^{-1}\), 30 mA current. ........................................................................................................122

Figure 4-17 Pareto chart for standardized effect of individual facto and combinations of factors........................................................................................................................................129

Figure 4-18 pH and ORP profiles for 4 different instant times (4 h, 6 h, 10 h and 16 h) in flow-through column set-up, 20 mA current, 0.02 M Na\(_2\)SO\(_4\) background electrolyte and 1.2 mL min\(^{-1}\) flow rate (a) using iron anode (b) using MMO (inert anode). ..............136

Figure 4-19 pH and ORP profiles for different currents (20 mA, 40 mA and 80 mA) in flow-through column set-up, iron anode, 0.02 M Na\(_2\)SO\(_4\) background electrolyte and 1.2 mL min\(^{-1}\) flow rate (a) time= 4 hours (b) time=6 hours (c) time=10 hours (d) time=16 hours.................................................................................................................139

Figure 4-20 pH and ORP profiles for different flow rates (1.2 mL min\(^{-1}\), 2 mL min\(^{-1}\) and 3.2 mL min\(^{-1}\)) in flow-through column set-up, iron anode, 0.02 M Na\(_2\)SO\(_4\) background electrolyte and 20 mA current (a) time= 1 hour (b) time=2 hours (c) time=4 hours.....143

Figure 4-21 pH and ORP profiles for different background electrolyte composition (0.02 M Na\(_2\)SO\(_4\) and 0.02 M NaHCO\(_3\)) in flow-through column set-up, iron anode, 20 mA current, (a) time= 1 hour (b) time=2 hours (c) time=4 hours (d) time=6 hours..............145

Figure 4-22 Hydraulic conductivity in the soil-packed column before and after electrolysis with different flow rate. Iron anode and MMO anode, 60 mA current, 0.02 M sodium sulfate electrolyte and 72 hours electrolysis duration.........................................................150

Figure 4-23 Hydraulic conductivity (k) in the column before and after electrolysis with different current values. Iron anode and MMO anode, 72 hours electrolysis duration, 0.02 M sodium sulfate electrolyte and 0.85±0.04 mL/min flow rate ...........................................151

Figure 4-24 Hydraulic conductivity in the soil-packed column before and after electrolysis with different electrolysis duration. Iron anode and MMO anode, 30 mA current, 0.02 M sodium sulfate electrolyte and 0.85±0.04 mL/min flow rate..............................................152
Figure 4-25 The iron precipitates and air pockets in the column due to iron electrolysis .................................................................................................................................153

Figure 4-26 The pressure difference during iron electrolysis. Iron-MMO couple is used as anode and cathode, 60 mA current, 0.5 flow rate, 20 mM sodium sulfate as electrolyte154

Figure 4-27 Effluent pH and ORP profiles with variable current conditions. a) MMO anode (Anode-1 in Reactor A) and porous copper cathode; b) Iron anode (Anode-1 in Reactor A) and porous copper cathode. Electrolyte contains 20 mg L⁻¹ Cl⁻, 0.172 g L⁻¹ CaSO₄ and 0.413 g L⁻¹ NaHCO₃. Flow rate is 2 mL min⁻¹ for all the experiments. ...........................................158

Figure 4-28 Effluent pH and ORP profiles of the three-electrode electrolytic system with different current distributions between anodes. Cast iron anode (Anode-1 in Reactor A), copper foam cathode and MMO iron anode (Anode-2 in Reactor A). Electrolyte contains 20 mg L⁻¹ Cl⁻, 0.172 g L⁻¹ CaSO₄ and 0.413 g L⁻¹ NaHCO₃. Flow rate is 2 mL/min for all the experiments. ..................................................................................................................160

Figure 4-29 a) Decay of aqueous TCE in the effluent with varying electrode configurations (samples are taken from Port-S4). b) The ORP profile of the electrolyte for corresponding electrode configurations (the samples are taken from Port-S3). 90 mA current and 4 mL min⁻¹ flow rate are applied for all experiments. For the three electrode arrangement, the total current is distributed equally between the anodes. A-1, C and A-2 in the legends refer to Anode-1, Cathode and Anode-2 positions in Reactor B. Electrolyte contains 0.172 g L⁻¹ of CaSO₄ and 0.413 g L⁻¹ of NaHCO₃.................................................................164

Figure 4-30 (a) TCE removal efficiency vs copper foam cathode thickness for different flow rates. (b) TCE treating capacity vs copper foam cathode thickness for different flow rates. Iron (A-1)-Copper foam (C)-MMO (A-2) electrode configuration and equal current distribution on the two anodes were used (90 mA total, 45 mA for each). Influent TCE concentration was 20 mg L⁻¹. Samples were collected from Port-S4 of Reactor B when steady-state TCE concentration was achieved in the reactor.........................................................167

Figure 4-31 Contour plots for TCE removal efficiencies with different current density and influent TCE concentration. Iron (A-1)-Copper foam (C)-MMO (A-2) electrode configuration and equal current distribution on the two anodes were used (90 mA total, 45 mA for each). Samples were collected from Port-S4 of Reactor B when steady-state TCE concentration was achieved in the reactor.........................................................169
ABSTRACT

Groundwater contamination with chlorinated solvents, such as trichloroethylene or TCE, is a major environmental challenge. The development of innovative, efficient, and sustainable remediation technologies is needed. In this study, iron electrolysis is assessed as a potential technology for the remediation of TCE contaminated groundwater.

A three-stage experimental program is conducted in this study: (i) the evaluation of chemical changes in the electrolyte due to iron electrolysis in batch reactors, as well as the investigation of TCE degradation rates; (ii) the optimization of electrochemical operating variables using a multivariable statistical approach; and (iii) the assessment of a proposed electrochemical system under flow conditions for the remediation of groundwater contaminated with TCE.

The first phase of this study focuses on the temporal chemical changes in the electrolyte due to iron electrolysis and TCE degradation kinetics with various electrode materials. Unlike an inert anode, an iron anode releases Fe (II) into the system and generates a highly reducing electrolyte condition (lower oxidation-reduction potential). This reducing electrolyte condition facilitates the reductive dechlorination of TCE. The TCE
dechlorination rate of various anode materials is investigated. The iron anode coupled with a copper foam cathode provides the best TCE dechlorination performance.

In the second stage, the significance of changes in operating variables on final TCE elimination efficiency (FEE) and specific energy consumption (SEC) is investigated using an iron anode-copper cathode couple. Under the same total charge conditions, changes in applied current impact FEE the most. For SEC, the ionic conductivity of the electrolyte is the most influential parameter.

In the final stage, a three-electrode (the sequence of an iron anode, a copper foam cathode, and an MMO anode) electrochemical system is implemented for the remediation of TCE in groundwater under flow conditions. Higher TCE removal efficiencies are reached at a lower flow rate, supporting the conclusion that a longer residence time of the electrolyte improves TCE removal efficiency. Conversely, the treating capacity of TCE is higher for a higher flow rate.
CHAPTER 1

1 Introduction

1.1 Overview

Groundwater is a crucial natural resource and a primary freshwater supply procured by humans. Groundwater is mostly utilized in irrigation (68% of total usage) and public water supply (19% of total usage). Groundwater was thought to be naturally protected from contamination under the assumption that soil provided a barrier to prevent the migration of contaminants released on or below land’s surface. However, groundwater was deemed very vulnerable to contamination as pollutants were detected in aquifers. Groundwater contamination can cause serious issues for the public and surrounding ecosystem, including poor drinking water quality, significant public health complications and problems, loss of clean water supply, and high cleanup and interventions costs.

Groundwater contamination is mainly due to human activities such as improper handling and disposal of hazardous substances. Table 1-1 lists activities that can cause groundwater contamination, differentiating between those that happen on the ground’s surface, in the ground above the water table, and in the ground below the water table.
Table 1-1 Activities that can cause groundwater contamination

<table>
<thead>
<tr>
<th>Ground surface</th>
<th>Infiltration of polluted surface waters; land disposal of wastes; stockpiles; dumps; sewage sludge disposal; de-icing salt use &amp; storage; animal feedlots; fertilizer &amp; pesticides; accidental spills; airborne source particulates.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Above water table</td>
<td>Septic tanks; cesspools &amp; privies; holding ponds &amp; lagoons; sanitary landfills; waste disposal in excavations; underground storage tank leaks; underground pipeline leaks; artificial recharge; sumps and dry wells; graveyards.</td>
</tr>
<tr>
<td>Below water table</td>
<td>Waste disposal in wells; drainage wells and canals; underground storage; mines; exploratory wells; abandoned wells; water supply wells; groundwater withdrawal.</td>
</tr>
</tbody>
</table>

A variety of hazardous substances have been detected in groundwater, including toxic organics such as dense non-aqueous phase liquids (DNAPLs), benzenes, and polycyclic aromatic hydrocarbons (PAHs); inorganic nonmetallic ions such as nitrate, perchlorate, and fluoride; and heavy metals such as lead, chromium, and arsenic. DNAPLs are a group of organic substances with two major characteristics: they are heavier than water and they are slightly soluble in water. Typical DNAPLs include chlorinated solvents, coal tar wastes, creosote-based wood-treating oils, and some pesticides. As a consequence of the widespread production, use, and disposal of hazardous DNAPLs, there are numerous DNAPL contamination sites in North America.
Sites contaminated with DNAPLs are among the major challenges in the field of environmental remediation as DNAPL source zones are difficult to find and characterize. The fate and movement of DNAPLs in the environment are unpredictable due to their physical and chemical properties. When they are released into the environment, they move downward via gravitational force through the layers of soil and groundwater until they reach an impermeable layer upon which to pool (Figure 1-1). As shown in Figure 1-1, DNAPL chemicals may be distributed in several phases: they can be dissolved in the groundwater, adsorbed to soils, or volatilized in the unsaturated zone. The phase of distribution impacts the fate of the contaminant in the aquifer and the required remediation technologies. Additionally, DNAPLs generally move within the aquifer in the direction of groundwater flow; due to the generally slow movement of groundwater, DNAPLs tend to remain in a concentrated form while at the same time producing a dissolved contamination plume. The size and speed of the plume depends on the hydrogeological characteristics of the aquifer as well as the type of contaminant. Aquifer permeability is a key hydrogeological property in the movement of groundwater. The contaminant plume can move faster within highly permeable aquifers, such as fractures within rocks, than in an aquifer of low permeability, such as consolidated clay.
Among DNAPLs, chlorinated solvents are the most prevalent groundwater contaminants. Chlorinated solvents are manmade, chlorine-containing organic compounds that are often used as solvents and degreasers in the electronics, defense, chemical, automotive, boat, food processing, textile, and dry cleaning industries. Typical chlorinated solvents include tetrachloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE), vinyl chloride (VC) and carbon tetrachloride (CT). Among these compounds, TCE and PCE are the most reported groundwater and soil contaminants. According to records from the United States Environmental Protection Agency (USEPA), TCE has been found in 325 (25%) of the 1,323 active National Priority List (NPL) sites by November 10, 2015. Similarly PCE has been recorded in 229 (17%) of the 1,323 active NPL sites.
Human exposure to chlorinated solvents may cause serious health problems because of their high toxicity levels. Adverse health effects include neurotoxicity, immunotoxicity, developmental toxicity, liver toxicity, kidney toxicity, endocrine effects, and several forms of cancer. For this reason, strict regulations have been orchestrated concerning the handling and disposal of chlorinated organic compounds to protect water from chlorinated solvent contamination. For example, waste containing these chlorinated compounds is classified as hazardous under the 1976 Resource Conservation and Recovery Act. Additionally, the 1984 Hazardous and Solid Waste Amendment requires the USEPA to restrict land disposal of untreated solvent wastes. To protect the public’s health, the USEPA set maximum contaminant levels allowed in drinking water at 0.005 mg L$^{-1}$ for TCE and PCE, 0.1 mg L$^{-1}$ for DCE and 0.002 mg L$^{-1}$ for VC.

Electrochemical treatment technologies, such as electrochemical oxidation and reduction, provide viable options for the in situ treatment of groundwater contaminated with chlorinated organic compounds. In electrochemical oxidation and reduction, closely arranged electrodes are inserted into the subsurface, perpendicular to the flow of the contaminant plume, to create an electrolytic reactive barrier. Applying an electrical current between the electrodes induces oxidation and reduction reactions at the electrodes that breakdown the respective contaminants.

The transformation of dissolved chlorinated compounds can be achieved mainly through two routes: anodic oxidation or cathodic reduction at the anode or the cathode, respectively. The anodic oxidation of chlorinated compounds may require anode materials with high
oxygen evolution overpotential, such as a boron-doped diamond, lead dioxide, or a ceramic electrode, to produce hydroxyl radicals that can cleavage carbon-halogen and carbon-carbon bonds. Although these anodes can reach high elimination efficiency, the high cost of the electrode is a primary concern for real application. On the other hand, cathodic reduction can provide a comparable electrocatalytic performance for the transformation of chlorinated compounds using more accessible and cost effective electrode materials. Low cost materials such as iron, copper, zinc, and carbon have been tested as cathodes for the reductive transformation of chlorinated compounds. In addition to these two transformation mechanisms, electrochemically-generated species such as oxygen and hydrogen can be utilized by other treatment methods including indirect biological, chemical, or physicochemical transformation in the electrolyte via electrochemically mediated reactions, such as electrochemically-assisted bioremediation, chemical reduction, and electrochemically-generated advanced oxidation.

The motivation for developing electrochemical technologies includes: (i) the potential ability to treat a broad range of contaminants through sequential oxidation and reduction reactions; (ii) the suitability of system variables, electrode potential, and cell current for facilitating process automation; (iii) the potential to produce a cost effective remediation alternative to current options; and (iv) environmental sustainability (the electron is the only reagent for the transformation reaction, therefore the electrochemical processes continue without continuous feed of redox chemicals). However, despite these promising advantages, the electrochemical treatment of groundwater contaminants is still considered an experimental technology, and the performance of electrochemical technologies in real-
world applications is still not verified due to limited testing in the field. Additionally, the electrochemical transformation of contaminants takes place at the interface of the electrode and the electrolyte, therefore the mass transfer of the target compound is crucial for efficient transformation. Since the concentration of chlorinated compounds in the natural aqueous media is relatively low, the performance of electrochemical processes may suffer from the limitations of mass transfer. As a result, research in this field focuses on efforts to improve the efficiency of electrochemical degradation. Generally, research on electrochemical water treatment has shown that the efficiency of electrochemical processes is affected not only by electrode surface reactivity and reactions, but also by temporary changes on the physical and/or chemical properties of the electrolyte. The performance of electrochemical remediation methods could be optimized by controlling the physicochemical conditions of the electrochemical redox system. Also, the anode and cathode materials greatly influence the chemical properties of the medium during the electrochemical remediation process. Anode and cathode materials change the dominant electrolysis reactions and the type and concentration of the species in the electrolyte during treatment.

Electrochemical treatment by iron electrolysis uses iron (cast iron, mild steel etc.) as an anode material. In the literature, iron electrolysis has mostly been reported for the remediation of heavy metals with electrocoagulation technology \(^{27, 28}\). The generated ferrous based species can also be utilized for the removal of other contaminants, such as chromium, arsenic, and selenate \(^{18, 20, 29}\). Although it has promising potential to improve the performance of the electrochemical reductive dechlorination of chlorinated
compounds, iron electrolysis has not been evaluated. Therefore, this study investigates different aspects of iron electrolysis in the electrochemical reductive dechlorination process, in which anodic reactions are utilized for regulating redox condition of the electrolyte for enhanced reductive dechlorination at the cathode. In this approach, ferrous species generated from the iron anode react with existing dissolved oxygen in the electrolyte, creating an oxygen-free, highly reducing environment. In a mixed electrolyte, the highly reducing condition accelerates the transformation of the chlorinated compounds at the cathode. In this study, TCE is used as a representative chlorinated compound.

1.2 Objectives of Research

The primary goal of this study is to test the performance of iron electrolysis for the treatment of TCE contaminated groundwater. The specific research objectives are as follows:

- To define the temporal chemical changes in pH, Oxidation-Reduction Potential (ORP), and conductivity with iron anodes in batch and under flow with varying operating conditions.
- To identify iron precipitates produced during the iron electrolysis process and to evaluate the potential adverse effect of the iron electrolysis on the physical characteristic of the aquifer, such as changes in hydraulic conductivity.
- To evaluate the TCE dechlorination kinetics for different anode and cathode materials and to investigate the effect of the operating variables on the TCE dechlorination rate constants.
• To optimize the operating variables of the iron electrolysis to find optimal operating condition.

• To test the performance of the iron electrolysis for the removal of TCE in the flow-through reactor.

1.3 Scope

This study consists of a series of experiments in batch and column reactors to evaluate the different aspects of iron electrolysis for the remediation of chlorinated solvents (TCE is a model chlorinated solvent) in groundwater. Batch experiments were conducted to evaluate chemical changes in the electrolyte due to iron electrolysis. Also, TCE dechlorination kinetics was investigated in a batch reactor with varying electrode materials and operating conditions. The effect of operating variables on TCE removal efficiency was investigated in a recirculation experimental setup. Flow-through column experiments were conducted to evaluate pH, ORP distribution, and TCE removal efficiency under flow. Additionally, the changes in hydraulic conductivity due to electrochemical processes were evaluated in this study.
1.4 Organization

This thesis consists of five chapters. Chapter 1 includes an introduction about chlorinated solvents (with a focus on TCE and PCE) to illustrate the necessity to develop new remediation methods. Electrochemical processes are also introduced, and the role of anode and cathode materials is emphasized. The goals and objectives of the research are defined in Chapter 1. Chapter 2 presents the general physical and chemical properties of chlorinated solvents with a literature review of remediation methods. Subsequently, an overview of electrochemical methods for the removal of chlorinated compounds from groundwater is presented.

Chapter 3 describes the experimental methods and procedures, analytical methods, sampling protocols. The experimental apparatus are explained in detailed. Used chemicals/reagents, materials and instruments are listed. The lists of experiments with variables and experimental conditions are provided.

Chapter 4 presents the results from batch and flow-through experiments for the evaluation of different aspect of iron electrolysis, including TCE removal efficiency as well as temporal physical and/or chemical changes due to iron electrolysis. The effect of operating variables on TCE reduction is presented. Chapter 5 provides the summary of the results, conclusions and future work recommendations.
CHAPTER 2

2 Background

2.1 Introduction

In this chapter, the physical and chemical properties of prevalent chlorinated contaminants are discussed. A general description of commonly used groundwater remediation technologies is then presented with a discussion of their advantages and limitations, followed by a brief explanation of the basic principles of electrochemistry. Finally, reported studies from the electrochemical remediation methods, mainly electrochemical reduction and electrochemical oxidation, are summarized.

2.2 Environmental Fate and Transport of Chlorinated Solvents

2.2.1 Basic Physical and Chemical Properties of Chlorinated Solvents

The fate and transport of chlorinated solvents in groundwater are determined by the physical and chemical properties of both the aquifer and the chlorinated solvents. These properties affect the selection of remediation technologies. A summary of basic physical and chemical properties of selected chlorinated solvents is presented in Table 2-1. Except VC, most are in liquid form at ambient temperature and their densities are larger than 1 g mL⁻¹. This means that they are heavier than water, and thus they can penetrate into the
aquifer by gravitational forces. Their solubility in water is relatively low, ranging between 0.15 g L\(^{-1}\) to 6.3 g L\(^{-1}\), and their dissolution in water is slow, indicating that when they reach the aquifer, they can contaminate a large volume of groundwater in the flow direction of groundwater. Henry’s Law constant (\(K_H\)) value is higher than 0.0002 atm-m\(^3\)mol\(^{-1}\) for all compounds listed in Table 2-1, implying that these compounds can be removed from water by air stripping\(^3\)\(^0\). The octanol-water partition coefficient (Log \(K_{ow}\)) is a measure of the hydrophobicity of the material. Lower Log \(K_{ow}\) values indicate that the compound sorbs less strongly onto aquifer solids compared to compounds with higher Log \(K_{ow}\) values.
## Table 2-1 Physical and chemical properties of chlorinated solvents

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Tetrachloroethene</th>
<th>Trichloroethene</th>
<th>cis-1,2-Dichloroethene</th>
<th>trans-1,2-Dichloroethene</th>
<th>1,1-Dichloroethene</th>
<th>Vinyl Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>PCE</td>
<td>TCE</td>
<td>cis-1,2-DCE</td>
<td>trans-1,2-DCE</td>
<td>1,1-DCE</td>
<td>VC</td>
</tr>
<tr>
<td>CAS Registry Number</td>
<td>127-18-4</td>
<td>79-01-6</td>
<td>156-59-2</td>
<td>156-60-5</td>
<td>75-35-4</td>
<td>75-01-4</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>C₂Cl₄</td>
<td>C₂HCl₃</td>
<td>C₂H₂Cl₂</td>
<td>C₂H₂Cl₂</td>
<td>C₂H₂Cl₂</td>
<td>C₂H₃Cl</td>
</tr>
<tr>
<td>Molar Weight</td>
<td>165.83</td>
<td>131.4</td>
<td>96.95</td>
<td>96.95</td>
<td>96.95</td>
<td>62.5</td>
</tr>
<tr>
<td>Appearance @20 °C</td>
<td>Colorless liquid</td>
<td>Colorless liquid</td>
<td>Colorless liquid</td>
<td>Colorless liquid</td>
<td>Colorless liquid</td>
<td>Colorless gas</td>
</tr>
<tr>
<td>Odor</td>
<td>Ethereal</td>
<td>Ethereal; sweet</td>
<td>Ethereal, slightly acrid</td>
<td>Ethereal, slightly acrid</td>
<td>Mild sweet odor</td>
<td>Sweet</td>
</tr>
<tr>
<td>Density, g mL⁻¹ @ 20 °C</td>
<td>1.6227</td>
<td>1.465</td>
<td>1.2837</td>
<td>1.2565</td>
<td>1.213</td>
<td>0.9106</td>
</tr>
<tr>
<td>Boiling Point, °C</td>
<td>121</td>
<td>86.7</td>
<td>60.3</td>
<td>48</td>
<td>31.7</td>
<td>-13.37</td>
</tr>
<tr>
<td>Melting Point, °C</td>
<td>-19</td>
<td>-87.1</td>
<td>-80.5</td>
<td>-50</td>
<td>-122.5</td>
<td>-153.8</td>
</tr>
<tr>
<td>Vapor Pressure, mmHg</td>
<td>18.47 (@25 °C)</td>
<td>74 (@25 °C)</td>
<td>180 (@20 °C)</td>
<td>265 (@20 °C)</td>
<td>500 (@20 °C)</td>
<td>2530 (@20 °C)</td>
</tr>
<tr>
<td>Solubility in water, g L⁻¹ @ 25 °C</td>
<td>0.15</td>
<td>1.366</td>
<td>3.5</td>
<td>6.3</td>
<td>2.5</td>
<td>2.763</td>
</tr>
<tr>
<td>Henry's Law Constant, atm·m³ mol⁻¹ @ 25 °C</td>
<td>0.018</td>
<td>0.011</td>
<td>0.0041</td>
<td>0.0094</td>
<td>0.19</td>
<td>0.0278</td>
</tr>
<tr>
<td>Log Kow</td>
<td>3.4</td>
<td>2.42</td>
<td>1.86</td>
<td>2.09</td>
<td>1.32</td>
<td>1.36</td>
</tr>
</tbody>
</table>

2.2.2 Environmental Fate of Chlorinated Solvents

The chlorinated solvents released into the environment tend to sink through the saturated and unsaturated layers of soil until they reach an impermeable layer where they can create a source zone containing DNAPL either as a separate phase or adsorbed to soil. The source zone behaves as a long term contamination source due to the low solubility of DNAPLs in the groundwater and the low desorption rate from the soil. In the subsurface, the chlorinated solvents seek phase equilibrium between soil, groundwater, and air in void spaces. The potential phases involve adsorbed to soil, dissolved in groundwater, or volatilized into soil gas. The distribution between the phases is determined by chemical and physical properties of the individual chlorinated solvent and the subsurface environment. Therefore, the extent of distribution in each phase may change with time and location.

In addition to the partitioning of chlorinated solvents among the three phases, they can migrate in the subsurface in their partitioned phases through various processes, such as advection, dispersion, and diffusion. Through advection and dispersion, the aqueous phase will migrate through groundwater flow under a hydraulic gradient. Their transport by diffusion can occur due to concentration gradients. The permeability of soil and the reactivity and mobility of the contaminants are the key properties that affect the extent of contaminant transport in groundwater. In general, advective processes govern the overall rate of transport in aquifers. Along with the physical transport processes, dissolved chlorinated solvents can be attenuated naturally through physical (volatilization), chemical (sorption, abiotic degradation), and biological (degradation) processes in groundwater.
Natural attenuation is discussed later in this chapter (see Section 2.3.2 Monitored Natural Attenuation (MNA)).

Adsorption and desorption are key reactions between the contaminant and aquifer solids that affect the fate and transport of the dissolved phase in the subsurface. The adsorption-desorption properties of contaminants are commonly explained using isotherms, which are equations showing the relationship between the equilibrium concentration of contaminant in liquid and solid phases at constant temperature. In practice, the adsorption isotherms can be used to determine the mass of contaminated soil by knowing or estimating the amount of chemical spilled and the dissolved concentration of the chemical. The most frequently used models are linear isotherm, Freundlich isotherm, and Langmuir isotherm, given by:

2-1 Linear isotherm: \( S = K_d C \)

2-2 Freundlich isotherm: \( S = K C^n \)

2-3 Langmuir isotherm: \( S = \frac{\alpha \beta C}{1+\alpha C} \),

where \( S \) is the mass sorbed on solid surface per mass of solids (mg g\(^{-1}\)), \( C \) is the equilibrium concentration of the solution (mgL\(^{-1}\)), \( K_d \) and \( K \) are the partitioning coefficients of linear isotherm (Lkg\(^{-1}\)) and Freundlich isotherm, respectively, \( n \) is the Freundlich exponent, usually ranging between 0.7 to 1.2, \( \alpha \) is a coefficient known as Langmuir constant, and \( \beta \) is the maximum sorption capacity of the solid surface (mg kg\(^{-1}\)).

Sorption of TCE and PCE mainly depends on the content of fine- and coarse-grained soil fractions and the organic carbon content. The sorption behavior of TCE and PCE follows linear isotherm in sandy aquifer\(^{31}\). Kret et al\(^{31}\) reported the stronger PCE adsorption on
sandy soil in comparison to TCE due to the higher hydrophobicity of PCE (See Log $K_{ow}$ values of corresponding compounds in Table 2-1). The study by Lu et al. 32 concluded that Freundlich isotherm fits slightly better than linear isotherm for the sorption of PCE, TCE, DCE and VC on natural clayey till. The chlorinated solvents tend to adsorb stronger on the soil particles as the organic carbon content of soil increases 33.

2.3 Remediation of Chlorinated Solvents

2.3.1 In Situ Bioremediation

During bioremediation, organic contaminants are reduced or oxidized by oxidation-reduction reactions facilitated by microorganisms. In these reactions, chlorinated organic compounds may undergo biodegradation either as an electron donor, an electron acceptor, or through cometabolism. Highly chlorinated solvents such as PCE and TCE are not likely to serve as electron donors for microbial degradation reactions. Therefore, the most important process for biodegradation of these compounds is reductive dechlorination under anaerobic conditions. During this process, the chlorinated compound is used as an electron acceptor by the microorganism and a chlorine atom is removed and replaced by a hydrogen atom. The reductive dechlorination usually occurs by sequential dechlorination from PCE to TCE to DCE to VC and then to ethene. Since PCE and TCE are used as electron acceptors during reductive dechlorination, there must be an appropriate carbon source and electron donor for the microbial growth and bioremediation to occur. PCE and TCE have been shown to undergo reductive dechlorination with various anthropogenic or native electron donors/carbon sources. These electron donors include a variety of soluble organic
compounds (lactate, acetate, methanol, benzoate), materials such as vegetable oil, natural organic solids such as compost, and commercially available products such as hydrogen release compounds.

Relatively low oxidation state chlorinated compounds such as DCE and VC may undergo aerobic biodegradation rather than reductive dechlorination. During this process, chlorinated compounds are used as an electron donor and oxygen is used as the primary electron acceptor. Since aerobic degradation rates are usually faster than reductive dechlorination for these products, aerobic conditions can be induced by air injection into the subsurface for relatively faster degradation of these compounds.

The effectiveness of this system depends on the hydraulic conductivity, the contaminant type and the location of the contamination in the subsurface. In situ bioremediation is most effective in high permeable aquifers because of the ease of distribution of essential substrates. Less permeable aquifers need a longer time for cleanup. Additionally, the physical and chemical characteristics of the contaminant significantly affect the performance of in situ bioremediation. The biodegradability of the contaminants is a measure of its ability to be metabolized by microorganisms. The water solubility, partitioning coefficient, and adsorption characteristics of contaminants are other chemical properties that influence in situ bioremediation efficiency. Groundwater pH, temperature, and mineral content affect the microbial activity. Optimal microbial activities occur at neutral pH conditions, while extreme groundwater temperatures negatively affect microbial activities.
2.3.2 Monitored Natural Attenuation (MNA)

Monitored Natural Attenuation is defined as the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. “Natural attenuation” has also been referred to as “intrinsic remediation”, “intrinsic bioremediation”, “passive bioremediation”, “natural recovery”, and “natural assimilation” 49.

Natural attenuation is a combination of a variety of chemical, physical, and biological processes. Processes that only reduce the concentration of the contaminant are termed “nondestructive,” such as volatilization, hydrodynamic dispersion, and sorption. Processes that reduce the mass of contaminants such as biodegradation and abiotic degradation are termed “destructive” 49.

The advantages of MNA include the in situ destruction of contaminants, lower volumes of remediation waste, applicability to all or part of the given site, and lower overall remediation costs. The disadvantages of MNA encompass a longer clean-up time frame, costly and complex site characterization processes, and the potential change of hydrologic and geochemical conditions over time.

Despite those potential disadvantages, MNA can be an effective way to remediate several organic and inorganic contaminants under favorable conditions. Aerobic and anaerobic biological processes play a significant role in the removal of organic contaminants. Successful natural attenuation of PCE and TCE with a combination of aerobic and
anaerobic biotransformation has been reported at the Area 6 test site at Dover Air Force Base (Dover, DE) \(^{47}\).

### 2.3.3 *In situ* Chemical Oxidation

Remediation by chemical oxidation is defined as the contact between oxidizing chemicals with subsurface contaminants to transform the contaminant into a non-toxic form. Some oxidizing agents for chemical oxidation of TCE include potassium ferrate \(^{50}\), ozone \(^{51}\), potassium permanganate \(^{52}\), and persulfate \(^{53}\). The TCE oxidation reaction can be accelerated by adding a catalyst such as mixing ferrous ions with hydrogen peroxide (Fenton’s reagent). The reactions between ferrous \((Fe^{2+})\) and hydrogen peroxide \((H_2O_2)\) produce several oxidants. The possible reactions occurring in a \(Fe^{2+}/H_2O_2\) solution are as follows:

\[
\begin{align*}
2-4 & \quad Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + HO^- \\
2-5 & \quad Fe^{2+} + HO^- = Fe^{3+} + OH^- \\
2-6 & \quad H_2O_2 + HO^- = H_2O + HO_2 \\
2-7 & \quad Fe^{2+} + HO_2 = Fe^{3+} + HO_2^- \\
2-8 & \quad Fe^{2+} + HO_2 = Fe^{2+} + H^+ + O_2 \\
2-9 & \quad Fe^{3+} + H_2O_2 = Fe^{2+} + HO_2^- + H^+
\end{align*}
\]

Hydroxyl radicals \((HO^-)\), hydroperoxyl radicals \((HO_2^-)\), hydrogen peroxide\((H_2O_2)\), and oxygen \((O_2)\) are all possible oxidants produced by these reactions \(^{54}\). The hydroxyl radical \((HO^-)\) is a very unstable and strong oxidant that can react immediately with target organic compounds and oxidize them. The rate constant of the hydroxyl radical with TCE
is $4 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$. The rate constant of TCE oxidation can be enhanced by combining different oxidants such as ozone with hydrogen peroxide or ozone with UV radiation, which is referred to as an advanced oxidation process (AOP). The rate constant of ozone (O$_3$) with TCE is 17 M$^{-1}$ s$^{-1}$, which is much less than that of the hydroxyl radical. Yasunaga et al. reported that the TCE oxidation efficiency of the O$_3$/H$_2$O$_2$ system is only 40% better than that of O$_3$. The overall reaction between O$_3$ and H$_2$O$_2$ results in the production of hydroxyl radicals, as shown in the following equation:

$$2\text{O}_3 + \text{H}_2\text{O}_2 = 2\text{HO}^+ + 3\text{O}_2$$

Ozone can be used with UV radiation to enhance the oxidation of TCE as well. Ozone absorbs UV radiation at a wavelength of 254 nm and produces hydrogen peroxide; the hydrogen peroxide then decomposes to a hydrogen radical, which is a strong oxidant.

Potassium permanganate is another chemical utilized for TCE oxidation. The oxidation of TCE with permanganate follows the sequential reactions below:

$$2\text{HO}^+ + 3\text{Cl}^- \rightarrow \text{aCA} + \text{MnO}_2 + 2\text{CO}_2$$

where $a$ and $b$ are stoichiometric coefficients, $I$ is Cyclic complex, and $CA$ are various carboxylic acids.

The effectiveness of the chemical oxidation depends on the strength of the oxidant, contact time of the oxidant with the contaminants, and site hydrogeologic conditions. The oxidant should be transformed to the target zone without consumption, implying that the total
oxidant demand should be estimated carefully for full transformation of the contaminant. The targeted location has to be explored and structured to ensure the delivery of the oxidant does not go to a non-targeted zone \(^\text{58}\).

The primary advantages of chemical oxidation are \(^\text{59}\):

- Rapid in situ destruction of the contaminants,
- No significant waste production except Fenton’s Reagent,
- Reduced operation and monitoring costs, and
- Minimal disturbance to site operations.

Some disadvantages are \(^\text{59}\):

- Higher initial and overall cost compared to other in situ treatment technologies,
- Ineffectiveness in low permeability soils,
- Production of a significant amount of explosive off-gas by Fenton’s Reagent,
- Health and safety concerns associated with applying oxidants,
- A significant amount of oxidant loss as a result of reacting with non-toxic organics, and
- The possibility of change to aquifer geochemistry (reduction of porosity of aquifer with precipitation).

### 2.3.4 Permeable Reactive Barriers

The technology termed Permeable Reactive Barriers (PRB) is defined as: “an embracement of reactive materials in the subsurface designed to intercept a contaminant plume, provide
a preferential flow path through the reactive media, and transform the contaminants into environmentally acceptable forms to attain remediation concentration goals at points of compliance\(^6\).

A permeable reactive barrier is placed in the subsurface across the flow of the contaminated groundwater path, which moves through it as it flows under its natural gradient, creating a passive treatment system. As the contaminants move through the reactive barrier, the reactive medium degrades or traps the contaminants. The principal contaminant transformation processes in the reactive barrier involve: (i) reductive degradation of organic contaminants, (ii) oxidative degradation of organic contaminants, (iii) retardation and biodegradation of organic contaminants, (iv) sorption of organic or inorganic contaminants, and the (v) reduction and/or precipitation of heavy metal compounds\(^6\).

Based on the target contaminant and the removal mechanism, the reactive medium used in PRBs may include iron based materials (zero-valent iron, cast iron, steel wool, amorphous ferric oxide, etc.)\(^{62-66}\), organic based materials\(^{67-69}\), zeolites\(^{70,71}\), clay\(^{72}\), and metal oxides\(^{73}\).

Zero-valent iron (ZVI) is the most commonly used reactive material in PRB; with a record of over 200 field installations as of 2011, at least 120 used iron based materials\(^{74,75}\). During the degradation process by ZVI, two redox reactions result in the chlorinated organic compounds-iron-water mix. The first redox reaction is the reduction of water by oxidation
of ZVI (Equation 2-13). The second one is the reduction of chlorinated organic \((RCl)\) by oxidation of iron (Equation 2-14).

\[
2-13 \quad Fe^0 + 2H_2O = Fe^{2+} + 2OH^- + H_2
\]

\[
2-14 \quad RCl + Fe^0 + H^+ = Fe^{2+} + RH + Cl^- \quad \text{or} \quad Cl_2 \quad \text{or} \quad Fe^0 + H^+ = Fe^{2+} + RH + Cl^-
\]

Table 2-2 lists the standard reduction potentials of common reactions likely to occur during ZVI based dechlorination process. ZVI is highly reduced and the carbon of the chlorinated organic compound is in oxidized form; therefore, thermodynamically, Equation 2-14 is more favorable for many chlorinated contaminants \(^7\).

Three possible pathways were suggested during dechlorination of chlorinated compounds with ZVI \(^7\) (Figure 2-1). The first pathway (Figure 2-1A) involves the electron transfer from the metal surface to adsorbed contaminants. The second pathway (Figure 2-1B) is the reduction of the contaminant by intermediate product of corrosion (Fe\(^{2+}\)) in aqueous system. The third pathway (Figure 2-1C) is the reductive dechlorination by produced hydrogen as a product of corrosion with water.
Table 2-2 The standard reduction potentials at standard state (25 ºC, pH 7 and 1 M)

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>$E^\circ$, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{2+} + 2e^- = \text{Fe}$</td>
<td>-440</td>
</tr>
<tr>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O}$</td>
<td>816</td>
</tr>
<tr>
<td>$\text{PCE} + \text{H}^+ + 2e^- = \text{TCE} + \text{Cl}^-$</td>
<td>574</td>
</tr>
<tr>
<td>$\text{TCE} + \text{H}^+ + 2e^- = \text{DCE} + \text{Cl}^-$</td>
<td>550-527</td>
</tr>
<tr>
<td>$\text{DCE} + \text{H}^+ + 2e^- = \text{VC} + \text{Cl}^-$</td>
<td>420-397</td>
</tr>
<tr>
<td>$\text{VC} + \text{H}^+ + 2e^- = \text{C}_2\text{H}_4 + \text{Cl}^-$</td>
<td>450</td>
</tr>
</tbody>
</table>
Figure 2-1 The proposed pathways by Matheson and Tratynek \cite{77} for reductive dehalogenation.
In addition to chemical reduction by ZVI, TCE and PCE can be degraded by biological reactions in PRBs. Reactive media considered in PRBs to promote the biological treatment of chlorinated compounds in the groundwater include peat, cane molasses, sludge cake, and vegetable oil 78-80.

Despite the promising efficiency and applicability of ZVI, there are many uncertainties in predicting the long term performance of the ZVI system, which is affected by the loss of reactivity of iron fillings and the loss of permeability 81-85. Studies have shown that the loss of permeability in ZVI based barriers is mainly due to gas entrapment and mineral precipitation 84-89.

Other technologies for the remediation of chlorinated solvents in groundwater include pump and treat, in situ air sparging, in situ thermal treatment and in situ flushing. Pump and treat involves the installation of a series of extraction wells to pump contaminated groundwater to the ground surface for subsequent aboveground treatment. In situ air sparging technology strips VOCs from the groundwater physically by the injection of air into the saturated zone to volatilize and transfer groundwater contaminants to the vadose zone. This technology is generally coupled with a soil vapor extraction (SVE) that enables extraction of volatilized vapor from the vadose zone. In situ thermal treatment methods use heat to enhance the recovery of volatile and semivolatile contaminants from the subsurface. In situ flushing involves the injection or infiltration of an aqueous solution into contaminated soil/groundwater, followed by down gradient extraction of the mixture of groundwater and flushing solution and subsequent aboveground treatment.
2.4 Electrochemical Remediation Methods

2.4.1 Fundamental Concepts of Electrochemical Remediation Methods

Electricity was first proposed for the treatment of wastewater in the UK in 1889\(^9_0\). However, due to the high cost and shortage of electricity at that time, using electricity was not preferred for the wide application of treatment processes. Significant research has been achieved over recent decades and electrochemical based processes are recognized as viable technologies to remove, transform, or immobilize contaminants in soil or groundwater. The motivation to develop electrochemical remediation technologies stems from\(^9_1\): 

(i) The potential ability to treat a broad range of contaminants through sequential oxidation and reduction reactions;

(ii) The avoidance of the injection of chemicals into the subsurface as electrochemical remediation uses a clean reagent, the electron, as a reactant;

(iii) The potential to produce a cost effective remediation alternative to current options, given that the remediation system can be powered by renewable energy sources (e.g., solar power);

(iv) The ability to use more than a pair of electrodes to enhance the contaminant transformation performance; and

(v) The rate of electrochemical reactions at the electrodes can be controlled by adjusting the electrical potential difference between electrodes, thus the groundwater chemistry can be regulated to achieve desired conditions for the degradation of target contaminants.
Electrochemical process has been proposed in the form of a permeable reactive barrier for groundwater remediation, also called an electrochemically induced redox barrier or e-barrier. The e-barrier consists of closely placed electrodes across the flow direction of contaminated groundwater. Applying direct electrical current between the electrodes induces oxidation reactions at the anode (positive sign electrode) and reduction reactions at the cathode (negative sign electrode). As the plume of contaminated groundwater passes through the barrier, the dissolved contaminants are subject to sequential oxidation-reduction or reduction-oxidation, depending on the sequence of the charges applied to the electrode set. For instance, dissolved TCE can be reduced at the cathode by electrochemical processes as in Equation 2-17. In addition to TCE reduction, other electrochemical reactions such as water oxidation (Equation 2-15) and water reduction (Equation 2-16) are most likely to occur at corresponding electrodes in the aqueous solution.

\[
\begin{align*}
2-15 & \quad 2H_2O = 4H^+ + O_2 + 4e^- \quad \text{(at the anode)} \\
2-16 & \quad 2H_2O + 2e^- = 2OH^- + H_2 \quad \text{(at the cathode)} \\
2-17 & \quad C_2HCl_3(TCE) + 7H_2O + 10e^- \rightarrow 2CH_4 + 3Cl^- + 7OH^- \quad \text{(at the cathode)}
\end{align*}
\]

The relationship between charge passed and the amount of substance oxidized or reduced at the corresponding electrode is defined by Faraday’s Law. According to Faraday’s Law (Equation 2-18), the amount of charge transfer is proportional to the amount of product formed from the corresponding electrode reaction. Generally, the electrochemical processes at an individual electrode involve more than one reaction; in that case, a term called current efficiency (CE), given in Equation 2-19, indicates the efficiency of a specific
electrode reaction. In Equation 2-19, theoretical chemical change is calculated by Faraday’s Law, and actual chemical change is a measured value in the electrochemical cell:

\[
2-18 \quad J_{sub} = \frac{It}{nFV}
\]

\[
2-19 \quad CE = \frac{\text{actual chemical change}}{\text{theoretical chemical change}} \times 100
\]

where \( J_{sub} \) is the rate of substance production per unit electrolyte volume (mol L\(^{-1}\)), \( I \) is the electric current (Amp or C sec\(^{-1}\)), \( t \) is elapsed time (sec), \( n \) is the number of electrons transferred for a specific electrochemical reaction, \( F \) is faraday’s constant (96,485 C mol\(^{-1}\)) and \( V \) is the volume of background electrolyte (L).

The electrode-electrolyte interface is the most important phenomena in electrochemistry since all electrochemical reactions happen at a layer adjacent to the electrode surface. A simple model of the electrode-electrolyte interface consists of mainly two layers, namely the double layer and the diffusion layer. The double layer consists of the two layers of opposite charges lined up within a scale of nanometers to the electrode surface \(^{95}\). The double layer has large potential difference, which is the driving force behind the electrochemical reactions and governs the rate of charge transfer reactions \(^{95}\). The diffusion layer exists between the double layer and bulk electrolyte in the order of micrometers due to the concentration gradient between the double layer and bulk solution. Mass transfer and charge transfer occur simultaneously during an electrochemical reaction. The slower of these two processes is the rate-limiting step for the electrochemical reaction. Diffusion layer thickness is a significant parameter determining the mass-transfer limiting current density. The mass-transfer limiting current density is independent of potential and defined as;
2-20 \[ i_l = \frac{n F D C^*}{\delta}, \]

where \( i_l \) is the limiting current density (A cm\(^{-2}\)), \( D \) is the diffusion coefficient (cm\(^2\) sec\(^{-1}\)), \( \delta \) is the thickness of the Nerst diffusion layer (cm), and \( C^* \) is the concentration of reactant in the bulk solution (mM).

In the absence of mass transfer limitations, the potential dependence of the electrochemical reaction rate at an electrode is described by the Butler-Volmer equation \(^{96}\),

\[
2-21 \quad i = i_0 \left[ e^{\alpha_a F (E-E_{eq})/RT} - e^{-\alpha_c F (E-E_{eq})/RT} \right],
\]

where \( i \) is the overall rate of the electrochemical reaction (A cm\(^{-2}\)) or the net current associated with the reaction, \( i_0 \) is the exchange current density (A cm\(^{-2}\)), \( E \) is the electrode potential (V), \( E_{eq} \) is the equilibrium potential (V), \( R \) is the gas constant (8.314 V C mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature (K), and \( \alpha_a \) and \( \alpha_c \) are the transfer coefficients for the anodic and cathodic reactions, respectively (dimensionless).

The equilibrium reduction potential \( (E_{eq}) \) is calculated using Nernst equation, shown in Equation 2-22:

\[
2-22 \quad E_{eq} = E^o + \frac{RT}{nF} \ln \left[ \frac{\prod a_{ox,i}^{s_{ox,i}}}{\prod a_{red,i}^{s_{red,i}}} \right],
\]

where \( E^o \) is the standard electrode potential, \( a_{ox,i}^{s_{ox,i}} \) is chemical activity of the oxidized species, \( a_{red,i}^{s_{red,i}} \) is chemical activity of the reduced species, and \( s \) is the stoichiometric coefficient of relevant species.
For a reversible electrochemical reaction, the reaction favors in both directions simultaneously, therefore the first term in Equation 2-21 gives the rate of oxidation reaction while the second term gives the rate of reduction. The electrochemical reactions for the transformation of chlorinated compounds are irreversible; so Equation 2-21 can be further simplified. For instance, for the cathodic reduction of TCE, the applied electrode potential, $E$, is negative and relatively high, so the first term in the bracket is negligible in comparison with the second term. In this case, the electrode potential dependence of TCE reduction rate ($i_r$) can be rewritten as:

$$i_r = i_0 e^{-\alpha_c F (E - E_{eq}) / RT}$$

The term $(E - E_{eq})$ in the equation refers to the overpotential of the electrochemical reaction, where $E_{eq}$ is determined by the Nerst equation (Equation 2-22). The kinetic variables $\alpha_a$, $\alpha_c$, and $i_0$, are a function of electrode potential; they are determined by fitting experimental data on the $i$ vs. $(E - E_{eq})$ plot for a specific electrochemical reaction. The transfer coefficients ($\alpha_a$ and $\alpha_c$) depend on the symmetry factor ($\beta$) and the number of electrons transferred before and after the rate limiting step. The symmetry factor, which is the fraction of the potential across the double layer promoting the cathodic reaction, ranges from 0 to 1 for a single step electron transfer reaction. The transfer coefficients have been estimated for various chlorinated compounds for specific electrochemical processes. For instance, cathodic reduction of chlorinated compounds on porous nickel cathode showed the transfer coefficient values as 0.13 for PCE, 0.14 for TCE and 0.27 for CT (carbon tetrachloride). The exchange current density, $i_0$, is dependent on the concentration of both reactants and products, in addition to the type of electrode. It is a
measure of the kinetic ability of the reaction, meaning that a system with large $i_0$ achieves equilibrium on a shorter time scale. The exchange current density typically ranges between 0.2 to 2 A m$^{-2}$

Anodic oxidation and cathodic reduction are common electrochemical remediation processes investigated to clean-up chlorinated compounds in water/groundwater. In the following sections, these electrochemical processes will be summarized, with a discussion of the influence of operating parameters.

2.4.2 Electrochemical Remediation Processes

2.4.2.1 Electrochemical Oxidation or Anodic Oxidation

Electrochemical oxidation (EO) or anodic oxidation has attracted great attention especially for the treatment of wastewater containing organic contaminants due to its potential advantages such as versatility, energy efficiency, amenability to automation, environmental compatibility, and cost effectiveness.

Since anode material greatly influences the selectivity and efficiency of electrochemical oxidation, researchers have intensely investigated the efficiency of different anode materials on the oxidation of environmentally concerned organics. Generally, these anode materials can be classified mainly into two groups based on electrocatalytic capacity for oxygen evolution reaction: low oxygen evolution overpotential (also called active anodes) and high oxygen evolution overpotential (also called nonactive anodes). Table
2-3 lists the commonly used anode materials and corresponding oxidation evolution potentials. Ruthenium-based oxides (RuO₂), iridium-based oxides (IrO₂), platinum (Pt), and graphite, which are active anodes, have relatively low oxygen evolution potential. At an applied voltage, these active anodes show a higher tendency for oxygen evolution compared to nonactive electrodes (andipony-doped tin oxide (SnO₂), lead dioxide (PbO₂), and boron-doped diamond (BDD)).

Table 2-3 Potential for oxygen evolution of different anode materials

<table>
<thead>
<tr>
<th>Anode Material</th>
<th>Oxygen Evolution Potential (V/SHE)</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO₂</td>
<td>1.47</td>
<td>0.5 M H₂SO₄</td>
</tr>
<tr>
<td>IrO₂</td>
<td>1.52</td>
<td>0.5 M H₂SO₄</td>
</tr>
<tr>
<td>Pt</td>
<td>1.6</td>
<td>0.5 M H₂SO₄</td>
</tr>
<tr>
<td>Graphite</td>
<td>1.7</td>
<td>0.5 M H₂SO₄</td>
</tr>
<tr>
<td>SnO₂</td>
<td>1.9</td>
<td>0.05 M H₂SO₄</td>
</tr>
<tr>
<td>PbO₂</td>
<td>1.9</td>
<td>1 M H₂SO₄</td>
</tr>
<tr>
<td>BDD</td>
<td>2.3</td>
<td>0.5 M H₂SO₄</td>
</tr>
</tbody>
</table>

Standard electron potential for oxygen evolution is 1.23 V/NHE.
EO of organic compounds can be achieved by two main mechanisms: (i) direct oxidation, where contaminants exchange electrons with the anode surface without involvement of other substances or (ii) indirect oxidation, where contaminants do not exchange electrons with the anode surface but rather via the involvement of some electroactive species regenerated in the cell, which acts as a mediator for electron shuttling between the electrode and the organic compound.

The direct oxidation of a contaminant involves the adsorption of the organic compound (R) on the anode (Equation 2-24), followed by direct electron transfer between the anode and the adsorbed compound (Equation 2-25). Direct anodic oxidation is theoretically possible only at low potentials before oxygen evolution can cause a decrease in the catalytic activity of the anode, due to the formation of a polymer layer on the anode surface, called
a poisoning effect. The indirect oxidation usually includes the generation of a strong oxidant, mostly adsorbed hydroxyl radicals, by water discharge (Equation 2-26), followed by O-transfer reactions to the organic molecule (Equation 2-27) and evolution of oxygen as a side reaction (Equation 2-28). Also, other strong oxidants such as chlorine, hydrogen peroxide and ozone can be generated electrochemically.

\[
2-24 \quad M + R = M - R_{ads} \quad \text{(Adsorption of organic compound)}
\]

\[
2-25 \quad (M - R_{ads}) - ne^- \rightarrow \text{oxidation products} \quad \text{(Electron transfer)}
\]

\[
2-26 \quad M[.] + H_2O \rightarrow M[OH.] + H^+ + e^- \quad \text{(Hydroxyl radical generation)}
\]

\[
2-27 \quad M[OH.] + R \rightarrow M[.] + RO + H^+ + e^- \quad \text{(O-transfer reaction)}
\]

\[
2-28 \quad M[OH.] + H_2O \rightarrow M[.] + O_2 + 3H^+ + 3e^- \quad \text{(Oxygen evolution reaction)},
\]

where \( R \) is the target organic compound, \( M \) is the active site for the adsorption of the \( OH\cdot \) species, and \( RO \) is the oxidation product.

Indirect oxidation of chlorinated compounds via the hydroxyl radicals requires relatively costly anode materials such as BDD and ceramic. Although these anode materials show high oxidation performance, it is difficult, from a practical perspective, to balance the cost and efficiency for larger scale applications. Because of these challenges, very few researchers have studied the oxidation of chlorinated compounds via direct electron transfer or indirectly by electro-generated hydroxyl radicals. Lakshmipathiraj et al. studied the anodic oxidation kinetics of TCE on Ti/IrO\textsubscript{2}-Ta\textsubscript{2}O\textsubscript{5} anode in a undivided electrochemical cell, showing that TCE oxidation takes place on Ti/IrO\textsubscript{2}-Ta\textsubscript{2}O\textsubscript{5} anode via direct electron transfer for the potentials above 0.3 V vs. saturated calomel electrode (SCE).
a divided electrolytic cell demonstrated that TCE disappearance occurred via the reaction with electro-generated hydroxyl radicals and showed first order decay in TCE concentration for the anode potential between 2.5 to 4.3 V vs. SCE. In this study, TCE was transformed to CO₂, CO, Cl⁻, and ClO₃⁻. Furthermore, the oxidation of TCE on BDD film electrodes was investigated in the flow-through and rotating disk electrode reactors. This study demonstrates that the oxidation of TCE occurs via the direct electron transfer for voltage values less than 2 V vs. standard hydrogen electrode (SHE), both by direct electron transfer and indirectly by hydroxyl radicals at higher electrode potentials, producing formate, carbon dioxide, chlorate, and chloride as oxidation byproducts. Scialdone et al. evaluated the anodic oxidation of 1,2-dichloroethane with different anode materials, including Pt, Au, BDD, Ebonex, stainless steel, Ti/IrO₂-Ta₂O₅, and PbO₂. In this study, 1,2-dichloroethane was oxidized via chemisorbed active oxygen when Pt and Ti/IrO₂-Ta₂O₅ were used as anode materials. Among studied anode materials, BDD anode showed the highest electrocatalytic activity with chemical oxygen demand (COD) removal of about 97% at 5 mA cm⁻² and 15 mA cm⁻², while Au anode showed no COD removal. Saez et al. compared the efficiency of different electrochemical strategies (anodic, cathodic, and dual treatment) on PCE transformation using divided and undivided electrochemical cells employed with PbO₂ electrodes. At E=1.7 V vs. AgCl/Ag, relatively low total PCE degradation value was obtained with a value of 18% in the anodic compartment of the divided cell. The measured oxidation byproducts were CO₂, chloroacetic acid (ClCH₂CO₂H), and trace amounts of TCE. This study showed that cathodic reduction or dual treatment (cathodic and anodic degradation) was more preferable over only anodic oxidation in terms of PCE removal efficiency.
Hydrogen peroxide (H$_2$O$_2$) is another oxidant that can be generated electrochemically in acidic media by the cathodic reduction of O$_2$ (Equation 2-29). During this process, O$_2$ can be either produced at the anode or injected into the system. Furthermore, Fe$^{2+}$ is a common species in aquifers with concentration levels on the order of mg L$^{-1}$. The combination of electro-generated H$_2$O$_2$ and Fe$^{2+}$ produces hydroxyl radicals, a process known as electro-Fenton $^{110-112}$. Similarly, Yuan et al. $^{110}$ proposed a palladium-catalyzed electro-fenton process for the oxidation of TCE. In this process, in addition to electrochemical production of H$_2$O$_2$, Pd catalyzes the H$_2$O$_2$ production from the electro-generated O$_2$ and H$_2$ (Equation 2-31). Yuan et al. $^{112}$ proposed the three electrode system (one anode, two cathodes) to maintain low pH vicinity to promote the TCE oxidation with electro-fenton process. Similarly, electrochemically generated compounds can be utilized as an activator during a chemical oxidation process. For instance, electrochemically generated ferrous ion from iron anode activates the persulfate to produce strong radicals (sulfate radicals) for the oxidation of TCE in the groundwater $^{113}$. In other study, electrochemically generated ferrous ion from iron anode activated peroxymonosulfate for the oxidation of chlorophenol in groundwater $^{114}$.

$$
\text{2-29} \quad \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2
$$

$$
\text{2-30} \quad \text{Fe}^{2+} + \text{H}_2\text{O}_2 = \text{Fe}^{3+} + \text{OH}^- + \text{HO}^-
$$

$$
\text{2-31} \quad \text{H}_2 + \text{O}_2 \stackrel{\text{Pd}}{\rightarrow} \text{H}_2\text{O}_2
$$
2.4.2.2 Electrochemical Reductive Dechlorination or Cathodic Reduction

Compared to anodic oxidation and other reductive pathways such as ZVI, cathodic reduction has considerable advantages, including: (i) the provision of enhanced reduction kinetics, (ii) controllable electrode passivation to provide for longer service life, and (iii) easier accessibility of efficient cathode materials in comparison with anodes. Furthermore, previous studies demonstrated that cathodic reduction can be applied successfully to remediate a wide range of organic contaminants in environmental media including: chlorinated solvents, polychlorinated biphenyls, aliphatic chlorides, and polycyclic aromatic hydrocarbons. The cathodic reduction of chlorinated compounds has attracted the most attention due to the electronegative character of the chlorine group in the molecule. As a result, researchers have investigated the effectiveness of cathodic reduction of many chlorinated compounds including PCE, TCE, carbon tetrachloride, tetrachloromethane, chloroform, chlorobenzene, chlorinated phenols, and chlorobiphenyls. Literature on the electrochemical reduction of chlorinated compounds has mainly focused on (i) the determination of reductive electron transfer mechanisms and (ii) the improvement of electrochemical reduction efficiency.

2.4.2.2.1 Reductive electron transfer mechanisms

Two electrochemical reductive electron transfer mechanisms are reported: direct electron transfer and indirect electron transfer. Direct electron transfer reactions occur heterogeneously via electron transfer between targeted chemical species and solid-state
electrodes. The mechanism of the electrochemical cleavage of the R-Cl (chlorinated compound) via the direct electron transfer includes the adsorption step (Equation 2-32) followed by a reaction involving electron transfer and intermediate radical anion formation (Equation 2-33), and then, R-Cl bond cleavage (Equation 2-34). A second electron transfer may drive the formation of organic anion depending on the organic compound and on the working conditions such as supporting the electrolyte, electrode material, and potential (Equation 2-35). Both the anion and/or the radical can react with the solvent, hydrogen donors or other chlorinated compounds, to produce dechlorinated compounds as in Equations 2-36 to 2-38.

\[
\begin{align*}
&2-32 \quad RCl + M = M - RCl \quad \text{(Adsorption)} \\
&2-33 \quad M - RCl + e^- = (M - RCl)^- \quad \text{(Electron transfer)} \\
&2-34 \quad (M - RCl)^- \rightarrow M + R^- + Cl^- \quad \text{(R-Cl bond cleavage)} \\
&2-35 \quad R^- + e^- \rightarrow R^- \quad \text{(the organic anion formation)} \\
&2-36 \quad R(R^-) + HA \rightarrow RH + A(A^-) \\
&2-37 \quad R^- + RCl \rightarrow R - R + Cl^- \\
&2-38 \quad R^- + R^- \rightarrow R - R,
\end{align*}
\]

where \( M \) is the active site of the electrode for the adsorption of chlorinated organic compound.

Unlike direct electron transfer, indirect electron transfer takes place via electrolytic production of atomic hydrogen on the cathodes. The dechlorination mechanism via indirect electron transfer involves simultaneous reactions as shown in Equations 2-39 to 2-42. These reactions include the formation of adsorbed atomic hydrogen by electrolysis of water (Volmer discharge), molecular hydrogen evolution from electrochemical desorption
(Heyrovsky desorption), hydrogen evolution from the chemical recombination of atomic hydrogen (Tafel recombination), and the reaction between the adsorbed atomic hydrogen and the halocarbon molecule (hydrodechlorination).\textsuperscript{135-137}

\begin{align*}
2-39 & \quad H_2O + e^- + M \leftrightarrow M - H_{ads} + OH^- \text{ (Volmer discharge)} \\
2-40 & \quad M - H_{ads} + H_2O + e^- \leftrightarrow M + H_2 + OH^- \text{ (Heyrovsky desorption)} \\
2-41 & \quad M - H_{ads} + M - H_{ads} \leftrightarrow 2M + H_2 \text{ (Tafel recombination)} \\
2-42 & \quad RCl + 2(M - H_{ads}) \rightarrow RH + 2M + Cl^- + H^+ \text{ (Hydrodechlorination)},
\end{align*}

where \(M\) is an active site on the electrode surface and \(M - H_{ads}\) is atomic hydrogen adsorbed on the catalytic site of the electrode.

The type of reductive electron transfer mechanism is highly related to thermodynamic characteristics of the target compound, applied electrode potential and electrode material. For instance, Li and Farrell\textsuperscript{96} have reported that TCE and CT (carbon tetrachloride) follow different electrochemical reduction mechanisms in identical conditions. TCE is mainly transformed indirectly by atomic hydrogen adsorbed on the iron cathode; alternatively, CT is reduced via direct electron transfer following CT adsorption on the cathode surface. In another study, the investigation of the role of atomic hydrogen on TCE and PCE reduction with iron was carried out by Wang and Farrell\textsuperscript{121} using tafel analysis and electrochemical impedance spectroscopy; they concluded that PCE reduction occurred primarily via direct electron transfer. In contrast, TCE reduction occurred via atomic hydrogen at low pH values, and via atomic hydrogen and direct electron transfer at neutral pH values. Applied electrode potential also has a crucial effect on the type and efficiency of reductive electron
transfer. The reduction via atomic hydrogen occurs only at the potential, which is high enough for hydrogen evolution \(^{135}\). However, the reduction via direct electron transfer is affected adversely with more negative applied electrode potential. For instance, Saez \textit{et al.} \(^{115}\) reported that the dehalogenation mechanism of PCE, in the potential range from -1.2 V to +0.2 V, was a direct electron transfer onto glassy carbon, lead, and carbon electrode surfaces. A decrease in the current efficiency for PCE degradation was obtained with more negative applied potentials. The electrode potential for hydrogen evolution is mainly determined by the type of electrode material, and therefore electrode material is another significant parameter to evaluate the applicability and efficiency of cathodic degradation \(^{137}\). The next section discusses the performance of different electrode materials for the cathodic reduction of chlorinated compounds.

### 2.4.2.2.2 Electrode materials

Electrochemical reduction occurs mostly on the surface of the cathode, while reaction kinetics is a function of standard electrode potential (Equation 2-22 and 2-23). Therefore, the reduction efficiencies of aqueous contaminants are heavily dependent on the cathode material. Moreover, the selection of cathode material influences reaction pathway, process kinetics, selectivity, and specific energy consumption. Many cathode materials have been investigated for use in the cathodic reduction of chlorinated compounds. For instance, cathode materials such as Nickel-containing stainless steel \(^{124}\), nickel foam \(^{124}\), carbon cloth \(^{129}\), glassy carbon \(^{118}\), lead \(^{129}\), silver \(^{118, 128}\), iron \(^{15, 96}\), copper \(^{15}\), palladium \(^{138}\), BDD \(^{139}\), platinum- or palladium-coated ceramic \(^{122}\), copper foam \(^{136}\) bare- and polymer-coated nickel \(^{140}\), and mixed metal oxide (MMO)-coated titanium mesh cathodes \(^{25}\) demonstrate
different performances for reductive electrolytic dechlorination of chlorinated compounds in aqueous solution.

Saez et al. 141 have reported the influence of anode and cathode materials on the degradation of PCE in the recirculation system. Fast PCE decay was reported for cathodic copper and carbon in comparison with lead at short times, but the influence of the cathodic material disappeared at longer times. Saez et al. 141 also pointed out that the influence of studied anodic materials, DSA-O₂, DSA-O₂-Cl₂, and PbO₂, was not significant, suggesting that degradation performance was determined solely by cathode materials. Rajic et al. 124 reported that the nickel content in the stainless steel enhances the cathodic reduction efficiency of TCE. Liu et al. 15 investigated the selectivity and reactivity of cathode materials for electrolytic reduction of carbon tetrachloride (CT). This work concluded that, based on current efficiency, cathode materials can be ordered Zn>Cu>Fe>Zi. Zhang and Rusling 142, 143 reported that lead cathodes show better PCB dechlorination performance than carbon cloth cathodes, due to the higher hydrogen overpotential of lead. Additionally, Sonoyama and colleagues 144 investigated the reductive degradation efficiency of chloroform on 15 different kinds of metal cathodes. Their results show that Cu, Ag, Pd, Pb, and Ag have good catalytic activity of reduction of chloroform; however, Fe, Zr, and Al have relatively low catalytic activity.

Catalysts (palladium, zinc, etc.) have the unique property of promoting the dechlorination of organic compounds due to their ability to absorb hydrogen into its lattice to serve a high surface concentration of hydrogen 132. Therefore, catalyst-loaded electrodes have been
utilized to enhance the reductive dechlorination of chlorinated compounds. The dechlorination efficiency of palladium-loaded cathode materials including palladized graphite\textsuperscript{132}, palladized iron\textsuperscript{96}, palladized iron foam\textsuperscript{145}, palladized iron oxide\textsuperscript{123}, palladized carbon cloth\textsuperscript{130}, palladized Ti/TiO\textsubscript{2} nanotube\textsuperscript{146}, palladized titanium mesh\textsuperscript{130}, and zinc-modified carbon cloth\textsuperscript{129} have been investigated and compared with bare electrodes. Cheng\textsuperscript{132} illustrated that dechlorination of 4-chlorophenol is faster on palladized carbon cloth and palladized graphite electrodes than on bare electrodes. Sonoyomo\textsuperscript{147} investigated electrochemical dechlorination of chlorinated hydrocarbons using metal-impregnated (Zn, Ag, Cu) carbon fiber cathodes in flow cells; this study concluded that metal-impregnated electrodes can decompose all chloroform (0.25 µmol L\textsuperscript{-1}), however, bare metal electrodes could decompose only half of the initial chloroform in identical experimental conditions. It is also highlighted that Ag-impregnated cathode electrodes have shown optimal performance in comparison with Zn- and Cu-impregnated cathode electrodes. In another study, the enhancing effect of palladium on the iron oxide foam was reported for electrolytic degradation of TCE\textsuperscript{123}. Li and Farrell investigated the effectiveness of electrochemical reduction of TCE and CT using palladized-iron cathodes in a flow-through reactor and concluded that palladized-iron allows for a three times faster reduction rate in comparison to iron.

2.4.2.2.3 Operating Conditions

For a specific electrochemical cell, operating parameters include applied current density, background electrolyte composition, cathode potential, concentration of target compound, electrolyte pH, and electrode sequence. Since these parameters significantly impact the
performance of electrochemical systems, they have been extensively investigated and reported.

The applied current density influences the production rate of electrolysis products (H\textsubscript{2}, O\textsubscript{2}, H\textsuperscript{+} and OH\textsuperscript{-}), contaminant elimination rate, and current efficiency. The generation rate of electrolysis products increases with current based on Faraday’s Law. Contaminant elimination rate also increases with applied current\textsuperscript{148,149}. However, increases in current might affect current efficiency adversely. For instance, Cheng \textit{et al.}\textsuperscript{130} conducted experiments for hydrodehalogenation of 2,4-dichlorophenol (DCP) in 0.05 M Na\textsubscript{2}SO\textsubscript{4} aqueous solution in a Nafion 117 membrane flow cell with Pd/Ti mesh cathode. In that study, current efficiency showed a decreasing trend over electrolysis time. Also, the optimum current efficiency was reported at a relatively low current density, which could be explained by competing side reactions like hydrogen evolution at higher current densities. Accordingly, the energy consumption per reduced DCP increased with increasing current density. Electrode potential also has a significant influence on current efficiency. Since electrode potentials required for the reduction of halogenated compounds are quite negative, it is not always possible to prevent hydrogen evolution as a side reaction. As cathodic potential gets higher (more negative), water decomposition consumes a significant portion of the applied current. Chen\textsuperscript{122} reported that current efficiencies for the electrolytic reduction of chloroform (CF) and TCE were achieved at 100% when applied cathodic potential was -0.5 V, however current efficiencies dropped to 16.6% for CF and 24.4% for TCE when applied cathode potential was dropped to -1.4 V.
The pH and oxidation reduction potential of the solution can influence the cathodic reduction of chlorinated compounds \(^{122, 150}\). According to reduction experiments on iron and palladized-iron cathodes, Li and Farrell \(^{96}\) observed that the effect of pH was higher on TCE reduction than CT reduction, suggesting that CT reduction happens through direct electron transfer on the electrode surface. Al-Abed and Fang \(^{148}\) illustrated that acidic pH increased the reduction rate of TCE in an electrolyte, not involving cathodic reactions with protons and electrons. In the same study, higher pH values contributed to decreased cathodic hydrogen values, concluding that when reductive mechanisms utilize atomic hydrogen, current efficiency for TCE reduction is prone to decrease. Similarly, in comparing hydrogen surface coverage \(\Theta_H\) values of oxide-coated iron and nickel electrodes in neutral and low pH, Wang and Farrell \(^{151}\) concluded that the absorbed concentration of atomic hydrogen increases in low pH, enhancing the dechlorination of chlorinated solvents resulting from indirect electron transfer.

The electrolyte composition is another variable which might affect the cathodic reduction of chlorinated compounds due to electrode fouling. For instance, Chen \(^{122}\) investigated the sulfate and chloride poisoning effect on Pd-coated ebonex electrodes, concluding that reaction rates of TCE and CF reduction dropped significantly due to sulfate poisoning but chloride did not affect the catalytic activity of the Pd-coated electrode. Rajic \textit{et al}.\(^{145}\) reported that the presence of humic substances in the groundwater adversely affects the cathodic reduction of TCE on palladized iron foam cathodes. Mao \textit{et al}.\(^{93}\) indicated that the oxidative compounds such as dissolved oxygen and nitrate compete with TCE during
cathodic reduction of TCE in groundwater, therefore the oxidative compounds inhibit the cathodic degradation of TCE.

Additionally, the initial concentration of target chemicals might affect current efficiency due to mass transport limitations. Based on experiments in divided cell, Liu et al.\textsuperscript{15} posited that initial concentrations of CT proportionally influenced current efficiency of CT reduction due to the relatively higher amount of accumulation of by products and the displacement of water from the electrode surface by sorbed CT. In another study, current efficiency was doubled when initial DCP increased from 1 to 5 mM\textsuperscript{130}. Under the same conditions, energy consumption reduced by half when the DCP concentration increased from 1 mM to 5 mM. In contrast, Saez et al.\textsuperscript{141} studied a wide range of initial concentrations (150 – 452 µM) and observed that there was not a strong influence of initial concentration on the kinetics of PCE degradation in recirculation systems with an undivided filter-press reactor using a Pb cathode coupled with a PbO\textsubscript{2} anode.

Electrode sequence is an electrochemical system design parameter influencing both the electrochemical removal efficiency of target contaminant and the removal pathway. Rajic et al.\textsuperscript{152} investigated the impact of electrode sequence on TCE degradation in aqueous solution under a flowing condition. This study concluded that the installation of anode downstream of cathode significantly improves the cathodic reduction of TCE.
CHAPTER 3

3 Materials and Methods

3.1 Introduction

This chapter describes the experimental procedures followed to investigate the effect of iron electrolysis on temporal physiochemical changes in the electrolyte, as well as the capacity of iron electrolysis to degrade TCE in batch and flow-through column reactors. In this chapter, the components of experimental setup, chemicals, reagents, and materials used in this study are described. Experimental procedures and analytical methods utilized during the experiments are also explained in detail.

Figure 3-1 depicts the research flow followed in this study. The experiments were conducted in three phases: (i) batch experiments to evaluate the electrode effects on the physiochemical changes in the electrolyte and TCE degradation kinetics (Section 3.2.1 and Section 3.2.2), (ii) experiments in recirculation system to optimize the operating variables (Section 3.3), and (iii) flow-through column experiments to assess the temporal chemical changes and TCE transformation efficiency under flow (Section 3.4.1 and Section 3.4.3) and to examine the effect of iron electrolysis on hydraulic conductivity (Section 3.4.2).
Iron Electrolysis for Groundwater Remediation

Batch Experiments
- Chemical Changes
  - pH, ORP and conductivity
  - Identification of generated iron oxides
  - TCE degradation kinetics

Column Experiments
- Optimization of TCE removal in recirculation system
- Evaluation of TCE degradation under flow
- Chemical changes under flow
- Geotechnical changes
- pH and ORP
- Hydraulic conductivity

Figure 3-1 Flow chart of research phases within this study
3.2 Batch Experiments

3.2.1 Batch Experiment for Temporal Chemical Changes

3.2.1.1 Materials

The chemicals and reagents used include NaCl (100%, Fisher Scientific), Na₂SO₄ (99%, BDH), NaHCO₃ (99-100%, Fisher Scientific), o-Phenantrone (0.25% w/v, LabChem Inc.), hydroxylamine hydrochloride (98.5%, Fisher Scientific), ammonium acetate (98.1%, Fisher Scientific), hydrochloric acid (37.3%, Fisher Scientific), and glacial acetic acid (99.9%, Fisher Scientific). All solutions were prepared using deionized water and without pH adjustment. Cast iron (McMaster Carr, USA) and mixed metal oxides (mesh type, 3N International, USA) were used as electrodes. The working surface area for each electrode was 7 cm² with a length of 7 cm. The surface of the iron electrodes were polished with sand paper, etched in 1.3 M HCl, and then washed several times with distilled water prior to assembly.

3.2.1.2 Experimental Methods and Procedures

An experimental program (Table 3-1) was designed to evaluate the effect of electrode type, current density, background electrolyte composition, and polarity reversal on temporal changes in the pH and redox potential. To understand temporal changes in the electrolyte, the current density was evaluated and discussed with respect to electrolyte volume (mA L⁻¹), instead of using current density based on electrode surface.
The divided- and mixed-electrolyte batch experiments were conducted in a glass electrochemical cell with two electrode compartments as shown in Figure 3-2. In each compartment, the liquid and headspace volume were 200 mL and 100 mL, respectively. Gas from electrolysis was collected in 150 mL syringe connected to each compartment to maintain a closed system. The electrodes were placed in parallel such that the working surfaces were face to face. The center to center spacing between anode and cathode was 13 cm. Electrical current was applied by Agilent E3612A DC power supply. In the divided-electrolyte, the anolyte and catholyte were isolated by a Nafion® membrane (Nafion® 112, ElectroChem Inc, USA). The anolyte and catholyte compartments were continuously stirred at the same speed during testing.

pH and ORP values were recorded routinely with microprobes. The final conductivity was measured using a conductivity probe. Total dissolved iron and precipitated iron concentration were determined using 1, 10 Phenantroline method. For the measurement of total dissolved ferrous ions concentration, a 1 mL sample taken from the electrochemical cell was filtered with a 0.45 µm syringe filter and immediately diluted by 0.05 M H₂SO₄ solution, then placed in centrifuge tubes. Afterwards, a 200 µL ammonium acetate buffer (14.30 g ammonium acetate and 40 mL glacial acetic acid in 150 mL distilled water) and a 1 g L⁻¹ phenantroline solution were added subsequently to the centrifuge tube. The absorbance of solution at 510 nm wavelength was measured using UV-VIS spectrophotometer (UVmini-1240, Shimadzu). For measurement of the total dissolved iron concentration (ferrous and ferric), 25 µL hydroxylamine hydrochloride (15 g of hydroxylamine hydrochloride in 150 mL distilled water) was added to the filtered sample
as a reductant, and the sample was mixed for 5 minutes to allow all ferric ions to reduce to ferrous ions. Then, the same reagents (ammonium acetate buffer and phenantroline) were added prior to spectrophotometer measurement. For the determination of concentration of total iron precipitates, 1 mL samples were collected from the electrochemical cell and placed in 1.5 mL centrifuge tube; a 100 µL concentrated HCl was then added to the tube. The tube was stored for 1 day to allow all forms of iron precipitates to dissolve. The sample was then subjected to the same procedure explained above to measure the total iron concentrations (dissolved and solid form).

The identification of iron based precipitates was performed using an X-ray diffraction (XRD) instrument (Rigaku UltimaIV XRD) with Cu Ka radiation. After electrolysis, the electrolyte solution was filtered in a glove box using 1.5 µm pore size glass microfiber filter to collect the precipitates. The collected precipitates were placed on a XRD sample slide, and a thin layer of glycerol was applied to protect oxygen sensitive precipitates from oxidation during XRD measurement. The particle size of produced iron based precipitates was determined using Transmission Electron Microscopy (TEM). A 1 mL aqueous sample was diluted and placed on a carbon film on 300 mesh copper grids (CF300-Cu). The image of the sample on carbon film was then scanned using JEM 1010 Electron Microscopy.
Table 3-1 The experiment list for investigation of temporal chemical changes in batch setup

<table>
<thead>
<tr>
<th>Variables</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte (0.02 M)</th>
<th>Current (mA L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrode Types</strong></td>
<td>MMO</td>
<td>MMO</td>
<td>Na₂(SO₄)-mixed</td>
<td>112.5</td>
</tr>
<tr>
<td>MMO</td>
<td>MMO</td>
<td>Na₂(SO₄)-divided</td>
<td>112.5</td>
<td></td>
</tr>
<tr>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>112.5</td>
<td></td>
</tr>
<tr>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-divided</td>
<td>112.5</td>
<td></td>
</tr>
<tr>
<td><strong>Background Electrolyte</strong></td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>112.5</td>
</tr>
<tr>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>NaCl-mixed</td>
<td>112.5</td>
<td></td>
</tr>
<tr>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na(HCO₃)-mixed</td>
<td>112.5</td>
<td></td>
</tr>
<tr>
<td><strong>Current Density</strong></td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>37.5</td>
</tr>
<tr>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>75.0</td>
<td></td>
</tr>
<tr>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>112.5</td>
<td></td>
</tr>
<tr>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>150.0</td>
<td></td>
</tr>
<tr>
<td><strong>Polarity Reversal</strong></td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-divided</td>
<td>112.5</td>
</tr>
</tbody>
</table>
Figure 3-2 Divided glass electrochemical cell: 1) cathode side; 2) anode side; 3) electrolyte; 4) gas release port to the syringe; 5) magnetic stirrer; 6) membrane connection; 7) sampling port.

3.2.2 Batch Experiment for the Evaluation of Electrode Effects on Electrochemical TCE Dechlorination

3.2.2.1 Materials

The chemicals and reagents used include TCE (99.5%, Sigma-Aldrich), cis-DCE (97%, Sigma-Aldrich), VC (analytical standard, 200 μg mL$^{-1}$ in methanol, Supelco), hydrocarbon gas standard (analytical standard, 1% (w/w) methane, ethane, ethane, acetylene in nitrogen,
Supelco), NaHCO₃ (99-100%, Fisher Scientific), NaCl (100%, Fisher Scientific) and Na₂SO₄ (99%, BDH). Saturated TCE solution was prepared as stock solution by dissolving TCE in double-distilled water (18 MΩ cm). The stock solution was kept at a temperature of 20 °C to maintain 1.07 mg mL⁻¹ dissolution concentration. The conductive materials used as anode (Figure 3-3) include cast gray iron (McMaster Carr, USA), mixed metal oxide (mesh type, 3N International, USA), and lead dioxide. The cathode materials are copper foam (60 pores per inch (PPI), 99.5%, Aibixi Ltd., China), iron foam (45 PPI, 98% iron, 2% nickel, Aibixi Ltd., China), nickel foam (60 PPI, 99.9%, Lyrun Ltd., China), vitreous carbon foam (100 PPI, ERG, USA), copper plate (99.9%, VWR), and pure iron plate (3N5 purity, ESPI metals, USA) (Figure 3-4). The foam materials were cut to 4 cm length, 1 cm width, and 0.3 cm thickness. The working surface area of the plates was 4 cm² with 4 cm length, 1 cm width, and 0.1 cm thickness. A piece of copper wire was attached to the electrodes to connect to the DC source. A glass tube, 10 cm long, was placed around the electrode connection and filled with epoxy to prevent connection corrosion. The surfaces of the iron electrodes were polished with sand paper, etched in diluted HCl solution (10% by weight), and washed several times with distilled water. The copper foam electrodes were soaked in diluted H₂SO₄ solution (3 % by weight), cleaned with a 2% Micro-90 cleaning solution (Cole-Parmer, USA), and then washed several times with distilled water prior to assembly.
3.2.2.2 Experimental Methods and Procedures

The experimental plan was designed to evaluate the effect of various operating variables on TCE transformation. These variables include the type of anode and cathode materials,
current density, initial TCE concentration, background electrolyte type, and concentration
(Table 3-2). TCE transformation experiments were conducted in undivided glass
electrochemical cell (Figure 3-5) at ambient room temperature (25 °C). The liquid and
headspace volume were 115 mL and 67 mL, respectively. Although a 150 mL syringe was
connected to the electrochemical cell to enable gas expansion during electrolysis, no gas
expansion was observed during 5 hours of electrolysis. The anode and cathode were
pretreated prior to assembly and placed in parallel position with 1.7 cm between distance
to obtain homogeneous distribution of current on electrodes. The appropriate amount of
electrolyte solution (0.01 M NaHCO₃ for most of the experiments) was added, and then the
solution was spiked with saturated TCE solution. The solution was stirred 30 minutes with
a Teflon coated one inch magnetic stirring bar with a speed of 500 rpm to allow TCE
equilibrium between aqueous and gas phase. The initial concentration of TCE was checked
by withdrawing an aqueous sample. The electric current was then applied and TCE
concentration and hydrocarbon gas concentrations were routinely measured. For some of
the experiments, pH and ORP values were measured during the electrolysis by taking 0.2
mL aqueous samples. The final pH, ORP, conductivity, and chloride ion concentrations
were also measured.
Table 3-2 The experiment list for the evaluation of operating variables on TCE dechlorination kinetics

<table>
<thead>
<tr>
<th>Variables</th>
<th>Anode Material</th>
<th>Cathode Material</th>
<th>Current (mA)</th>
<th>Electrolyte</th>
<th>Initial TCE (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>NA</td>
<td>NA</td>
<td>no current</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>Anode type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>PbO₂</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>MMO</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cathode types</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous iron</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Pure iron (plate)</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous nickle</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous carbon</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Copper plate</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Initial TCE concentration and current density</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>5</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>10</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>20</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>60</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>5</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>10</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>20</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>60</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>5</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>10</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>20</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>60</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Background electrolyte type and concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>30</td>
<td>0.05 M Na(HCO₃)</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Porous copper</td>
<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Copper plate</td>
<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Copper plate</td>
<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Cast iron</td>
<td>Copper plate</td>
<td>30</td>
<td>0.01 M Na(HCO₃) +0.05 M NaNO₃</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>
Aqueous TCE, DCE, and VC concentrations were determined using the purge and trap method with gas chromatography (SRI GC 8610C, USA), which was equipped with a photo ionization detector (PID) and MXT-VOL stationary column (L=15 m, inner diameter=0.53 mm, DF=3). Helium was used as a carrier gas which was pretreated with a gas filter. The purge and trap autosampler system was equipped with a carbon-sieve trap and Tenax™ trap, which enable the detection of highly volatile compounds like VC. 50 μL aqueous samples were withdrawn from the electrochemical cell and injected into 5 mL of distilled water in a glass tube. The glass tube was loaded immediately to the 10 ports autosampler. The solution was purged at flow rate 1.5 mL min⁻¹ for 5 minutes before injection to the trap. The GC was set to hold at 40 °C for 6 minutes and then ramp to 60 °C in 2 minutes, then holding again at 60 °C for 10 minutes.
Hydrocarbon gases in the headspace of the electrolytic cell were analyzed by Model 310 GC (SRI, USA) with flame ionization detector (FID) and Haysep-T column. 100 μL gas taken from the headspace was injected to the GC directly through on-column port. The Model 310 GC was set to increase the temperature from 40 °C to 140 °C at a rate of 15 °C min⁻¹, holding at 140 °C for 1 minute, and then cooled to 40 °C at a rate of 20 °C min⁻¹.

Chloride ion concentration was analyzed by Dionex DX-120 ion chromatograph. A 0.5 mL aqueous sample was taken from the electrolytic cell after each experiment; the sample was diluted to 5 mL and filtered with 0.45 μm pore size filter paper prior to analysis.

pH and oxidation-reduction potential (ORP) values were measured using microprobes (Microelectrodes Inc., USA) and corresponding meters, and initial and final conductivity values were measured by using a corresponding conductivity meter and probe.

3.3 Recirculation Experiments for the Optimization of Electrochemical Operating Variables

3.3.1 Materials

The chemicals used include TCE (99.5%, Sigma-Aldrich), cis-DCE (97%, Sigma-Aldrich), VC (analytical standard, 200 μg mL⁻¹ in methanol, Supelco), hydrocarbon gas standard (analytical standard, 1% (w/w) methane, ethane, ethene, acetylene in nitrogen, Supelco), and anhydrous Na₂SO₄ (99%, BDH). Saturated TCE solution was prepared as stock solution by dissolving TCE in double-distilled water (18 MΩ cm). The stock solution was kept at a temperature of 20 °C to maintain 1.07 mg mL⁻¹ dissolution concentration. Cast
iron anode (mesh type, 3N International, USA) and copper foam (99.99%, 40 pores per inch (PPI), ERG, USA) were used as anode and cathode materials, respectively. The cast iron electrodes were round disks with a 5 cm diameter and 0.2 cm thickness. The copper foam electrodes were round disks with a 5 cm diameter and varying electrode thicknesses from 3.175 mm to 9.525 mm. The surface of the iron electrodes were polished with sand paper, etched in diluted HCl solution (1%), sonicated with 2% Micro-90 cleaning solution (Cole-Parmer, USA), and washed several times with distilled water. The copper foam electrodes were soaked in a diluted HCl solution (1%), washed with 2% Micro-90 cleaning solution, and finally washed several times with distilled water prior to assembly.

3.3.2 Experimental Methods and Procedures

The experimental setup consists of an electrochemical reactor, a peristaltic pump, and a sampling reservoir as seen in Figure 3-6. The electrochemical reactor was made of acrylic with a volume of 125 mL. The anode and cathode were pretreated prior to assembly and placed in parallel position with 4 cm distance between to obtain homogeneous distribution of current on electrodes. The electrodes were connected to a DC source (HP 3160, USA) from the backside of the electrode using two pieces of stainless steel and copper washers as shown in Figure 3-6b. Glass tube, PTFE tubing (Cole Parmer, USA), and Viton pump tubing (Cole Parmer, USA) were employed to minimize the loss of TCE due to adsorption. The head of the sampling reservoir was connected to a syringe, which allows for headspace gas expansion when the internal gas pressure is more than 12kPa. The appropriate amount of Na2SO4 solution (260 mL for most of the experiments) was added, and the solution was then spiked with saturated TCE solution to achieve the desired initial TCE concentration.
The total volume of Na₂SO₄ solution and saturated TCE was maintained at 270 mL for all experiments. The solution was circulated for 30 minutes at 320 mL min⁻¹ to allow for TCE equilibrium between the aqueous and gas phase. The initial concentration of TCE was checked by withdrawing an aqueous sample. The electric current was then applied. Aqueous and gas samples were taken routinely to measure aqueous TCE concentration, chloride ion concentration, hydrocarbon gas concentrations in the headspace of electrolytic cell, pH, ORP, conductivity, and dissolved oxygen (DO) using the instruments and methods explained in Section 3.2.2.2.
In this study, the effects of the operating variables including initial TCE concentration, foam cathode thickness, current intensity, and electrolyte ionic conductivity on the final elimination efficiency (FEE, %) and specific energy consumption (SEC, kW h kg\(^{-1}\)) were investigated. The following equations were used for FEE and SEC calculations:

\[ 3-1 \quad FEE = 1 - \frac{c_{aq(t)}}{c_{aq(0)}} \left[ 1 + \frac{H_{TCE} \Delta V_h}{V_{aq} + H_{TCE} V_h} \right] \times 100\% \]

\[ 3-2 \quad SEC = I \cdot U \cdot \frac{1}{C_{aq(0)} \cdot (V_{aq} + H_{TCE} V_h) \cdot FEE} \]
where $C_{aq}(0)$ and $C_{aq}(t)$ are the aqueous TCE concentration at zero time and $t$ time (mg L$^{-1}$), $V_{aq}$ and $V_h$ are the initial volume of liquid (270 mL) and initial headspace of reservoir (20 mL), respectively. $\Delta V_h$ is the volume of headspace expansion at time $t$ (mL), $H_{TCE}$ is the dimensionless Henry’s Law constant for TCE, $I$ is the applied current intensity (A), $U$ is the cell voltage of the cell, and $t$ is the electrolysis time (sec).

A multivariable statistical analysis was designed and used to investigate the effects of operating variables and to determine the optimal conditions in order to maximize TCE transformation efficiency. The range of parameters used in the experimental design are listed in Table 3-3. The experimental design matrix consists of three series of experiments$^{154,155}$: (i) a two level full factorial design 24 (all possible combination of codified values +1 and -1); (ii) six central, replicates of the central point (0); and (iii) eight axial points located at the center of both extreme levels of the experimental models. Table 3-4 lists the series of experiments and variables used for each experiment in this part.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Parameter</th>
<th>Low (-1)</th>
<th>Center (0)</th>
<th>High (+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>[TCE] (mg L$^{-1}$)</td>
<td>28</td>
<td>42</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Thickness of foam cathode, mm</td>
<td>3.175</td>
<td>6.35</td>
<td>9.525</td>
</tr>
<tr>
<td>C</td>
<td>Current (mA)</td>
<td>40</td>
<td>80</td>
<td>120</td>
</tr>
<tr>
<td>D</td>
<td>$[\text{Na}_2\text{SO}_4]$ (mol L$^{-1}$)</td>
<td>0.002</td>
<td>0.022</td>
<td>0.042</td>
</tr>
</tbody>
</table>
Table 3-4 List of experiments and operating parameters used for each experiment

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Variable levels</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A [TCE]</td>
<td>B Thickness</td>
<td>C Current</td>
<td>D [Na₂SO₄]</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>12</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>15</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>19</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>21</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>23</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>24</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>27</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>28</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>
3.4 Flow-Through Column Experiments

3.4.1 Sand-Packed Flow-Through Experiments for Chemical Changes

3.4.1.1 Materials

The column was machined using a 6.3 cm (2.5 in.) cast acrylic cylinder tube (McMaster Carr, USA) in the machine shop at Northeastern University. The column was composed of different sections to place the electrodes accordingly. PVC pipe fittings (McMaster Carr, USA) were used to connect the sections of the column. The pipe fittings were machined so that the electrodes were vertical to the flow direction as shown in Figure 3-7. Mixed metal oxide mesh electrodes and cast gray iron electrodes were cut to 8.3 cm in diameter with 0.64 cm thickness. The iron electrodes were perforated to maintain water flow through the electrodes. The column was packed with quartz sand (Ottawa testing sand) for the flow through column experiment. The solution was pumped with a peristaltic pump (Cole-Parmer, USA) equipped with 0.89 mm and 1.42 mm inner diameter tygon autoanalysis tubing (Cole-Parmer). The tubing allows for a flow rate between 0.36 to 4.9 mL min⁻¹.

3.4.1.2 Experimental Methods and Procedures

Table 3-5 presents a summary of the experimental variables used to evaluate the effect of anode type, current density, flow rate and electrolyte composition on temporal chemical changes (pH and ORP) in flow-through column setup. The main aim of this part was to understand the distribution of the chemical changes under flow and to mimic electrolysis in groundwater.
Figure 3-7 shows the schematic of the column. The column consists of 3 pieces. The pieces were combined using pipe fitting flanges and bolts. The flange was drilled from the side and 4 stainless steel screws were inserted through these holes to provide an electrical connection between the electrodes and the DC source as shown in Figure 3-7. The total length of the column was 82 cm, and the inner diameter was 6.35 cm. Six sampling ports were fabricated using Swagelok fittings and septa; 1 before the anode; 3 between the anode and cathode; and 2 after the cathode. Electrodes, 8.3 cm (3.25 in.) in diameter, were placed parallel to each other and vertical to the flow direction to provide 1-D transport of the electrolysis compounds and to maintain a homogeneous distribution of the electric fields. The distance between anode and cathode was 24 cm. Total amount of sand used for each experiment was around 4 kg, and the bulk density of air-dry sand in the column before the experiment was 1.56 g cm$^{-3}$. After the column was assembled, the solution was pumped through the column until the sand in the column was saturated. Then, the DC source was turned on and the pH and redox potential variables were measured by collecting 0.5 mL liquid solution from each sampling port.
Table 3-5 The experiment list with sand-packed flow-through column setup

<table>
<thead>
<tr>
<th>Variables</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte (0.02 M)</th>
<th>Current (mA)</th>
<th>Flow Rate (mL min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrode Types</strong></td>
<td>MMO</td>
<td>MMO</td>
<td>Na₂SO₄</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂SO₄</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td><strong>Current Density</strong></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂SO₄</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂SO₄</td>
<td>40</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂SO₄</td>
<td>80</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td><strong>Flow Rate</strong></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂SO₄</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂SO₄</td>
<td>20</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂SO₄</td>
<td>20</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td><strong>Background Electrolyte</strong></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>NaHCO₃</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
</tbody>
</table>
Figure 3-7 Schematic of sand-packed flow-through column
The pH and the oxidation reduction potential (ORP) were measured by microelectrode probes (Microelectrodes Inc., USA); an aliquot of 0.5 mL electrolyte was sampled from compartments for pH and ORP measurements. Total dissolved iron and precipitated iron concentrations were determined using 1, 10 Phenantroline method. Details of this method are explained in Section 3.2.1.2.

3.4.2 Experiments for the Assessment of Hydraulic Conductivity Change

3.4.2.1 Experimental Procedures

The ASTM D2434-68 constant-head permeability device was customized as seen in Figure 3-9 to evaluate iron electrolysis on the hydraulic conductivity in the sand-packed flow-through column. The experimental device consists of 3 parts: a base, column, and top that were connected to each other using a stainless steel threaded rod. The column dimensions
were 30.5 cm in height with a 6.35-cm inner diameter. MMO mesh electrodes and iron electrodes, 6.2 cm diameter, were placed parallel to each other and vertical to the flow direction at 7.5 cm and 11.5 cm from the inlet of the column. Iron electrodes were perforated to allow the water flow in the column. Four titanium rods (2.54 cm length, 6.35 mm diameter) were placed at electrode levels with quarter-inch Swagelok compression fittings to hold the electrodes in place and to provide electrical connection. Titanium was selected for the electrical connections due to its inert characteristic under electrical current. A porous stone (6.35-cm diameter and 0.64 cm thickness) and a filter paper were placed at the bottom of the column to provide homogeneous distribution of the flow in the column. The column was filled with Ottawa quartz sand (specific gravity is 2.67) up to the first electrode level before placing the first electrode. A 1-cm gap was left unfilled with sand on top of the first electrode to prevent sand from clogging the drilled holes on the iron electrodes. The column was filled with quartz sand after second electrode was placed. After the column was assembled, 20 mM sodium sulfate solution was pumped through the column until the sand in the column was completely saturated. Hydraulic conductivity of the sand in the column was measured before and after applying electrolysis using a ASTM constant head hydraulic conductivity test \(^{156}\). The total mass of the pumped solution was recorded to calculate average flow rate. Voltage values were also recorded manually during the experiment.

The permeability test is based the Darcy’s Law;

\[
3-3 \quad Q = -kiA,
\]
where \( k \) is the hydraulic conductivity of soil in the column (cm sec\(^{-1}\)), \( Q \) is discharge of solution through a cross section per unit time (cm\(^3\) sec\(^{-1}\)), \( i \) is the hydraulic gradient and equals \( h_L/L \), where \( h_L \) (cm) is the head loss along the flowpath and \( L \) (cm) is the length of the flowpath, and \( A \) is the cross-sectional area of the specimen (cm\(^2\)).

Figure 3-9 The experimental setup for permeability experiments
Table 3-6 Experiment list for the investigation of hydraulic conductivity change during iron electrolysis

<table>
<thead>
<tr>
<th>Variables</th>
<th>Electrodes (Anode-Cathode)</th>
<th>Current (mA)</th>
<th>Electrolysis Duration, h</th>
<th>Flow rate (mL min⁻¹)</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>Cast Iron-MMO</td>
<td>60</td>
<td>72</td>
<td>0.49±0.03</td>
<td>0.02 M Na₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Cast Iron-MMO</td>
<td>60</td>
<td>72</td>
<td>0.91±0.01</td>
<td>0.02 M Na₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Cast Iron-MMO</td>
<td>60</td>
<td>72</td>
<td>1.80±0.01</td>
<td>0.02 M Na₂SO₄</td>
</tr>
<tr>
<td>Current Intensity</td>
<td>Cast Iron-MMO</td>
<td>5</td>
<td>72</td>
<td>0.85±0.04</td>
<td>0.02 M Na₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Cast Iron-MMO</td>
<td>15</td>
<td>72</td>
<td>0.82±0.02</td>
<td>0.02 M Na₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Cast Iron-MMO</td>
<td>30</td>
<td>72</td>
<td>0.82±0.00</td>
<td>0.02 M Na₂SO₄</td>
</tr>
<tr>
<td>Electrolysis Duration</td>
<td>Cast Iron-MMO</td>
<td>30</td>
<td>6</td>
<td>0.94±0.02</td>
<td>0.02 M Na₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Cast Iron-MMO</td>
<td>30</td>
<td>12</td>
<td>0.91±0.01</td>
<td>0.02 M Na₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Cast Iron-MMO</td>
<td>30</td>
<td>24</td>
<td>0.89±0.01</td>
<td>0.02 M Na₂SO₄</td>
</tr>
<tr>
<td>Anode Material</td>
<td>MMO-MMO</td>
<td>30</td>
<td>3</td>
<td>0.92</td>
<td>0.02 M Na₂SO₄</td>
</tr>
</tbody>
</table>

3.4.3 Limestone Gravel-Packed Flow-Through Column Experiment for the Regulation of Chemical Properties in the Effluent and the Evaluation of TCE Transformation Under Flow

3.4.3.1 Materials

The chemicals used include TCE (99.5%, Sigma-Aldrich), sodium sulfate (reagent grade, Fisher chemical), sodium bicarbonate (reagent grade, Fisher chemical), and hydrocarbon gas standard (analytical standard, 1% (w/w) methane, ethane, ethene, acetylene in nitrogen, Supelco). Saturated TCE solution was prepared as stock solution by dissolving TCE in double-distilled water (18 MΩ cm). The stock solution was kept at a temperature of 20 °C to maintain 1.07 mg mL⁻¹ dissolution concentration. The electrode materials were cast iron
(McMaster Carr, USA), MMO (mesh type, 3N International, USA), copper plate (99.9% purity, VWR), and copper foam (99.99%, 40 pores per inch (PPI), ERG, USA). The electrodes were round disks with 6.2 cm diameter. The electrode thicknesses were 5 mm for the iron and copper plates and 1.27 mm for copper foam. The plate electrodes (iron and copper plate) were evenly perforated (21 holes with 4.6 mm diameter) to maintain water flow through the column. Limestone gravels, 4.75–9.5 mm particle size, were used to fill the column to mimic karstic aquifer conditions. The surface of the iron electrodes were polished with sand paper, etched in diluted HCl solution (1%), sonicated with 2% Micro-90 cleaning solution (Cole-Parmer, USA), and washed several times with distilled water. The copper electrodes were soaked in diluted HCl solution (1%), washed with 2% Micro-90 cleaning solution, and finally washed several times with distilled water prior to assembly.

3.4.3.2 Experimental Methods and Procedures

Two reactors were constructed for this part of testing, as shown in Figure 3-10. Reactor A was used for the pH and OPR regulation experiments in the effluent. Reactor B was used to test TCE transformation under flow. Reactor A was manufactured using 2 pieces of cast acrylic cylinder tubes (McMaster Carr, USA) which were connected to each other with PVC pipe fittings (McMaster Carr, USA). The bottom section was filled with limestone gravel up to anode-1 level, and then electrodes were placed vertical to the flow direction to achieve one-dimensional flow through the column as shown in Figure 3.3. The upper section of the column was connected to the bottom piece and filled with limestone gravel, providing space and time for chemical equilibrium before pH and ORP measurements after
the column. Reactor B was shorter and designed to quickly achieve steady-state condition in the transformation experiment. The void volume of reactors A and B were 0.80 and 0.50 L, respectively. Four stainless steel bolts were used for electrical connection to the electrodes. All sampling ports were sealed with Swaglok nuts and septa. The solution was pumped with a peristaltic pump (Cole-Parmer, USA) equipped with Viton tubing. Darcy’s velocities of the pumped solution in the column reactors were 0.9 m d⁻¹ and 1.8 m d⁻¹. Two and three electrode arrangements were tested in the columns. When the three-electrode arrangement (two anodes, one anode) was used, the applied current was distributed between two anodes by an adjustable resistance as shown in Figure 3-10. Simulated groundwater was prepared dissolving 0.413 g L⁻¹ NaHCO₃ and 0.172 g L⁻¹ CaSO₄ in deionized water or tap water. The concentrations of bicarbonate and calcium ions are representative of groundwater from karstic aquifers, resulting in a conductivity range of 800-920 µS cm⁻¹. The prepared solution was stored in a 10 L Tedlar bag and the contaminants were injected into the solution before starting each experiment. Solutions were pumped from the Tedlar bag into the column reactor for 30 minutes before starting the electricity, to produce a homogeneous distribution of the contaminants in the column. Control experiments without electricity were conducted to evaluate the significance of adsorption of contaminants on limestone, with results showing that contaminant loss due to adsorption was negligible within the duration of experiment.

Table 3-7 lists the experiments conducted for this investigation. pH and ORP changes in the effluent were continuously monitored using pH and ORP probes (Foundriest
Environmental Company) connected with a computer via the USB interface. Aqueous TCE concentration was analyzed using a SRI 8610 GC instrument equipped with a purge-trap system and FID detector. Hydrocarbon gases were analyzed using SRI 310 GC with FID detector. The details of GC operation programs for these analyses are explained in Section 3.2.2.2. Chloride ion concentrations were measured using a Dionex 5000 ion chromatography (IC) equipped with an AS20 analytical column. 35 mM KOH solution was used as mobile phase at a flow rate of 1 mL min⁻¹. The iron species in the effluent were determined using a spectrophotometer (Jasco spectrophotometer V550) (see Section 3.2.1.2 for details of this analysis).
Figure 3-10 Reactor A, Reactor B and schematic of electrical connection
Table 3-7 List of experiments for the evaluation of two- and three-electrode system for pH and ORP changes in effluent and TCE degradation efficacy

<table>
<thead>
<tr>
<th>Objective</th>
<th>Electrode configuration</th>
<th>TCE in influent (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Regulation of pH and ORP in effluent</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MMO (30 mA)</td>
<td>Cu foam (30 mA)</td>
<td>--</td>
</tr>
<tr>
<td>MMO (60 mA)</td>
<td>Cu foam (60 mA)</td>
<td>--</td>
</tr>
<tr>
<td>MMO (60 mA)</td>
<td>Cu foam (60 mA)</td>
<td>--</td>
</tr>
<tr>
<td>Cast iron (30 mA)</td>
<td>Cu foam (30 mA)</td>
<td>--</td>
</tr>
<tr>
<td>Cast iron (30 mA)</td>
<td>Cu foam (30 mA)</td>
<td>--</td>
</tr>
<tr>
<td>Cast iron (30 mA)</td>
<td>Cu foam (30 mA)</td>
<td>--</td>
</tr>
<tr>
<td>Cast iron (60 mA)</td>
<td>Cu foam (120 mA)</td>
<td>MMO (60 mA)</td>
</tr>
<tr>
<td>Cast iron (30 mA)</td>
<td>Cu foam (90 mA)</td>
<td>MMO (60 mA)</td>
</tr>
<tr>
<td>Cast iron (60 mA)</td>
<td>Cu foam (90 mA)</td>
<td>MMO (30 mA)</td>
</tr>
</tbody>
</table>

| **Assessment of three-electrode system for TCE degradation** | | |
| MMO | Cu foam | -- | 34.7 |
| -- | Cu foam | MMO | 34.9 |
| Cast iron | Cu foam | -- | 34.8 |
| -- | Cu foam | MMO | 35 |
| Cast iron (45 mA) | Cu foam | MMO (45 mA) | 34.8 |
| Cast iron (45 mA) | Cu foam | MMO (45 mA) | 34.8 |
| Cast iron (60 mA) | Cu foam | MMO (30 mA) | 34.7 |
| -- | Cu foam | MMO | 4.9 |
| Cast Iron | Cu foam | -- | 4.9 |
CHAPTER 4

4 Results and Discussion

4.1 Introduction

This chapter presents a summary and discussion of the experimental results in three main parts:

(i) Section 4.2 describes chemical changes and TCE degradation kinetics with varying operating conditions. Specifically, Section 4.2 discusses various anode and cathode materials in terms of chemical changes and TCE removal efficiencies. The section ends with a recommendation of the most effective electrode couple for TCE degradation.

(ii) Section 4.3 evaluates optimum operating conditions using the electrode couple selected in Section 4.2.

(iii) Section 4.4 presents a discussion of the physical and/or chemical changes and TCE removal efficiencies of the selected electrode couple under flow. Section 4.4 suggests three-electrode electrochemical system for the effective removal of TCE in groundwater.
4.2 Batch Experiments for the Evaluation of the TCE Dechlorination Effectiveness and Chemical Changes Due to Iron Electrolysis

4.2.1 Batch Experiment for Temporal Chemical Changes in pH and ORP

4.2.1.1 Effect of Electrode Types

Temporal chemical changes in divided- and mixed-electrolytes were evaluated in 0.02 M Na₂SO₄ background electrolyte. As shown in Figure 4-1a, the pH of mixed electrolyte with inert electrodes did not change significantly since the H⁺ produced at the anode neutralizes the OH⁻ produced at the cathode. The electrolyte pH with iron electrodes increased to 10.5 (Figure 4-1b) because there is no or limited formation of H⁺ ions at the iron anode to neutralize the OH⁻ released from the cathode. Instead, the dissolution of iron is the dominating reaction on the anode as given by,

\[
4-1 \quad \text{Fe} - 2e^- = \text{Fe}^{2+}
\]

Depending on the pH, ferrous ions may subsequently form ferrous hydroxides (Fe(OH)₂(s), pKso = 15.1)\(^{158}\). The ORP data in Figure 4-1 show critical differences. The ORP values of the mixed electrolyte with inert electrodes decreased from 217 mV to 160 mV in the first 2 hours, then stabilized around 150 mV (Figure 4-1a). In contrast, the ORP of the mixed electrolyte with iron electrodes steadily dropped to -444 mV in 5 hours (Figure 4-1b), showing buildup of reducing electrolyte condition.

When the anolyte and catholyte were divided by an ion exchange membrane (Figure 4-1a), the pH in the anolyte was acidic (≈ 2) and that in the catholyte was alkaline (≈11.5) when
MMO electrodes were used. The iron anode limits change in the anolyte pH due to little or no H\(^+\) production. A slight decrease was observed during the first 2 hours in the anolyte (Figure 4-1b). This is explained by the oxidation of the ferrous species by the dissolved oxygen in electrolyte. The formation of solid ferric hydroxides (pK\(_{so}\) of Fe(OH)\(_3\)\(_{(s)}\) is 38.8) induces the production of protons, leading to a slight pH drop, as given by:

\[
4Fe^{2+} + 10\text{H}_2\text{O} + \text{O}_2(g) = 4\text{Fe(OH)}_3(s) + 8\text{H}^+
\]

The ORP of the anolyte with MMO anode (Figure 4-1a) was highly oxidizing (≈450 mV) due to oxygen production from water electrolysis by the inert anode. By contrast, the anolyte ORP was low and more chemically reducing (11 mV, Figure 4-1b) with an iron anode. The main reason is that ferrous ions, instead of protons and oxygen gas, were produced at the anode. Ferrous species show reducibility to consume the oxidative components, such as dissolved oxygen (Equation 4-2), in the electrolyte. Furthermore, with increasing pH, the reducibility of ferrous species (such as ferrous hydroxides) increases progressively\(^{158}\). Changes in pH and ORP values in catholyte were consistent for both inert and iron electrodes because cathodic reactions are the same, water reduction (Equation 4-3). The pH increased to 11.5 and the ORP decreased to -340 mV in one case and -250 mV in the other case (Figure 4-1). The reducing potential (negative ORP) is due to the consumption of oxidative substances such as O\(_2\) through the reaction with iron species.

\[
2\text{H}_2\text{O} + 2\text{e}^- = 2\text{OH}^- + 2\text{H}_2
\]

The above observations show significant differences in the effect of using iron (reactive) versus MMO (inert) electrodes on the pH and redox change of the electrolytes. Water
oxidation is the main reaction at the anode of inert electrodes, therefore oxygen gas (O₂) and hydrogen ions (H⁺) are produced at the anode of inert electrodes. Iron dissolution is the governing reaction at the anode of iron electrodes and ferrous ions (Fe²⁺) are produced as the main product. The main cathodic reaction is water reduction, which is the same for iron and inert electrodes. The oxidation rates of iron and the flux of ferrous ions per electrolyte volume are controlled by the electric current. The rate can be calculated following Faraday’s law,

\[ \text{Equation 4-4} \quad J_{\text{Fe(II)}}^e = \frac{I}{n_{\text{Fe(II)}}V_a} = \alpha \frac{I}{2V_aF} \]

\[ \text{Equation 4-5} \quad \alpha = \frac{2V_aFJ_{\text{Fe(II)}}^e}{I} \]

\[ \text{Equation 4-6} \quad \bar{\alpha}_{0\rightarrow t} = \frac{2V_aFJ_{\text{Fe(II)}}^e}{I\Delta t} \]

where \( J_{\text{Fe(II)}}^e \) is the rate of electrolytic oxidation (in mol m⁻³ s⁻¹) of Fe(0) into Fe(II), \( n_{\text{Fe(II)}} \) is the number of electrons transferred, \( V_a \) is the volume of the anolyte (for divided-electrolyte) or total electrolyte volume (for mixed electrolyte), \( I \) is the electric current, \( \alpha \) is instant iron dissolution efficiency, and \( \bar{\alpha}_{0\rightarrow t} \) is the average iron dissolution efficiency from time zero to time \( t \). In Equation 4-4, the current is divided by the electrolyte volume to evaluate the current per volume of electrolyte (A m⁻³). This is mainly because it is important to evaluate the impact of electrolysis on the electrolyte chemistry.

Other electrolysis reactions that may occur at the anode include the oxidation of ferrous (Equation 4-7, \( E^\circ = 0.77 \) V vs. SHE) and water decomposition (Equation 4-8, \( E^\circ =1.23 \) V vs. SHE).
4-7 \[ Fe^{2+} = Fe^{3+} + e^- \]
4-8 \[ 2H_2O = 4H^+ + O_2 + 4e^- \]

Comparing the electrochemical standard potential shows that the electrolytic transformation of iron to Fe(II) has a significantly lower standard potential (+0.44 V). Therefore, oxidation of Fe(0) to Fe(II) is the dominant electrolytic reaction at the anode. As a result, the electrolyte pH and redox potential significantly change due to the ferrous species.
Figure 4-1 pH and ORP profiles in divided-electrolyte and mixed-electrolyte, 0.02 M Na$_2$SO$_4$ background electrolyte, 112.5 mA L$^{-1}$ current density (a) MMO electrodes (b) Iron electrodes.
4.2.1.2 Effect of Background Electrolyte on Iron Electrolysis

The electrolyte composition had significant effects on chemical and physicochemical changes induced by iron electrolysis due to the complexation of ferrous and ferric ions with existing anions and the precipitation of produced solid species. Mixed-electrolyte experiments were conducted using 0.02 M NaCl, Na₂SO₄, and NaHCO₃ solution; changes in electrolyte pH and ORP values were recorded. In addition, iron speciation and the average iron dissolution efficiency ($\alpha$) within 5 hours in different background electrolytes were compared. In Figure 4-2a, the pH of the mixed bicarbonate solution was stable around 8 in the first 4 hours due to its buffer capacity. Afterwards, the buffer capacity was exceeded by the OH⁻ released from the cathode and pH subsequently increased to 8.9. The pH values of the mixed sulfate and chloride electrolytes increased steadily as a result of electrolysis. At the end of the experiment, the pH of the Na₂SO₄ (∼10.5) electrolyte was slightly higher than that of the chloride solution (∼10.0).

Initially, the ORP value of the mixed bicarbonate solution was lower (87 mV) than sulfate and chloride solutions (Figure 4-2a). Over time, the sulfate electrolyte showed a constant decrease in ORP, and by the end of testing, the sulfate electrolyte was the most reducing (-444 mV).

Although chloride, sulfate, and carbonate anions can form ferrous ion complexes, based on the equilibrium data, the primary metal ligands in the solution were ferrous hydroxides (Table 4-1). Some ferrous ions can be further oxidized to ferric ions with the presence of dissolved oxygen. Ferric ions produced some ferric complexes with existing ligands as
well. Ferric hydroxide precipitations (yellow to brownish color) were observed in the early stage of the experiment and ferrous hydroxide precipitations (dark green color) were observed at the end of the experiment. Dissolved iron, ferrous, and ferric precipitates are summarized in Table 4-2 for varying electrolyte composition. Dissolved iron was not observed in the bicarbonate solution because of the high initial pH (≅8). Dissolved iron was detected in the sulfate solution (7.3%) and in the chloride solution (4.4%) in the first hour; however, in later stages of the experiments, all dissolved iron precipitated due to the pH increase. At the end of 5 hours of electrolysis, the ratio of ferrous precipitates to ferric precipitates was higher in the chloride and sulfate solutions compared to the bicarbonate solution, leading to a more reducing condition. Total iron concentrations were 8.9 mM for the sulfate solution, 6.9 mM for the chloride solution and 9.6 mM for the bicarbonate solution. The average iron dissolution efficiencies were 85%, 66%, and 92% in the sulfate, chloride, and bicarbonate solutions, respectively.
Table 4-1 The equilibrium constants of the ferrous and ferric complexes with sulfate, chloride and bicarbonate anions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe^{2+} + 2H_2O = 2H^+ + Fe(OH)_2 (aq)</td>
<td>-20.494</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe^{3+} + 2H_2O = 2H^+ + Fe(OH)_2^+</td>
<td>-5.75</td>
<td>LiuMill99</td>
</tr>
<tr>
<td>Fe^{2+} + 3H_2O = 3H^+ + Fe(OH)_3^-</td>
<td>-30.991</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe^{3+} + 3H_2O = 3H^+ + Fe(OH)_3 (aq)</td>
<td>-15</td>
<td>LiuMill99</td>
</tr>
<tr>
<td>Fe^{3+} + 4H_2O = 4H^+ + Fe(OH)_4^-</td>
<td>-22.7</td>
<td>LiuMill99</td>
</tr>
<tr>
<td>2Fe^{3+} + 2H_2O = 2H^+ + Fe_2(OH)_2^2+</td>
<td>-2.894</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>3Fe^{3+} + 4H_2O = 4H^+ + Fe_3(OH)_4^+</td>
<td>-6.288</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe^{2+} + Cl^- = FeCl^+</td>
<td>-0.2</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe^{3+} + Cl^- = FeCl^2</td>
<td>1.48</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe^{2+} + H_2O = H^+ + Fe(OH)^+</td>
<td>-9.397</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe^{3+} + H_2O = H^+ + Fe(OH)_2^+</td>
<td>-2.02</td>
<td>LiuMill99</td>
</tr>
<tr>
<td>Fe^{3+} + 2SO_4^2- = Fe(SO_4)_2</td>
<td>5.38</td>
<td>Nord 90</td>
</tr>
<tr>
<td>Fe^{2+} + SO_4^2- = Fe(SO_4) (aq)</td>
<td>2.39</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe^{3+} + SO_4^2- = Fe(SO_4)^+</td>
<td>4.25</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe^{2+} + CO_3^2- + H^+ = FeHCO_3^+</td>
<td>11.429</td>
<td>NIST 46.7</td>
</tr>
</tbody>
</table>
Table 4-2 Iron speciation in sulfate, chloride and bicarbonate solutions at different times, 112.5 mA L$^{-1}$ current density, mixed-electrolyte (total volume 400 mL), and cast iron electrodes

<table>
<thead>
<tr>
<th>Time h</th>
<th>0.02 M Na$_2$SO$_4$</th>
<th>0.02 M NaCl</th>
<th>0.02 M NaHCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dissolved</td>
<td>Fe$^{2+}$</td>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td></td>
<td>Iron</td>
<td>precipitates</td>
<td>percent</td>
</tr>
<tr>
<td>1</td>
<td>7.3</td>
<td>13.2</td>
<td>79.5</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>33.5</td>
<td>66.5</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>45.0</td>
<td>55.0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>52.4</td>
<td>47.6</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>59.7</td>
<td>40.3</td>
</tr>
</tbody>
</table>
Figure 4-2 pH and ORP profiles (a) in different electrolyte compositions using iron electrodes, 112.5 mA L⁻¹ current density, mixed-electrolyte; (b) with different current densities (mA L⁻¹), using iron electrodes, in 0.02 M Na₂SO₄ mixed-electrolyte.
4.2.1.3 Effect of Different Current Densities on Iron Electrolysis

The electrolyte pH decreased slightly from 5.6 to 4.9 for the lowest current density (37.5 mA L$^{-1}$) in the first 2 hours (Figure 4-2b), because ferrous ion oxidation with existing oxygen lead to H$^+$ production. The pH value then increased slightly to 5.8 and stabilized. When the current density was increased, OH$^-$ production and pH at the cathode increased. The maximum observed pH was 10.7 for 150 mA L$^{-1}$ (Figure 4-2b). The ORP values for different current densities also showed a similar trend as with pH. The most reducing solution was observed under 150 mA L$^{-1}$. According to the pe-pH diagram$^{158}$ of iron species, the basic pH enables more Fe(OH)$_2$ (s) precipitation and a more reducing condition (lower ORP).

Dissolved iron species were detected in the electrolyte after 1 hour (Figure 4-3) for all current densities. As electrolysis progressed, the dissolved iron gradually disappeared and only 37.5 mA L$^{-1}$ shows dissolved iron after 5 hours electrolysis. The data is in agreement with the pH data in Figure 4-2b. According to the pH data, the pH values after 2 hours under 37.5 mA L$^{-1}$ and 75 mA L$^{-1}$ were less than 7, which allows for the presence of dissolved ferrous ions.
Figure 4-3 Iron speciation at different current densities (37.5, 75, 112.5, 150 mA L\textsuperscript{-1}). The asterisk (*) means under detection limit.
4.2.1.4 Polarity Reversal with Iron Electrolysis

Polarity reversal is a convenient and useful method to clean the scale and fouling on electrodes and prevents the passivation of iron electrode. The effect of polarity reversal of iron electrolysis on redox and pH conditions in divided anolyte and catholyte was also evaluated. After application of the current for 5 hours, the polarity was reversed for the next 5 hours. In the first 5 hours, the pH in the anolyte dropped from 5.4 to 4.2 in 2 hours and then increased up to 5.8 (Figure 4-4a) due to the formation of ferrous and ferric hydroxides; additionally, pH in the catholyte increased up to 12 (Figure 4-4b) due to water electrolysis. After polarity reversal, the pH in the new catholyte (Figure 4-4a) was stable for about one hour because the OH– being produced reacted with existing ferrous and ferric ions. The pH then sharply increased up to 12, and all ferrous ions immediately precipitated, mostly in the form Fe(OH)\textsubscript{2} (s). As shown in Figure 4-4b, the pH change in the new anolyte was not significant for the first 2 hours, but the pH dropped after that because of precipitation of ferrous hydroxides. The final pH in the anolyte was around 6.5 (Figure 4-4b).

The ORP value in the anolyte (Figure 4-4a) decreased to -150 mV in the first 5 hours due to ferrous production at the anode, and the ORP in the catholyte (Figure 4-4b) dropped to below -300 mV in the first 5 hours due to H\textsubscript{2} (g) generation in the basic environment. When the polarity was reversed, the ORP in the new catholyte (Figure 4-4a) continued to decrease to -600 mV while the pH increased. The ORP in the anolyte (Figure 4-4b) was stabilized at around -400 mV. At the end of the experiment, a neutral pH and a highly reducing environment (Figure 4-4b) were achieved in the anolyte.
Figure 4-4 pH and ORP profiles under polarity reversal using iron electrodes, 112.5 mA L-1 current density and 0.02 M Na2SO4 background electrolyte: (a) first 5 hours served as anolyte then polarity reversed and then served as catholyte from 5 hours to 10 hours (b) first 5 hours served as catholyte then polarity reversed served as anolyte from 5 hours to 10 hours.
4.2.1.5 Identification of the Iron Precipitates

In order to understand geochemical formation during iron electrolysis, iron based precipitations during iron electrolysis in different background solutions were identified using X-ray diffraction (XRD). When a 20 mM NaCl or 20 mM NaSO₄ solution was used as the background electrolyte with an iron anode, black iron precipitates were predominantly observed in the electrochemical cell. Based on visual observation, these precipitates had magnetic properties and were more resistant to oxidation, compared to ferrous hydroxide, when they were exposed to air. According to the XRD analysis on these precipitates, for NaCl and NaSO₄, the XRD pattern in Figure 4-5a and Figure 4-5b exhibited that magnetite and iron hydroxides were the major precipitates generated during iron electrolysis. When a 0.02 M sodium bicarbonate was used as a background electrolyte, ferric based precipitations such as lepidocrocite and/or iron-oxide-hydroxide mineral were the major precipitations formed during the iron electrolysis.

The occurrence of magnetite in the Na₂SO₄ and NaCl electrolyte can be associated with an ample supply of Fe²⁺ from the anodic dissolution in electrochemically-generated alkaline and reducing conditions. The magnetite formation reactions include the lepidocrocite (FeOOH) formation by the oxidation of ferrous ions with dissolved oxygen, and the transformation lepidocrocite. Cathodic OH⁻ neutralizes H⁺ from Equation 4-9 and 4-10, which maintains the alkaline condition and promotes the magnetite formation. Iron hydroxide, Fe(OH)₂, detected in the NaCl and Na₂SO₄ electrolyte, is due to the precipitation of anodic Fe²⁺ with cathodic OH⁻ as shown in Equation 4-11.
4-9 \[ \text{Fe}^{2+} + \frac{1}{2} \text{O}_2(aq) + 3\text{H}_2\text{O} = 2\text{FeOOH} + 4\text{H}^+ \] (Lepidocrocite formation)

4-10 \[ 2\text{FeOOH} + \text{Fe}^{2+} = \text{Fe}_3\text{O}_4 + 2\text{H}^+ \] (Transformation of lepidocrocite to magnetite)

4-11 \[ \text{Fe}^{2+} + \text{OH}^- = \text{FeOH}_2(s) \] (Iron hydroxide formation)

In order to verify the proposed magnetite formation pathway and to evaluate the initial dissolved oxygen presence on the type of precipitation formation, an additional experiment was conducted with sulfate solution with no initial dissolved oxygen in the electrolyte. For this case, green colored precipitates were observed in the cell. The XRD pattern in Figure 4-6 shows that ferrous hydroxide and ferroxyhyte are the main precipitates produced for this case, concluding that the magnetite formation did not occur in the absence of oxygen. In this way, the lepidocrocite formation (Equation 4-9) and subsequently the lepidocrocite transformation to magnetite (Equation 4-10) were ceased, and the iron hydroxide formation (Equation 4-11) was promoted. Ferroxyhyte can be formed due to the oxidation of ferrous hydroxide. Since the color of the sample changed from green to a yellowish-brown color during the XRD analysis, ferroxyhyte detection in the sample was likely due to the oxidation of the sample during the XRD analysis. As seen in the Transmission Electron Microscopy (TEM) images in Figure 4-7, magnetite was observed as round, relatively dense crystals with size ranging between 20 nm to 60 nm.

When the NaHCO3 electrolyte was used, the magnetite was not identified in the electrolyte. Since a higher amount of ferrous ion is required for magnetite formation compared to ferric ion, this lack of magnetite formation might be due to insufficient ferrous ion release to the electrolyte. The initial pH of NaHCO3 was \( \approx 8 \), and ferrous ion creates a layer of iron oxides on the anode surface very quickly that decreases anodic Fe\(^{2+}\) efficiency. A passivated iron
anode acts like an inert anode and releases oxygen. Oxygen oxidizes Fe$^{2+}$ in the electrolyte and as a result, lepidocrocite is primarily formed. As seen in Figure 4-7, lepidocrocite (lath) in NaHCO$_3$ was less structured than the magnetite and iron hydroxide in the sulfate and chloride solution. Each dispersed formation size ranges between 200 nm to 700 nm.
Figure 4-5 X-Ray diffraction patterns of produced precipitates during iron electrolysis in a) 0.02 M Na2SO4 electrolyte; b) 0.02 M NaCl electrolyte; c) 0.02 M NaHCO3 electrolyte. 5 hours of electrolysis, 90 mA current, iron anode and MMO cathode, final pH $\approx$10 for Na2SO4 and NaCl, $\approx$9 for NaHCO3
Figure 4-6 X-Ray diffraction patterns of produced precipitates during iron electrolysis in pre-purged (oxygen free) 0.02 M Na2SO4 electrolyte. 5 hours of electrolysis, 90 mA current, iron anode and MMO cathode, final pH ≈10
Figure 4-7 Transmission Electron Microscopy (TEM) images of precipitates formed by iron electrolysis in: a) 0.02 M Na2SO4; b) 0.02 M NaCl; c) 0.02 M NaHCO3 electrolyte. 5 h of electrolysis, 90 mA current, iron anode and MMO cathode.
4.2.2 Batch Experiments for the Evaluation of Electrochemical TCE Dechlorination

4.2.2.1 Effect of Anode Type

Three types of anode materials (cast iron, lead dioxide, and mixed metal oxide) were tested by applying a 90 mA constant current in a 10 mM sodium bicarbonate solution and then comparing their electrochemical efficiency for TCE degradation in a mixed-electrolyte cell. Porous copper was used as a cathode for this part of the study.

The decay of aqueous TCE in the cells using a copper cathode and variable anode materials is presented in Figure 4-8a. TCE loss in the control cell (no electricity) was negligible with 3.56% within 5 hours. For the iron anode, the TCE concentration decreased by 50% in the first 0.5 hour, and to under the detection limit (0.1 mg L⁻¹) after 5 hours of electrolysis. With inert anodes, aqueous TCE in the cell decreased from 40 mg to 15.6 mg when lead dioxide (PbO₂) anode was used and to 16.7 mg when mixed metal oxide (MMO) anode was used. The TCE removal efficiencies were 61%, 57%, and >99% for PbO2, MMO, and iron anodes, respectively. Lead dioxide, as a high oxygen evolution overpotential anode material, did not show significant improvement on TCE degradation, suggesting that anodic oxidation is not a TCE degradation pathway when iron anodes are used.

Oxidation-reduction potential (ORP) of the electrolyte cell was also monitored during electrolysis. The ORP value is a key parameter to explain the increased degradation efficiency by the iron anode. ORP values during electrolysis decreased from 121 mV to –
750 mV (Figure 4-8b) for the iron anode due to the production of $\text{Fe}^{2+}$ which consumes oxidative substances in the electrolyte, such as dissolved oxygen. PbO$_2$ and MMO did not induce significant changes in redox potential (-37 mV for PbO$_2$ and -83 mV for MMO) compared with the iron anode. As discussed in Section 4.2.1.1, PbO$_2$ and MMO are inert anodes, which means that the main anodic reaction is water decomposition (Equation 4-8) and the main products are protons and oxygen gas. Continuous production of oxygen gas at the anode can limit the reduction of TCE because oxygen (O$_2$) has a high oxidation potential, and thus, is susceptible to reduction. The reduction potential of O$_2$ is 1.229 V vs SHE (Equation 4-12) higher than the reduction potential of TCE (0.42 V vs SHE) (Equation 4-13). Therefore, the reduction of O$_2$ is more favorable than TCE reduction in the electrolyte, which negatively affects TCE degradation.

\begin{align*}
4-12 & \quad \text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O} \\
4-13 & \quad \text{TCE} + 2\text{e}^- = 1,1\text{DCE}
\end{align*}
Figure 4-8  a) Aqueous TCE (Ca) electroreductive dechlorination profile; b) ORP profile with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, initial TCE concentration 39 mg L\(^{-1}\), 90 mA current, 0.01 M NaHCO\(_3\) electrolyte. The control experiment was conducted without an electrical current.
The produced hydrocarbons (ethane, ethene, methane and acetylene) were monitored to understand the transformation mechanism of TCE. Ethane, ethene and methane were observed (Figure 4-9) as the main TCE transformation by-products. The by-products produced from the different anode materials within a 0.5 hour are presented in Figure 4-9. Higher levels of hydrocarbon gases indicate higher degradation rates. As evidenced in Figure 4-9, the iron anode exhibits the better TCE degradation performance compared to both the MMO and PbO₂ anodes.

![Figure 4-9 The concentrations of hydrocarbon gases after 0.5 hour with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, 90 mA current, 0.01 M NaHCO₃ electrolyte.](image-url)
For the PbO₂ anode, ethene and ethane concentrations increased to 103 and 41 µmol L⁻¹ within 5 hours (Figure 4-10). Similarly, when the MMO anode was used, ethene and ethane accumulation in the headspace were detected at 90 and 45 µmol L⁻¹, respectively. For the cast iron anode, ethene and ethane concentrations increased within the first 2 hours to 83 and 220 µmol L⁻¹, respectively, and then decreased during the following 3 hours. The decreases in the detected ethane and ethene concentrations for the iron anode towards the end of experiment may be the result of headspace volume expansion. In comparison with ethane and ethene, monitored methane gas in the headspace was less significant with varying concentrations between 2 to 4 µmol L⁻¹ for all anode types. The high concentrations of ethene and ethane in the cell using the cast iron anode support the proposition that faster TCE degradation occurred in this cell. Additionally, during electrolysis, cis-DCE and VC were monitored as possible degradation intermediates of TCE; however, no visible accumulation of these chlorinated intermediates was found in any of the three cells.
Figure 4-10 Aqueous TCE decay and main by-products with copper foam cathode and a) PbO2 anode; b) MMO anode; and c) iron anode; initial TCE concentration 298 µmol L\(^{-1}\) (39 mg L\(^{-1}\)), 90 mA current, 0.01 M NaHCO\(_3\) electrolyte.
According to our hypothesis, atomic hydrogen formation on the surface of the cathode due to water reduction (Equation 4-14) is the main mechanism for TCE degradation in the cell. The generated atomic hydrogen can be used mainly for the formation of hydrogen gas (Equation 4-15) and for the reduction of other compounds present in the cell such as oxygen and TCE. In the absence of oxygen, atomic hydrogen mostly contributes to TCE reduction (Equation 4-16) and faster degradation is achieved.

4-14  \[ \text{H}_2\text{O} - \text{e} = \text{H}^\cdot + \text{OH}^- \]

4-15  \[ \text{H}^\cdot + \text{H}^\cdot = \text{H}_2 \]

4-16  \[ 2\text{H}^\cdot + \text{RCl} = \text{RH} + \text{H}^+ + \text{Cl}^- \]

This hypothesis can be verified by checking the molar ratios of produced hydrocarbons in the headspace of each cell. Ethene requires four hydrogen atoms to be chemically formed while ethane needs six hydrogen atoms. More ethane gas (with 6 hydrogens) in the headspace means that more atomic hydrogen is available for TCE reduction. As shown in Figure 4-11, the molar ratio of ethene to ethane was less than 1 (i.e. the ethane concentration was higher than the ethene concentration) for the iron anode. However, the ethene:ethane ratio with inert anodes signaled different behaviors; the ratios were 2.8 and 2 for PbO2 and MMO, respectively. Although the same amount of atomic hydrogen was produced under the same electrolysis conditions, less atomic hydrogen was used for TCE reduction for the PbO2 and MMO anodes, which shows that some part of the atomic hydrogen was consumed by oxidative compounds in the electrolytes of the PbO2 and MMO anodes.
Figure 4-11 Molar ratio of ethene to ethane at time 0.5 h with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, 90 mA current, 0.01 M NaHCO₃ electrolyte.

4.2.2.2 Effect of Cathode Type

Bench-scale experiments were conducted under 90 mA current in a mixed-electrolyte cell with a 10 mM bicarbonate solution to compare the electro-reductive TCE dechlorination performance of four foam (iron, nickel, copper, carbon) and two planar (copper, pure iron) cathode materials with a cast iron anode. As seen in Equation 4-16, pseudo-first order transformation kinetics can be used to describe TCE decay with various cathode materials coupled with an iron anode. The pseudo-first order model for TCE degradation can be modified for our experimental procedures as follows:

$$-\frac{d(V_eC_a + V_hC_h)}{dt} = kC_a + gC_h,$$
where $C_a$ and $C_h$ are TCE concentrations in the aqueous solution and headspace (mg L$^{-1}$), respectively; $V_a$ and $V_h$ are the volumes of the aqueous solution and the headspace, respectively (L); $k$ is the first order rate constant for TCE degradation (L h$^{-1}$); $g$ is the headspace expansion rate (L h$^{-1}$); and $t$ is the electrolysis time (in hours).

The total amount of TCE at any time during the electrolysis is the sum of TCE in the aqueous solution ($C_a$) and in the headspace ($C_h$). The change in total TCE over time can be linked to the degradation of aqueous TCE due to electrocatalytic activity and the expansion of headspace volume. The TCE equilibrium between an aqueous and a gas state can be expressed with Henry’s law (Equation 4-18) where $H_{TCE}$ is the dimensionless Henry’s constant.

4-18 \[ C_h = H_{TCE} C_a \]

The model can be further simplified and rearranged by substituting Equation 4-18 into Equation 4-17;

4-19 \[ \ln \frac{C_{a(t)}}{C_{a(0)}} = - \frac{k + g H_{TCE}}{V_a + V_h H_{TCE}} t \]

where $C_{a(t)}$ and $C_{a(0)}$ are the TCE concentrations in the aqueous solution at time $t$ and $t=0$, respectively. The headspace expansion rate ($g$) can be assumed as zero in this case because no expansion was observed during the experiments. The final equation (Equation 4-20) for the pseudo-first order model for TCE reduction is:

4-20 \[ -\ln\left(\frac{C_{a(t)}}{C_{a(0)}}\right)(V_a + V_h H_{TCE}) = kt \]
Figure 4-12b presents \(-\ln(Ca(t) / Ca(0))(V_a + V_hHTCE)\) versus time for tested cathode materials; the slope of this plot indicates the first order rate constants, \(k\), for TCE reduction. The corresponding \(k\) values are listed in Table 4-3. Copper foam and iron foam showed the best TCE dechlorination efficiencies across the six cathode materials tested. In addition, the copper plate and pure iron plate evidenced surprisingly high performances (88.9% for the copper plate and 82.3% for the pure iron plate), despite their limited surface area. The copper and iron foams both performed better than their corresponding plate materials, lending support to the conclusion that the transformation rate could be further improved by adopting high surface area electrodes. Although the vitreous carbon foam and nickel foam had high surface areas to be used for TCE reduction, their overall performances (82.4% for the vitreous carbon foam and 74.9% for the nickel foam) were not high in comparison to the copper and iron foams. Relatively little information is available about electrocatalytic reactions of TCE on different cathodes, however, our results with the copper cathode are in agreement with similar studies on aqueous dechlorination. Zinc and copper cathodes were shown to have the highest electrocatalytic performance in studies on electrolytic reduction of carbon tetrachloride\(^{15}\). Another study compared the performance of 15 metals on the electroreduction of chloroform, with copper being reported as one of the most efficient cathode materials\(^{144}\).
Figure 4-12 a) Electro-reductive dechlorination profile of aqueous TCE (Ca) with variable cathode types and cast iron anode b) Pseudo-first order TCE degradation kinetics with variable cathode materials and cast iron anode, the initial TCE concentration 39 mg L\(^{-1}\), 90 mA current, 0.01 M NaHCO\(_3\) electrolyte.
A summary of other relevant information from the experiment is presented in Table 4-3. In addition to the discussion above, a considerable pH rise was observed in all experiments using the iron anode. As discussed in Section 4.2.1.1, when an inert anode is used, the protons generated from the anode neutralize the hydroxyl ions generated from the cathode. When the iron anode is used, ferrous ions generated from the anode are not completely combined with hydroxyl ions produced from the cathode, forming iron-based precipitates and complexes. As a result, electrolyte pH did not show significant changes for inert anodes (MMO and PbO2), with a decrease from 7.7 to 6.9 for PbO2 and from 7.7 to 7.1 for MMO. However, for the iron anode, pH increased sharply to 11.3 within 5 hours of electrolysis. In parallel with the changes seen in pH levels, a significant rise in the ionic conductivity of the electrolyte was observed in the experiments using the iron anode due to the generation of iron-based ions and hydroxyl ions. As for the chloride ions, higher chloride ion accumulation was measured in the experiments with higher final TCE removal rates, agreeing with prior expectations. However, chloride mass recovery rates were relatively low when the iron anode was used (54% for nickel foam cathode). These low values can be explained by the formation of ferric and ferrous chloride in the solution.
Table 4-3 The list of pseudo-first order rate constants and final dechlorination efficiencies for different anode and cathode materials.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
<th>(C_a) (mg L(^{-1})) (ini-fin)</th>
<th>pH (ini-fin)</th>
<th>ORP (mV/AgCl) (ini-fin)</th>
<th>(Z) ((\mu)S cm(^{-1})) (ini-fin)</th>
<th>Final Chloride (mg L(^{-1}))</th>
<th>Cl(^-) recovery (%)</th>
<th>FDE (%)</th>
<th>(k) (x10(^{-3}) L h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMO</td>
<td>Copper foam</td>
<td>38.9-16.7</td>
<td>7.7-7.1</td>
<td>91-(-83)</td>
<td>853-840</td>
<td>16.2</td>
<td>90.2</td>
<td>56.1</td>
<td>NA</td>
</tr>
<tr>
<td>PbO(_2)</td>
<td>Copper foam</td>
<td>40.0-15.6</td>
<td>7.7-6.9</td>
<td>102-(-37)</td>
<td>853-911</td>
<td>11.7</td>
<td>59.2</td>
<td>59.8</td>
<td>NA</td>
</tr>
<tr>
<td>Cast iron</td>
<td>Copper foam</td>
<td>40.2-0.1</td>
<td>7.7-11.3</td>
<td>121-(-744)</td>
<td>853-1590</td>
<td>34.7</td>
<td>&gt;99.9</td>
<td>&gt;99.7</td>
<td>212.5±3.8</td>
</tr>
<tr>
<td>Cast iron</td>
<td>Iron foam</td>
<td>40.2-1.8</td>
<td>7.7-10.1</td>
<td>-</td>
<td>853-950</td>
<td>19.5</td>
<td>62.7</td>
<td>95.5</td>
<td>90.1±1.6</td>
</tr>
<tr>
<td>Cast iron</td>
<td>Nickel foam</td>
<td>40.3-10.1</td>
<td>7.7-9.5</td>
<td>-</td>
<td>853-858</td>
<td>13.2</td>
<td>54.0</td>
<td>74.9</td>
<td>39.5±1.6</td>
</tr>
<tr>
<td>Cast iron</td>
<td>Vitreous carbon foam</td>
<td>40.4-7.1</td>
<td>7.7-11.1</td>
<td>-</td>
<td>853-1393</td>
<td>22.8</td>
<td>84.6</td>
<td>82.4</td>
<td>54.1±3.7</td>
</tr>
<tr>
<td>Cast iron</td>
<td>Copper plate</td>
<td>38.6-4.3</td>
<td>7.7-10.1</td>
<td>-</td>
<td>867-970</td>
<td>30.5</td>
<td>109.8</td>
<td>88.9</td>
<td>64.6±2.2</td>
</tr>
<tr>
<td>Cast iron</td>
<td>Pure iron plate</td>
<td>40.0-7.1</td>
<td>7.7-9.7</td>
<td>-</td>
<td>853-866</td>
<td>19.6</td>
<td>73.6</td>
<td>82.3</td>
<td>54.4±2.2</td>
</tr>
</tbody>
</table>

*:FDE (Final Dechlorination Efficiency) = \(\left(\frac{C_{a(0)} - C_{a(t=60)} / C_{a(0)}}{C_{a(0)}}\right) \times 100\)
4.2.2.3 Effect of Current and Initial TCE Concentration

Applied current and initial substrate concentration are two important variables that can impact the electrochemical process. The effects of initial TCE concentration and current density on TCE degradation were evaluated in a 10 mM bicarbonate solution using three levels of initial TCE concentration (20, 39, and 74 mg L\(^{-1}\)) and six levels of current value (5, 10, 20, 30, 60, and 90 mA). The iron anode coupled with a copper foam cathode was used in this part of the study. The pseudo-first order rate constants and final dechlorination efficiencies (FDE) are summarized in Table 4-4. FDE values are increasing up to more than 99% as a result of increases in the applied current for all three initial TCE concentrations. As the initial TCE concentration increases, it becomes relatively harder to achieve more than 99% TCE deformation within 5 hours of electrolysis. For the pseudo-first order rate constants, as the initial concentration of TCE increases, the rate constants generally decrease for the same applied current value. In summary, the rate constants are directly proportional to the applied current; however, they are inversely proportional to the initial TCE concentration.

The rate of hydrodechlorination (\(r_{TCE}\)) on the iron cathode surface occurring with the participation of atomic hydrogen can be expressed as \(^{135}\):

\[
4-21 \quad r_{TCE} = k_{TCE} \Theta_H^n \Theta_{TCE},
\]

where \(\Theta_H\) and \(\Theta_{TCE}\) represent the surface coverage of adsorbed hydrogen (or atomic hydrogen) and adsorbed TCE, respectively, and \(n\) is the reaction order of hydrogen in the hydrodechlorination reaction. If the dechlorination of TCE on the copper surface is
assumed to show the same mechanism as that of an iron surface, the change in values of $k$ can be explained. As the applied current increases, more atomic hydrogens cover the surface of the cathode so the adsorbed TCE molecules are more likely to acquire atomic hydrogens. Other investigators have also reported higher dechlorination rate constants with higher current density $^{148,149}$. On the other hand, increasing initial TCE concentration has an adverse effect on $k$ values, suggesting that surface coverage of adsorbed TCE is not directly proportional with bulk TCE concentration in the electrolyte. The TCE reduction mechanism on the cathode surface requires chemisorption, thus involving longer TCE interaction with the cathode surface rather than physical adsorption $^{135}$.

Table 4-4 The list of pseudo-first order rate constants and final dechlorination efficiencies with different current densities and initial TCE concentration.

<table>
<thead>
<tr>
<th>Current (mA)</th>
<th>$C_{a(0)}$ ≈20 mg L$^{-1}$</th>
<th></th>
<th>$C_{a(0)}$ ≈39 mg L$^{-1}$</th>
<th></th>
<th>$C_{a(0)}$ ≈74 mg L$^{-1}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$ (×10$^{-3}$ L h$^{-1}$)</td>
<td>FDE (%)</td>
<td>$k$ (×10$^{-3}$ L h$^{-1}$)</td>
<td>FDE (%)</td>
<td>$k$ (×10$^{-3}$ L h$^{-1}$)</td>
<td>FDE (%)</td>
</tr>
<tr>
<td>5</td>
<td>51.55±6.03</td>
<td>65.9</td>
<td>19.39±1.67</td>
<td>42.2</td>
<td>18.98±1.92</td>
<td>38.7</td>
</tr>
<tr>
<td>10</td>
<td>57.51±1.25</td>
<td>83.9</td>
<td>39.81±3.13</td>
<td>72.1</td>
<td>45.58±1.33</td>
<td>76.5</td>
</tr>
<tr>
<td>20</td>
<td>116.5±4.06</td>
<td>98.0</td>
<td>113.8±11.49</td>
<td>99.2</td>
<td>64.45±3.62</td>
<td>84.6</td>
</tr>
<tr>
<td>30</td>
<td>150.12±2.7</td>
<td>&gt;99.4</td>
<td>149.33±2.96</td>
<td>&gt;99.7</td>
<td>105.18±1.89</td>
<td>96.7</td>
</tr>
<tr>
<td>60</td>
<td>241.4±6.49</td>
<td>&gt;99.4</td>
<td>128.24±4.67</td>
<td>&gt;99.7</td>
<td>150.05±5.13</td>
<td>99.2</td>
</tr>
<tr>
<td>90</td>
<td>287.6±9.58</td>
<td>&gt;99.4</td>
<td>212.51±3.81</td>
<td>&gt;99.7</td>
<td>245.15±7.23</td>
<td>&gt;99.8</td>
</tr>
</tbody>
</table>
Despite lower final dechlorination under lower current densities, the application of low currents results in higher current efficiencies and consequently lower energy consumption per mass of transformed TCE. Average current efficiency (ACE) of TCE reduction at a given time (t) can be defined by the following formula:

\[
ACE_t = \left( \frac{F(V_a + V_{HTCE})(C_{a(0)} - C_{a(t)})}{1000itM_{TCE}} \sum m_jx_j \right) * 100 
\]

where \( ACE_t \) is the average current efficiency at time \( t \) (%); \( F \) is Faraday’s constant (96485 C mol\(^{-1}\)); \( m_j \) is the number of electrons transferred from TCE to the hydrocarbon compounds; \( x_j \) is the molar percentage of species \( j \) in the hydrocarbon gases; \( M_{TCE} \) is the molecular weight of TCE (131.4 g mol\(^{-1}\)); \( i \) is the current (ampere), and \( t \) is electrolysis time (s).

The reductive dechlorination of TCE on the cathode, indirectly with atomic hydrogen, is a process involving electrons and proton transfer, eventually producing non-toxic hydrocarbons. The reaction can be expressed by:

\[
C_2HCl_3 + me^- + (m - 3)H^+ = C_2H_{m-2} + 3Cl^- 
\]

In our case, acetylene is not detected and the amount of methane production is negligible, so only ethene (m=6) and ethane (m=8) are considered in our \( ACE_t \) calculation. The molar percentage of ethene and ethane in the headspace is measured at time \( t \). Figure 4-13 presents ACE values for TCE reduction for different current densities at different electrolysis times. The basic observation is that the lower current densities exhibit higher average current efficiencies during the experiment. The ACE values of 5 mA range from 43.3% at 0.5 h to 14.7% at 5 h. On the other hand, the ACE values of the highest investigated current, 90
mA, remain between 11.0% at 0.5 h and 2.0% at 5 h. The observed trend in ACE can be explained by cathodic side reactions. Hydrogen evolution is the major parasitic reaction in the cathodic reduction of contaminants. As cathodic potential gets higher (more negative), water decomposition consumes a significant part of the applied current. On the other hand, electrode potential required for TCE dechlorination is quite negative. Therefore, cathodic potential is a significant factor for current efficiency as well as TCE dechlorination efficiency. From a practical viewpoint, the applied current should be optimized to achieve desired TCE transformation with minimum energy consumption or optimum current efficiency. In our experiments, 30 mA seems to be the threshold value that achieves an FDE value above 95% for three different initial concentration values.

**Figure 4-13** Time profiles of average current efficiency (ACE) of TCE electroreductive dechlorination with variable applied current values, cast iron anode and copper foam as electrodes, the initial TCE concentration 39 mg L\(^{-1}\), 0.01 M NaHCO\(_3\) electrolyte.
Other relevant information regarding the effect of current density on the electrochemical process is depicted in Figure 4-14. In Figure 4-14a, the ORP values of the electrolyte at different current conditions are presented. The first observation is that the ORP values decrease at all currents and provide a relatively more reducing electrolyte condition due to ferrous ion generation from the anode. However, the change rate of the ORP value depends on the applied current. For 5 mA, 10 mA, and 20 mA, the ORP decreases gradually from around 100 mV to -68 mV, -135 mV, and -484 mV, respectively. In contrast, the 30 mA, 60 mA, and 90 mA currents result in a drastic drop of ORP in 0.5 hour, show the buildup of the very reducing condition in 2 hours, and then level off around -468 mV, -625 mV, and -745 mV at corresponding currents. Assuming the current efficiency for iron dissolution is 100%, the molar concentration of total iron (in dissolved and solid [precipitation] form) in the cell should increase linearly as depicted in Figure 4-14a (dashed line). Since the ferrous ion generated from the iron anode is the primary reason for the decreasing trend in the ORP of the electrolyte, in parallel to ferrous iron concentration, the constant decrease of ORP is supposed to occur for all current conditions. However, the profile of electrolyte ORP in Figure 4-14a gradually stabilizes at later stages of electrolysis instead of following a constantly decreasing pattern. This suggests that the possible side reactions at the anode, such as O₂ evolution, prevent continuous decreases in ORP. Figure 4-14b presents the effect of current density on the final electrolyte pH. Noting that the initial electrolyte pH is 7.7 for all current conditions, the final pH value ranges between 7.4 and 11.3. The pH vs. current plot (Figure 4-14b) shows that a higher current results in a higher final pH value. Negligible or no change in electrolyte pH for 5 mA, 10 mA, and 20 mA suggests that a buffer capacity of electrolyte compensates the hydroxyl ion released
from the cathode. Considering that maintaining a neutral pH value is essential for groundwater remediation, choosing an appropriate current that does not induce significant pH increases but still attains a reasonable TCE removal rate is an important design issue. In our system, 30 mA is the optimum current that balances these two aspects.
Figure 4-14 (a) ORP profile, (b) final pH values with variable applied current values, cast iron anode and copper foam as electrodes, the initial TCE concentration 39 mg L$^{-1}$, 0.01 M NaHCO$_3$ electrolyte.
4.2.2.4 Effect of Electrolyte Type and Electrolyte Concentration

For a specific electrochemical cell, background electrolyte type and concentration are two significant variables that can impact the electrochemical process. In this section, the effects of background electrolyte concentration (ionic conductivity of electrolyte) and electrolyte type on TCE removal rate were tested.

Figure 4-15a shows the electrochemical TCE degradation profile with an MMO anode and a copper cathode in different electrolyte compositions including NaHCO₃, NaNO₃, and KCl. When the MMO anode was used, TCE removal efficiencies were 41%, 35%, and 30% in the NaHCO₃, KCl, and NaNO₃ compositions, respectively. Among these electrolytes, HCO₃⁻ is almost an inert supporting electrolyte and does not impact TCE dechlorination through chemical routes, because of its low reactivity on either anode or cathode. Unlike NaHCO₃, NO₃⁻, an oxidizing compound, has a tendency to reduce through cathodic reactions. Since TCE reduction is also through cathodic reactions, NO₃⁻ competes with TCE resulting in lower TCE removal efficiency in NO₃⁻ compared to HCO₃⁻. Similarly, Cl₂, an oxidative compound, might be generated at the MMO anode. Cl₂ diminishes the reductive degradation efficiency of TCE by creating more oxidizing electrolyte. When the iron anode was used, the electrolyte composition effect on TCE degradation rate was minimal as shown in Figure 4-15b indicating that ferrous specious generated at the iron anode show reducibility to consume all oxidative compounds in the electrolyte including O₂, Cl₂, and NO₃⁻.
The effect of electrolyte concentration on TCE degradation was evaluated using three levels of NaHCO₃ concentration: 10 mM, 50 mM, and 100 mM. Figure 4-16 presents normalized TCE concentration versus time in different NaHCO₃ concentrations with an iron anode and copper foam cathode. As seen in Figure 4-16, TCE degradation rate was faster when the NaHCO₃ concentration in the electrolyte was higher. The final dechlorination efficiency of TCE increases to >99% within 3 hours of electrolysis in the 50 mM and 100 mM NaHCO₃ electrolyte. This trend can be explained by the ionic conductivity of the electrolyte. If the mass transport of the reactants in electrolyte governs the kinetics of the desired reaction, the limiting current for a specific electrochemical reaction is related to the bulk ion concentration in the supporting solution. The higher ionic conductivity can achieve faster reaction kinetics. This phenomena will be further explained in Section 4.3.1.1.
Figure 4-15 Normalized aqueous TCE concentration profile with variable background electrolyte type, a) MMO anode coupled with copper plate cathode; b) Cast ron anode with copper plate cathode, initial TCE concentration ≈66 mg L$^{-1}$, 30 mA current.
Figure 4-16 a) Normalized aqueous TCE concentration profile with variable background electrolyte concentration, cast iron and copper foam cathode, initial TCE concentration ≈66 mg L⁻¹, 30 mA current.

4.3 Optimization of Operating Variables for Electrochemical Dechlorination of TCE

4.3.1 Regression Model and Assessment of the Main Factors

The copper foam cathode coupled with the iron anode resulted in the highest TCE dechlorination efficiency compared to the other electrode materials tested. In addition to electrode material, the electrochemical process is affected by operating variables such as the flow rate of aqueous solution, current density, influent TCE concentration, background electrolyte type, electrolyte ionic conductivity and temperature, and electrode surface area.
These operating variables can be further optimized using a multivariable experimental design; however, for the scope of this study, initial TCE concentration (A), electrode surface area (or foam cathode thickness, B), current intensity (C), and ionic conductivity (or NaSO4 concentration, D) were selected for further investigation. Three levels from each parameter were selected and the influence of the tested parameters on final elimination efficiency (FEE) and specific energy consumption (SEC) was statistically evaluated using factorial regression. The following equations are used to determine the FEE and SEC of the electrochemical process:

\[
FEE = 1 - \frac{C_{aq}(t)}{C_{aq}(0)} \left[ 1 + \frac{H_{TCE} \Delta V_h}{V_{aq} + H_{TCE} V_h} \right] \times 100\%
\]

\[
SEC = \frac{I \cdot U \cdot t}{C_{aq}(0) (V_{aq} + H_{TCE} V_h) FEE},
\]

where \(C_{aq}(t)\) and \(C_{aq}(0)\) are the aqueous TCE concentrations at time \(t\) and zero (mg L\(^{-1}\)); \(V_{aq}\) and \(V_h\) are the initial volume of solution (270 mL) and initial headspace volume of reservoir (20 mL); \(\Delta V_h\) is the expanded volume of headspace gas at time \(t\); \(I\) is the current intensity (A); \(U\) is the cell voltage of the electrochemical cell (V); \(H_{TCE}\) is the dimensionless Henry’s constant for TCE; and \(t\) is the electrolysis time (s).

The range of parameters used in the experimental design is listed in Table 4-5. Since the surface area of the foam electrode is directly proportional to its thickness, thickness is used to represent the variation in the surface area of the foam electrode. The specific surface areas of the foam electrodes were 145 cm\(^2\) (3.175 mm), 290 cm\(^2\) (6.35 mm), and 435 cm\(^2\) (9.525 mm). Different electrolysis times (6 h for 40 mA, 3 h for 80 mA, and 2 h for 120 mA) were used to maintain an identical total applied current charge (240 mA h). The ionic
conductivity levels used were 480 μS cm\(^{-1}\) (2 mM), 4.31 μS cm\(^{-1}\) (22 mM), and 7.6 μS cm\(^{-1}\) (42 mM). The experimental design matrix consisted of three series of experiments\(^{154,155}\): (i) a two level full factorial design \(2^4\) (all possible combinations of codified values +1 and -1); (ii) six replicates of the central point (0); and (iii) eight axial points located at the center of both extreme levels of the experimental models.

Table 4-5 The range of variation of the parameters used in the experiment design

<table>
<thead>
<tr>
<th>Notation</th>
<th>Parameter</th>
<th>Low (-1)</th>
<th>Center (0)</th>
<th>High (+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>[TCE] (mg L(^{-1}))</td>
<td>28</td>
<td>42</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Thickness of foam cathode, mm</td>
<td>3.175</td>
<td>6.35</td>
<td>9.525</td>
</tr>
<tr>
<td>C</td>
<td>Current (mA)</td>
<td>40</td>
<td>80</td>
<td>120</td>
</tr>
<tr>
<td>D</td>
<td>([\text{Na}_2\text{SO}_4]) (mol L(^{-1}))</td>
<td>0.002</td>
<td>0.022</td>
<td>0.042</td>
</tr>
</tbody>
</table>

Experimental design and results are summarized in Table 4-6. Using Minitab software, statistical regressions were conducted, resulting in the following model regression equations for the responses of FEE (Equation 4-26) and SEC (Equation 4-27):

\[
4-26
\]

\[
FEE = 88.606 + 1.018 A + 4.004 B - 4.921 C + 4.904 D - 0.267 AB + 0.059 AC - 0.254 AD + 1.269 BC - 1.067 BD + 1.992 CD + 0.877 ABC + 0.061 ABD - 0.333 ACD - 1.103 BCD + 0.262 ABCD
\]
SEC = 178.4 - 78.8 A - 22.5 B + 156.1 C - 229.5 D + 10.2 AB - 59.9 AC + 78.8 AD - 18.5 BC + 23.4 BD - 167.0 CD + 9.3 ABC - 10.3 ABD + 58.4 ACD + 18.9 BCD - 9.4 ABCD,

where A, B, C, and D take values between -1 and 1, representing the level of each factor.

The two, three, and four-way interactions of these variables were also included in the analysis. The FEE and SEC models produced $R^2_{\text{adj}}$ values of 98.8% and 77.4%, respectively, meaning that the FEE model explained 98.8% of the variation in FEE values while the SEC model explained only 77.4% of the variation in SEC values. Based upon these results, the FEE model is more successful in terms of explanatory power than the SEC model. This result is expected given that the SEC values were calculated using average cell voltage and the variation of cell voltage due to anodic corrosion reactions was not considered in the SEC calculation.
Table 4-6 Summary of the variables and results of the experiment design

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Variable levels</th>
<th>Expended gas volume (ml)</th>
<th>Cell voltage (V)</th>
<th>Y1 (FEE) (%)</th>
<th>Y2 (SEC) (kW h kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A [TCE]</td>
<td>B Thickness</td>
<td>C Current</td>
<td>D [Na₂SO₄]</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>78</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td>8</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td>10</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>84</td>
</tr>
<tr>
<td>11</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>80</td>
</tr>
<tr>
<td>12</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>85</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>14</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>84</td>
</tr>
<tr>
<td>15</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>81</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>82</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>80</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>83</td>
</tr>
<tr>
<td>19</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>78</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td>21</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>82</td>
</tr>
<tr>
<td>22</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>84</td>
</tr>
<tr>
<td>23</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td>24</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>82</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>80</td>
</tr>
<tr>
<td>26</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>27</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td>28</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>80</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>80</td>
</tr>
</tbody>
</table>

The significance level of each factor and the model’s interaction terms are presented in Figure 4-17 as a pareto chart. The vertical lines at 2.14 and 2.145 denote the critical value of the Student’s t-distribution at which the regression coefficients are significant at an
\( \alpha=0.05 \) confidence level (i.e. 95% level of confidence), indicating that a factor with a standardized effect (t-statistic) overpassing these vertical lines has a significant influence on the response variable. The \(+\) and \(-\) signs represent the positive and negative effect of the corresponding factors on the response variable. A positive effect denotes that values of the factor are positively associated with values of the response variable, more specifically saying that a unit increase in the factor will be associated with a unit increase in the response variable; the numerical value of the coefficient (seen in Equations 4-26 and 4-27) corresponds to the amount (in standardized units) in which the response variable increases in association with a unit increase in the factor variable. Similarly, a negative effect means that the factor and the response variables are negatively associated, resulting in an observed decrease in the response variable as the factor variable increases.

As depicted both in the regression equations and in Figure 4-17a, the most influential single factor on FEE is applied current (C) \([\beta=-4.921; \ p < .001]\), followed by Na2SO4 (D) \([\beta=4.904; \ p < .001]\), and foam cathode thickness (B) \([\beta=4.004; \ p < .001]\). Different from the other individual factors, applied current (C) has a negative influence on the response variable (FEE), indicating that the current efficiency for TCE reduction drops with increasing current intensity. Initial TCE concentration (A) has a much smaller influence on FEE compared to the other individual factors, although still significant \([\beta=1.018; \ p < .001]\). Additionally, the model also shows that FEE is significantly affected by some two-way (CD, BC, and BD) and three-way (BCD and ABC) interactions of the factors, however their coefficients are of a much smaller magnitude in comparison to the single factor items.
In Figure 4-17b, SEC is significantly affected by changes in the level of Na2SO4 concentration (D) \([\beta=-229.5; p < .001]\), the current intensity (C) \([\beta=156.1; p < .001]\), and initial TCE concentration (A) \([\beta=-78.8; p < .05]\). It is not surprising that the Na2SO4 concentration has the largest effect on SEC since the cell voltage is mostly affected by the ionic conductivity of the supporting electrolyte. The remaining individual factor of electrode thickness (B) \([\beta=-22.5; p > .50]\) did not have a significant effect on the SEC response variable since electrode thickness has a limited effect on cell voltage. Additionally, the two-way interaction of C (current intensity) and D (Na2SO4) \([\beta=-167.0; p < .001]\) had noticeable effect on SEC, suggesting that applying a lower current and increasing ionic conductivity could be an effective strategy to design energy efficient electrochemical remediation systems.
Figure 4-17 Pareto chart for standardized effect of individual factor and combinations of factors

(a) Pareto chart for standardized effect of individual factor and combinations of factors (response is FEE, $\alpha = 0.05$)

(b) Pareto chart for standardized effect of individual factor and combinations of factors (response is SEC, $\alpha = 0.05$)

<table>
<thead>
<tr>
<th>Term</th>
<th>Standardized Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.14</td>
</tr>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td></td>
</tr>
<tr>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>ABC</td>
<td></td>
</tr>
<tr>
<td>ACD</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td></td>
</tr>
<tr>
<td>BCD</td>
<td></td>
</tr>
<tr>
<td>BD</td>
<td></td>
</tr>
<tr>
<td>CD</td>
<td></td>
</tr>
<tr>
<td>ABCD</td>
<td></td>
</tr>
<tr>
<td>ABC</td>
<td></td>
</tr>
<tr>
<td>ABD</td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Factor</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>TCE</td>
</tr>
<tr>
<td>B</td>
<td>Thickness</td>
</tr>
<tr>
<td>C</td>
<td>Current</td>
</tr>
<tr>
<td>D</td>
<td>$[\text{Na}_2\text{SO}_4]$</td>
</tr>
</tbody>
</table>
4.3.1.1 Na$_2$SO$_4$ Concentration

As mentioned above, the Na$_2$SO$_4$ concentration significantly affects the FEE of TCE and SEC of the electrolysis. Higher FEE values and lower SEC are observed with increasing concentrations of Na$_2$SO$_4$. Since Na$_2$SO$_4$ is an inert supporting electrolyte, it does not involve the electrochemical TCE degradation process through chemical routes because of its low reactivity on either the anode or the cathode. However, the ionic conductivity is directly related to Na$_2$SO$_4$ concentration existing in the electrolyte, and ionic conductivity can impact the electrochemical process. When copper foam is used as a cathode, the cathode potential ($E$) is constant throughout the copper foam electrode since the conductivity of the copper phase is much greater than that of the electrolyte. The cathode potential consists of four components 159, as shown in Equation 4-28: the equilibrium potential of the rate-limiting reaction step ($E_{eq}$), the concentration overpotential ($\eta_c$), the solution potential ($\eta_s$), and the charge transfer overpotential ($\eta$).

$$4-28 \ E = E_{eq} + \eta_c + \eta_s + \eta$$

The concentration overpotential, $\eta_c$ is the change in overpotential due to reactant concentration differences between the bulk solution and the electrode surface. The concentration overpotential can be assumed to be minimal when the reaction rate is primarily determined by the charge transfer. The solution potential, $\eta_s$, is related to the ionic conductivity, and increases from the surface of the foam electrode to the inner side of the foam. The charge transfer overpotential, $\eta$, increases throughout the outer part of the electrode (closer layer to the anode) to maintain electrode potential constant. Higher charge
transfer overpotential indicates a faster reaction rate for TCE reduction at the outmost layer of the electrode. Higher ionic conductivity of the electrolyte provides a more homogeneous charge transfer overpotential through the layers of the foam electrode, which results in more electrode surface area for TCE reduction. For the specific energy consumption, SEC, the increase in the ionic conductivity causes a drop in the cell voltage, resulting in lower SEC values.

4.3.1.2 Current Intensity

In the studied range, current intensity is another parameter significantly affecting FEE and SEC of the electrochemical process. As seen in Figure 4-17, under a constant-charge but different current conditions, a higher current intensity results in lower FEE and higher SEC values. Higher cathodic potential needs to be applied for higher current intensity. As cathodic potential gets higher, hydrogen evolution reaction consumes a big portion of the applied current, which negatively affects current efficiency. Additionally, excessive hydrogen gas released at the cathode has an isolation effect, limiting mass transport of TCE to the cathode surface. Finally, low current causes less voltage drop (iR) due to electrical resistance in the solution, resulting in a more homogeneous current distribution, increasing the probability of TCE acquiring the atomic hydrogen. In conclusion, low current is more preferable if the retention time of the contaminated water is not a primary concern.
4.3.1.3 Thickness of Foam Electrode

The foam electrode thickness has no significant influence on SEC since it has a negligible effect on cell voltage. Unlike SEC, the foam thickness significantly affects the FEE; the thicker electrode results in higher FEE values. However, the FEE values are not linearly increasing with electrode thickness. For instance, comparing experiment No 1 and Experiment No 15 in Table 4-6, the 200 % increase in cathode thickness leads to only an 8.8 % increase in FEE value and a 7.8 % decrease in the cell voltage. This suggests that for thicker electrodes, it may be difficult to achieve sufficient electron transfer potential for the inner part of the foam electrode because of increasing iR drop.

4.3.1.4 Initial TCE Concentration

For the experimental range of 28 mgL⁻¹ to 56 mgL⁻¹, the initial TCE concentration had an impact on both FEE and SEC. At higher initial TCE concentration, due to high surface area of the foam electrode, the chemisorption of TCE was enhanced, indicating the improvement of mass transport of TCE, and high current efficiency accordingly. Therefore, a positive impact on FEE and negative impact on SEC was observed.

In summary, based on the results of multivariable experiments, the optimal operating conditions for response FEE and SEC is: 40 mA current, 9.525 mm foam cathode thickness, and 0.042 M Na₂SO₄ (ionic conductivity of 7.60 mS cm⁻¹) concentration. Among studied conditions, the initial TCE concentration has the least effect on FEE, indicating that a high surface area cathode has potential applicability for a wide range of TCE concentrations.
4.4 Flow-Through Column Experiments

4.4.1 Sand-Packed Flow-Through Column Experiment for Chemical Changes

4.4.1.1 Effect of Electrode Type

Temporal chemical changes in sand-packed flow-through column with iron and MMO (inert) anodes were evaluated in a 0.02 M Na₂SO₄ electrolyte solution with flow rate 1.2 ml min⁻¹. Electrolyte passed first through the anode and then through the cathode (Figure 3.2). Figure 4-18 shows the distribution of pH and ORP values in the column for different times (4 h, 6 h, 10 h, and 16 h).

As shown in Figure 4-18a, the pH of the electrolyte between the electrodes with the iron anode did not change significantly, which is almost the same as the influent pH. The pH after the cathode increased sharply to 11.3 (Port 5) in 4 hours due to OH⁻ production at the cathode. The pH for the last port (Port 6) after 4 hours was still similar to the initial value (5.9) because produced OH⁻ ions did not reach the last port. It took 6 hours for the OH⁻ ions to reach the last port and generate a basic environment (pH=11.8). At this time, the whole section after the cathode was alkaline. The pH in pore water in the first port after the cathode dropped to around 5.6 (Figure 4-18a) after 10 and 16 hours because ferrous ions produced at the anode were transported up to this port with advection and the carried ferrous ions mostly reacted with OH⁻ and precipitated as Fe(OH)₂(s) in the highly alkaline zone.

On the other hand, when the MMO anode was used, the pH between the electrodes decreased to 2.8 (Figure 4-18b) due to water oxidation at the anode. pH decreased at Port
1 before the anode as well due to H⁺ diffusion from the anode and H⁺ production due to little electric field at the outer surface of the anode. The pH of the region beyond the cathode decreased after 10 hours and 16 hours because H⁺ flux from the anode reached the ports after cathode (Port 5 and Port 6) and neutralized the OH⁻ released from the cathode.

The main differences between pH distribution in the column with the iron anode and the MMO (inert) anode are:

- Little or no pH drop was observed between the electrodes and before the anode when the iron anode was used. However, a highly acidic environment between the electrodes and a slight pH drop before the anode were seen when the MMO anode was used.

- After a certain time, a pH drop was observed around the cathode when the iron anode was used, which was an indication of precipitation (mostly in the form of ferrous hydroxides) around the cathode. However, a pH drop was observed not only around the cathode but also in all sections after the cathode due to water formation when the MMO (inert) anode was used.

The ORP value with the MMO anode increased (Figure 4-18b) from 254 mV (influent value) to 371 mV for the port before the anode (Port 1) and up to 480 mV between the electrodes in 4 hours due to O₂(g) release from the MMO anode. The ORP value after the cathode was relatively reducing (-246 mV for Port 5 and -119 mV for Port 6) after 4 hours due to the alkaline condition. Then, ORP started to increase up to 427 mV for Port 5 and 164 mV for Port 6 in 16 hours because O₂ flux from the MMO anode reached Port 5 and
Port 6. In contrast, the ORP value with the iron anode dropped (Figure 4-18a) from 254 mV to 200 mV for the port just before anode (Port 1) and to 100 mV between the electrodes in 4 hours. The ORP value after the cathode dropped from 254 mV to -194 mV for Port 5 and -206 mV for Port 6 in 4 hours. After that, ferrous ions released from the anode reached Port 5 and Port 6 and made redox potential more reducing compared to the MMO anode (after 16 hours: -33 mV for Port 5 and -106 mV for Port 6).

The main differences between ORP distribution in the column with the iron and the MMO (inert) anode are:

- The ORP value was highly oxidizing before the anode and between the electrodes when the MMO anode was used. However, the ORP was relatively more reducing before the anode and between the electrodes when the iron anode was used.

- The ORP value was reducing after the electrodes at the early stage of the experiment when the MMO electrode was used. Then, the ORP started to increase and made the whole column oxidizing until the end of testing (16 hours). However, the ORP after the cathode was reducing at the early stage of the experiment and at the end of the experiment.
Figure 4-18 pH and ORP profiles for 4 different instant times (4 h, 6 h, 10 h and 16 h) in flow-through column set-up, 20 mA current, 0.02 M Na$_2$SO$_4$ background electrolyte and 1.2 mL min$^{-1}$ flow rate (a) using iron anode (b) using MMO (inert anode).
4.4.1.2 Effect of Current Density

Figure 4-21 shows the distribution of pH and ORP in the column with the iron anode for 3 different currents (20 mA, 40 mA, and 80 mA) and 4 different times (4 h, 6 h, 10 h, and 16 h). The pH decrease between the electrodes was not significant for all three current densities. pH values between the electrodes decreased from 5.73 to around 5 in 4 hours (Figure 4-21a). Then, pH was stable around 5 in 16 hours for all current densities and did not show significant differences for different current densities (Figure 4-21d) because the main reaction at the anode was iron dissolution and little or no H+ was production occurred at the iron anode. The slight drop in pH data was because of the formation of ferric hydroxides with the presence of dissolved oxygen (Equation 4-2). pH value after the cathode showed a similar trend for 4 and 6 hours. pH values at Port 5 were 5.63 for 20 mA, 5.73 for 40 mA, and 11.2 for 80 mA in 10 hours (c). This pH drop for low current densities was due to ferrous hydroxides precipitation observed after the cathode. Relatively high current density (80 mA) did not show a significant pH drop.

The redox potential between the electrodes was more reducing for high current density (80 mA) because of more ferrous ions released at the anode (Figure 4-21). The ORP dropped (Figure 4-21a) to -194 mV, -268 mV, and -263 mV in 4 hours for 20 mA, 40 mA, and 80 mA, respectively. The current density and anodic reaction effects were more dominant at the later stage of the experiment. After 16 hours, the ferrous flux reached Port 5 and Port 6, and the redox potential at Port 6 was -106 mV, -190 mV, and -286 mV for 20 mA, 40 mA, and 80 mA, respectively.
Inlet...Port 1...>...>...>...>...Port 5...Port 6

(a) 4 h

(b) 6 h
Figure 4-19 pH and ORP profiles for different currents (20 mA, 40 mA and 80 mA) in flow-through column set-up, iron anode, 0.02 M Na$_2$SO$_4$ background electrolyte and 1.2 mL min$^{-1}$ flow rate (a) time= 4 hours (b) time=6 hours (c) time=10 hours (d) time=16 hours.
4.4.1.3 Effect of Flow Rate

Figure 4-20 shows the distribution of pH and ORP in the column for three different flow rates (1.2 mL per min, 2 mL per min, and 3.2 mL per min) for three different times (1 h, 2 h, and 4 h). The pH between the electrodes and after the cathode (Figure 4-20a) did not show significant changes for relatively low flow rates (1.2 mL min\(^{-1}\) and 2 mL min\(^{-1}\)) because the flux of electrolysis products did not reach the sampling ports in 1 hour. However, the pH increased up to 10.94 at Port 5 for the flow rate 3.2 mL min\(^{-1}\). The pH between the electrodes started to decrease slightly (Figure 4-20b) for all flow rates in 2 hours. The pH values at Port 5 were alkaline for all flow rates (Figure 4-20c). At that time, the pH of lower flow rates showed a more basic pH (11.27 for 1.2 mL min\(^{-1}\), 10.97 for 2 mL min\(^{-1}\), and 10.9 for 3.2 mL min\(^{-1}\)).

ORP data (Figure 4-20) is critical to understand the effect of flow rate on electrochemical dechlorination of chlorinated compounds. At the initial stage of testing (Figure 4-20b), ORP values between the electrodes were mostly oxidizing for low flow rates (at port 2 around 200 mV for 1.2 mL min-1, 152 mV for 2 mL min\(^{-1}\), and around 105 mV for 3.2 mL min\(^{-1}\)) because ferrous ion distribution through the column was not complete as a result of slow transport of the reducing compounds like ferrous ions in the column. As electrolysis continues, ferrous ions and other electrolysis compounds were transported and distributed through the column. As seen in Figure 4-20c, the ORP values between the electrodes were similar for all flow rates. This can be explained by the retention time of electrolyte in the electric fields. The same volume of electrolytes with lower flow rate was subjected to more electrolysis when compared to higher flow rate. On the other hand, the total mass of
electrolysis compounds like OH- and Fe2+ released from the electrodes were the same for all flow rates at a specific time because current densities were same for all flow rates.
Figure 4-20 pH and ORP profiles for different flow rates (1.2 mL min⁻¹, 2 mL min⁻¹ and 3.2 mL min⁻¹) in flow-through column set-up, iron anode, 0.02 M Na₂SO₄ background electrolyte and 20 mA current (a) time= 1 hour (b) time=2 hours (c) time=4 hours.

4.4.1.4 Effect of Electrolyte Composition

Electrolyte composition has a significant effect on the distribution of the chemical properties in the column due to precipitation and complexation of the ferrous and ferric ions with existing anions in the background electrolytes. Figure 4-21 shows the distribution of pH and redox potential in the column with two different
background electrolytes (sodium bicarbonate and sodium sulfate) in time (1 h, 2 h, 4 h, and 6 h). The pH dropped from 7.7 to 6.9 between the electrodes for the bicarbonate solution (Figure 4-21b); however the pH decrease between the electrodes was not significant for the sulfate solution. This behavior can be explained by the precipitation zone of the sulfate and bicarbonate solutions. The decrease in pH with the iron anode is mainly due to iron hydroxide precipitation. Initial pH values were 5.73 for sodium sulfate and 7.7 for sodium bicarbonate, therefore the zone of iron oxides precipitation differs for the sulfate and bicarbonate solutions. Although it had a high buffer capacity, the main precipitation products such as ferrous hydroxides and ferric hydroxides (green and yellowish color precipitates) were observed between the electrodes for the sodium bicarbonate solution. In contrast, precipitations were observed after the cathode for the sulfate solution. Precipitation of highly reducible species like Fe(OH)\textsubscript{2(s)} greatly affects the ORP distribution in the column as well. As shown in Figure 4-21b, the ORP at Port 2 dropped sharply from 87 mV to -187 mV for the bicarbonate solution. However, the ORP decreased at Port 2 from 254 mV to 140 mV for the sulfate solution. Based on Figure 4-21, the redox potential was more reducing between the electrodes when bicarbonate was used as the background electrolyte instead of sulfate. On the other hand, redox potential with the sulfate solution was more reducing after the cathode compared to the bicarbonate solution.
Figure 4-21 pH and ORP profiles for different background electrolyte composition (0.02 M Na₂SO₄ and 0.02 M NaHCO₃) in flow-through column set-up, iron anode, 20 mA current, (a) time= 1 hour (b) time=2 hours (c) time=4 hours (d) time=6 hours.
4.4.2 The Assessment of Hydraulic Conductivity Change During Iron Electrolysis

As explained in Section 4.2.1.1, ferrous ions and hydrogen gas are the two main products during iron electrolysis. Generated ferrous ions react with existing anions in the electrolyte and precipitate in the form of various iron oxides, such as iron hydroxide, ferric lepidocrocite, and magnetite. In addition to iron precipitates filling the pore space, electrochemically generated gas can be temporarily entrapped in the aquifer resulting in local unsaturated zones in the aquifer. The generated iron precipitates and the entrapment of gas during electrolysis may adversely affect the physical characteristics of the aquifer, such as permeability or hydraulic conductivity. For instance, previous studies have shown that the loss of permeability in the ZVI system, which is an example of an electrochemical redox system, results mainly from gas entrapment and mineral precipitation. In this section, the effect of iron electrolysis on hydraulic conductivity was evaluated in the sand-packed flow-through column. Experiments were conducted with various flow rates, electric currents, and electrolysis duration with an iron anode and an MMO cathode. The hydraulic conductivity values before and after the electrolysis were tested and compared. Table 4-7 summarizes the experimental parameters and hydraulic conductivities before and after the electrolysis.

Iron electrolysis was conducted at three different flow rate values: 0.49 mL min⁻¹, 0.91 mL min⁻¹, and 1.9 mL min⁻¹. As depicted in Figure 4-22, the hydraulic conductivities decreased within 72 hours from $4.04 \times 10^{-2}$ to $6.25 \times 10^{-3}$ cm s⁻¹ for
0.49 mL min⁻¹, from 4.04×10⁻² to 6.25×10⁻³ cm s⁻¹ for 0.49 mL min⁻¹ and from 4.25×10⁻² to 4.52×10⁻³ cm s⁻¹ for 1.9 mL min⁻¹. For the current intensity, as shown in Figure 4-23 the hydraulic conductivities decreased within from 3.86×10⁻² to 1.90×10⁻² cm s⁻¹ for 5 mA, from 3.93×10⁻² to 8.47×10⁻³ cm s⁻¹ for 15 mA, from 4.25×10⁻² to 4.81×10⁻³ cm s⁻¹ for 30 mA and from 3.71×10⁻² to 6.88×10⁻³ cm s⁻¹ for 60 mA. The effect of current increased until 30 mA. After 30 mA, the impact of current on hydraulic conductivity reached steady state. The change in hydraulic conductivity increases as the current increases because more iron precipitates and gas are generated electrochemically at higher current values.

Electrolysis duration is another important parameter that affects the amount of iron precipitates and gas formation that could influence temporary changes in hydraulic conductivity. Figure 4-24 compares the hydraulic conductivity before and after iron electrolysis with different electrolysis durations. Hydraulic conductivity decreased from 4.43×10⁻² to 1.68×10⁻² cm s⁻¹ within 6 hours, from 4.17×10⁻² to 1.89×10⁻² cm s⁻¹ within 12 hours and from 3.53×10⁻² to 8.15×10⁻³ cm s⁻¹ within 24 hours. As electrolysis continues over time, the decrease in hydraulic conductivity becomes larger due to an increase and buildup in the iron precipitates and entrapped gas in the column.

The experimental results with the iron anode indicate that iron electrolysis could decrease the hydraulic conductivity of the system. Iron electrolysis induces ferrous ions from the anode and hydrogen gas from the cathode. As shown in Figure 4-22,
the iron oxides accumulated mainly in the vicinity of the cathode and the entrapped
gas created air pockets in the vicinity after the cathode.

Assuming 100% iron dissolution efficiency, 1.5 g ferrous ions were generated per
day from the iron anode for 60 mA current. However, as shown in Section 4.4.1.4,
iron dissolution efficiencies might decrease to 66% in 5 hours, suggesting that the
ferrous ion in the system is much lower than the theoretical amount. At the same
time, the generated gas at the cathode was 600 mL per day at standard temperature
and pressure (0 °C and 1 atmosphere pressure). Comparing the generated gas
volume and ferrous ion during iron electrolysis, the adverse effect of gas
entrapment in the system is more likely to happen. An additional experiment was
carried out with the MMO anode to further investigate the effect of gas generation
on hydraulic conductivity. When the MMO anode was used, the voltage of the cell
increased from 10 Volts to above 100 Volts within 3 hours, proving that the
generated gas accumulates in the system and creates unsaturated and electrically
nonconductive zones. These unsaturated zones result in a decrease in the hydraulic
conductivity of system. To further analyze these changes, pore pressure was
monitored during iron electrolysis at three locations: before the anode, between the
electrodes, and after the cathode. Pore pressure did not change through the column
within 72 hours (Figure 4-26), indicating that the observed changes in hydraulic
conductivity tests are mainly due to the gas generated in the column.
Table 4-7 Summary of initial (k<sub>initial</sub>) and final (k<sub>final</sub>) hydraulic conductivity values with different flow rates, electrical current and electrolysis duration

<table>
<thead>
<tr>
<th>Current, mA</th>
<th>Electrolysis Duration, h</th>
<th>Q, mL/min</th>
<th>v&lt;sub&gt;s&lt;/sub&gt;, cm/h</th>
<th>ρ&lt;sub&gt;d&lt;/sub&gt;, g/cm³</th>
<th>n</th>
<th>e</th>
<th>k&lt;sub&gt;initial&lt;/sub&gt;, cm/s</th>
<th>k&lt;sub&gt;final&lt;/sub&gt;, cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>72</td>
<td>0.49±0.03</td>
<td>2.09±0.02</td>
<td>1.51±0.06</td>
<td>0.45</td>
<td>0.80</td>
<td>4.04E-02 ±5.52E-03</td>
<td>6.25E-03 ±3.21E-03</td>
</tr>
<tr>
<td>60</td>
<td>72</td>
<td>0.91±0.01</td>
<td>3.81±0.02</td>
<td>1.48±0.01</td>
<td>0.45</td>
<td>0.82</td>
<td>3.71E-02 ±1.65E-03</td>
<td>6.88E-03 ±8.55E-04</td>
</tr>
<tr>
<td>60</td>
<td>72</td>
<td>1.80±0.01</td>
<td>7.75±0.04</td>
<td>1.51±0.00</td>
<td>0.44</td>
<td>0.79</td>
<td>4.25E-02 ±2.45E-03</td>
<td>4.52E-03 ±1.10E-04</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>0.85±0.04</td>
<td>3.60±0.02</td>
<td>1.49±0.06</td>
<td>0.45</td>
<td>0.82</td>
<td>3.86E-02 ±2.40E-03</td>
<td>1.90E-02±4.31E-03</td>
</tr>
<tr>
<td>15</td>
<td>72</td>
<td>0.82±0.02</td>
<td>3.57±0.04</td>
<td>1.52±0.04</td>
<td>0.44</td>
<td>0.78</td>
<td>3.93E-02±6.25E-03</td>
<td>8.47E-03±1.32E-03</td>
</tr>
<tr>
<td>30</td>
<td>72</td>
<td>0.82±0.00</td>
<td>3.51±0.06</td>
<td>1.51±0.02</td>
<td>0.44</td>
<td>0.79</td>
<td>4.25E-02±1.02E-02</td>
<td>4.81E-03±1.29E-03</td>
</tr>
<tr>
<td>30</td>
<td>6</td>
<td>0.94±0.02</td>
<td>4.07±0.03</td>
<td>1.52±0.03</td>
<td>0.44</td>
<td>0.77</td>
<td>4.43E-02±1.77E-03</td>
<td>1.68E-02±8.27E-03</td>
</tr>
<tr>
<td>30</td>
<td>12</td>
<td>0.91±0.01</td>
<td>3.96±0.00</td>
<td>1.53±0.01</td>
<td>0.44</td>
<td>0.77</td>
<td>4.17E-02±1.80E-03</td>
<td>1.89E-02±2.00E-04</td>
</tr>
<tr>
<td>30</td>
<td>24</td>
<td>0.89±0.01</td>
<td>3.75±0.04</td>
<td>1.50±0.03</td>
<td>0.45</td>
<td>0.82</td>
<td>3.53E-02±2.25E-03</td>
<td>8.15E-03±1.36E-03</td>
</tr>
<tr>
<td>30*</td>
<td>3</td>
<td>0.92</td>
<td>4.07</td>
<td>1.53</td>
<td>0.43</td>
<td>0.75</td>
<td>6.16E-2</td>
<td>NA</td>
</tr>
</tbody>
</table>

*: MMO is used as an anode material and the experiment could not be completed because voltage increased over 100 V in 3 hours.
Figure 4-22 Hydraulic conductivity in the soil-packed column before and after electrolysis with different flow rate. Iron anode and MMO anode, 60 mA current, 0.02 M sodium sulfate electrolyte and 72 hours electrolysis duration.
Figure 4-23 Hydraulic conductivity (k) in the column before and after electrolysis with different current values. Iron anode and MMO anode, 72 hours electrolysis duration, 0.02 M sodium sulfate electrolyte and 0.85±0.04 mL/min flow rate.
Figure 4-24 Hyraulic conductivity in the soil-packed column before and after electrolysis with different electrolysis duration. Iron anode and MMO anode, 30 mA current, 0.02 M sodium sulfate electrolyte and 0.85±0.04 mL/min flow rate.
Figure 4-25 The iron precipitates and air pockets in the column due to iron electrolysis
Figure 4-26 The pressure difference during iron electrolysis. Iron-MMO couple is used as anode and cathode, 60 mA current, 0.5 flow rate, 20 mM sodium sulfate as electrolyte.
4.4.3 Regulation of the Effluent ORP and pH Under Flow

The effluent ORP and pH changes in Reactor A (Figure 3-10) during electrolysis with varying current conditions are presented in Figure 4-27. Since the cathode is placed closer to the effluent of the reactor, the pH probe measures the electrolyte within the vicinity of the cathode electrode first, followed by the measurement of mixed electrolytes from the anodic and cathodic reactions. When the MMO anode and copper foam are used as electrodes, the effluent pH decreases slightly from around 8 and stabilizes around 7.4 under a 60 mA and 120 mA current, and stabilizes around 7.6 under 30 mA current (Figure 4-27a). The decrease in effluent pH starts within 2 hours for 30 mA and 60 mA current conditions, but is delayed 6 hours for the 120 mA current condition. The pH change appears to be due primarily to the sequential passing of the simulated groundwater flow. In the meantime, an increase in the effluent ORP is observed when using the MMO anode. As presented in Figure 4-27a, the ORP value initially increases from around 40 mV to ≈70 mV, ≈90 mV, and ≈125 mV within 5 hours for 30 mA, 60 mA, and 120 mA current, respectively, with the effluent ORP stabilizing around those values. It is clear that the higher current creates higher ORP values, indicating that the rate of oxidative substances generated at the anode is dependent on current density. As discussed in Section 4.2.1 of this study, when the MMO anode is used, the main cathodic reaction, water reduction, produces hydroxyl ions and hydrogen gas, while the main anodic reaction produces protons and oxygen gas. Also, in the presence of the chloride ion in the electrolyte, chlorine gas can be generated at the anode. Among those electrochemical products, chlorine, oxygen, and hydrogen gases have a direct
effect on the effluent ORP. Due to the oxidative characteristics of chlorine and oxygen gases, their presence increases the electrolyte ORP in the reactor. On the other hand, hydrogen gas is a reductive substance, thus making the electrolyte more reducing.

When cast iron is used as an anode material, the pH and ORP measurements are very different than those obtained when the MMO anode is used. Figure 4-27b presents the effluent pH and ORP under different current conditions. For 30 mA and 60 mA, the effluent pH increases sharply to a peak value within 3 hours, then decreases gradually, reaching the steady state condition towards the end of the experiment. The peak pH values are 9.6 for 30 mA and 10.4 for 60 mA. However, for 90 mA, the pH increases sharply within 3 hours, maintaining a steady state alkaline condition until the end of the experiment (pH>11). Unlike the MMO anode, the effluent ORP continuously decreases to a very reducing condition when the iron anode is used. This trend is further enhanced under higher currents since the rate of the electrochemical process is accelerated. As mentioned earlier in this study, the ORP decrease is mainly due to the formation of ferrous ions from the anodic reaction. Ferrous ions generated from the anodic reaction show reducibility to consume oxidative components in the electrolyte, such as dissolved oxygen. Therefore, within our experiments, the dissolved oxygen decreases from more than 8 mg L\(^{-1}\) in the influent to less than 1 mg L\(^{-1}\) in the effluent. Furthermore, the Fe(II)/Fe(III) ratios in the effluent are 0.82 under 90 mA, 0.48 under 60 mA, and 0.24 under 30 mA, after 18 h of electrolysis.
It is shown that when an electrolytic system with two electrodes (cast iron anode, copper foam cathode) is used, the effluent ORP decreases to reducing values, which can enhance TCE dechlorination. However, the effluent pH reaches an alkaline condition, which may adversely affect the physical, chemical, and biological characteristics of groundwater. Therefore, the electrolytic system with 3 electrodes (2 anodes, one cathode) is investigated as an alternative to the two electrodes system.
Figure 4-27 Effluent pH and ORP profiles with variable current conditions. a) MMO anode (Anode-1 in Reactor A) and porous copper cathode; b) Iron anode (Anode-1 in Reactor A) and porous copper cathode. Electrolyte contains 20 mgL\(^{-1}\) Cl\(^-\), 0.172 gL\(^{-1}\) CaSO\(_4\) and 0.413 gL\(^{-1}\) NaHCO\(_3\). Flow rate is 2 mL min\(^{-1}\) for all the experiments.
Figure 4-28 presents the changes on the effluent pH and ORP from the three-electrode electrochemical system (two anodes, one cathode). For all current distributions, the effluent pH reaches a peak value within 5 hour of electrolysis, and then decreases to values around 8.5 to 9 after 21 hour of operation. This is slightly higher than the influent pH value of 8.4, indicating that the production of protons from the MMO anode limits the generation of the alkaline condition in the effluent. While the pH is being neutralized, the ORP profiles decrease and reach steady state condition at values ranging from -150 to -300 mV vs Ag/AgCl. In contrast to the two electrodes system, two anodic processes, including iron dissolution and oxygen evolution, occur simultaneously with the three-electrode system. The rate of these anodic processes can be controlled by varying the total current between two anodes. The larger part of the total current passing through the iron anode leads to lower effluent ORP levels, compared to when the larger current passes through the MMO anode, leading to higher ORP values. These findings are further validated by the Fe (II)/Fe (III) ratios in the effluent with varying current distributions between the iron and MMO anodes. After 20 h of electrolysis, the ratios of Fe (II) concentration to Fe (III) concentration are 0.15 (60 mA MMO anode: 30 mA iron anode), 0.83 (60 mA MMO anode: 60 mA iron anode), and 0.96 (30 mA MMO anode: 60 mA iron anode).

In summary, the effluent pH and ORP can be regulated by adopting a three-electrode system with two anodes (one iron anode, one MMO anode), allowing for
a more suitable electrolyte chemistry for the transformation of the target contaminant.

Figure 4-28 Effluent pH and ORP profiles of the three-electrode electrolytic system with different current distributions between anodes. Cast iron anode (Anode-1 in Reactor A), copper foam cathode and MMO iron anode (Anode-2 in Reactor A). Electrolyte contains 20 mgL⁻¹ Cl⁻, 0.172 gL⁻¹ CaSO₄ and 0.413 gL⁻¹ NaHCO₃. Flow rate is 2 mL/min for all the experiments.

### 4.4.4 Transformation of TCE Under Flow

In this part, the transformation of TCE in simulated groundwater is further evaluated in Reactor B under flow conditions with varying electrode configurations. In the flow through system, the removal efficiency (RE, %) of
aqueous TCE, the treating capacity (TC, mg h\(^{-1}\)) of TCE, and energy consumption (EC, kW h \(g_{\text{TCE}}^{-1}\)) are used as analytical parameters, defined as follows:

\[
\begin{align*}
4-29 \quad RE &= \frac{(C_{in} - C_{ef})}{C_{in}} \times 100 \\
4-30 \quad TC &= Q \times (C_{in} - C_{ef}) \\
4-31 \quad EC &= I \times U \times TC,
\end{align*}
\]

where \(C_{in}\) and \(C_{ef}\) are the aqueous TCE concentrations (mg L\(^{-1}\)) in the influent and in the effluent, respectively; \(Q\) is the flow rate of simulated groundwater (L h\(^{-1}\)); \(I\) is the applied current (A); and \(U\) is the average cell voltage (V).

Figure 4-29a exhibits the decay of aqueous TCE in Reactor B. TCE concentrations (measured at Port-S4 in Reactor B) decreased after passing through the electrodes and reached steady state conditions within 3.5 h. The pair of iron electrodes (No. 1) and MMO electrodes (No. 2) resulted in a limited RE of only 4.9% and 15.1%, respectively, suggesting that a high surface area cathode is necessary for improving TCE transformation. When copper foam was adopted as a cathode for the experiments, the RE of TCE is enhanced significantly. Additionally, when the copper foam cathode was coupled with the MMO anode, TCE removal efficiency was affected by the sequence of the electrodes. For the MMO anode-copper foam cathode sequence (No. 3), 23.1% RE and 1.93 mg h\(^{-1}\) TC were obtained; however, for the copper foam cathode-MMO anode sequence (No. 4), RE and TC values increased to 33.7% and 2.82 mg h\(^{-1}\), respectively. This is due to the fact that the TCE transformation occurs mostly in the vicinity of the copper foam cathode, and that placing the MMO anode downstream of the copper cathode concludes the
availability of anodic oxygen in the cathode region. The anodic oxygen reduces TCE removal efficiency through the electron competition effect on the electro-reduction reaction. Using the iron anode with the copper cathode (No. 5) further enhanced TCE transformation efficiency, obtaining RE and TCE values up to 40.5% and 3.51 mg h\(^{-1}\), respectively. To further investigate the promoting effect of the iron anode on TCE removal, ORP values were measured after the anode and before the cathode at Port-S3 for cases No. 3 to No. 7. As shown in Figure 4-29b, for the cases in which iron was used as Anode-1 (No. 5 and No. 7), the solution ORP creates a relatively more reducing solution. In parallel with the ORP values, the dissolved oxygen concentration between Anode-1 and the cathode are measured to be lower than 1 mg L\(^{-1}\) after 3.5 h of operation. These observations proffer that there are two main reasons behind the significant improvement in TCE removal efficiencies using the iron anode: (i) iron dissolution is the main anodic reaction instead of oxygen evolution for this case and the adverse effect coming from anodic oxygen with the MMO anode is eliminated, and (ii) the ferrous species generated from the iron anode has a deoxygenating effect on the dissolved oxygen existing in the influent (downstream from the cathode). To further verify the deoxygenating effect of the iron anode, a deoxygenated solution containing TCE was used as influent (No. 6). For this case, the RE and TC values were 41.5% and 3.5 mg h\(^{-1}\), respectively. Additionally, using a deoxygenated influent solution with the copper cathode-MMO anode sequence showed a very similar TCE decay profile with that of the iron anode-copper cathode sequence (No. 5), suggesting that the enhancing effect of the iron anode is due to the disappearance of the dissolved oxygen in the
influent solution (around 8.5 mg L⁻¹). In addition to using the iron anode before the cathode, the placement of the secondary anode (Anode-2 position) after the cathode further improves TCE removal efficiency (No. 7). For this case, the iron anode (Anode-1 position)-copper foam cathode (Cathode position)-MMO anode (Anode-2 position) were placed sequentially and the total current is split evenly between the anodes. For this three electrode arrangement, the RE and TC values increased to 45.4% and 3.79 mg h⁻¹, respectively. In the experiment with arrangement No. 7, the MMO electrode at the Anode-2 position did not adversely affect the TCE transformation at the cathode since no oxygen gas was generated downstream from the cathode. In addition to improvements in TCE removal efficiency, a decrease in cell voltage (lower energy consumption) was recorded for the three-electrode system (Table 4.5) in comparison to the two-electrode system.
Figure 4-29 a) Decay of aqueous TCE in the effluent with varying electrode configurations (samples are taken from Port-S4). b) The ORP profile of the electrolyte for corresponding electrode configurations (the samples are taken from Port-S3). 90 mA current and 4 mL min⁻¹ flow rate are applied for all experiments. For the three electrode arrangement, the total current is distributed equally between the anodes. A-1, C and A-2 in the legends refer to Anode-1, Cathode and Anode-2 positions in Reactor B. Electrolyte contains 0.172 gL⁻¹ of CaSO₄ and 0.413 gL⁻¹ of NaHCO₃.
Table 4-8 Summary of TCE transformation under flow experiments with different electrode arrangement (4 mL min\(^{-1}\), 90 mA current, Reactor B, 1.27 cm thick foam cathode).

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Electrode configuration</th>
<th>TCE in influent (mg/L)</th>
<th>Cell Voltage (V)</th>
<th>Treating Capacity (mg/h)</th>
<th>Removal Efficiency (%)</th>
<th>Energy Consumption (kW h/g TCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Anode-1 -- Cast iron</td>
<td>34.9</td>
<td>8.7-9.0</td>
<td>0.41</td>
<td>4.9</td>
<td>1.94</td>
</tr>
<tr>
<td>2</td>
<td>Anode-1 -- MMO</td>
<td>35</td>
<td>13.7-13.2</td>
<td>1.27 ± 0.13</td>
<td>15.1 ± 1.3</td>
<td>0.95</td>
</tr>
<tr>
<td>3</td>
<td>MMO -- Cu foam</td>
<td>34.7</td>
<td>11.5-9.7</td>
<td>1.93 ± 0.05</td>
<td>23.1 ± 0.4</td>
<td>0.49</td>
</tr>
<tr>
<td>4</td>
<td>MMO -- Cu foam</td>
<td>34.9</td>
<td>11.4-10.5</td>
<td>2.82 ± 0.05</td>
<td>33.7 ± 0.3</td>
<td>0.35</td>
</tr>
<tr>
<td>5</td>
<td>Cast iron -- Cu foam</td>
<td>34.8</td>
<td>9.3-8.9</td>
<td>3.39 ± 0.05</td>
<td>40.5 ± 0.3</td>
<td>0.24</td>
</tr>
<tr>
<td>6</td>
<td>Cu foam -- MMO</td>
<td>35</td>
<td>9.5-9.1</td>
<td>3.51 ± 0.09</td>
<td>41.2 ± 0.2</td>
<td>0.24</td>
</tr>
<tr>
<td>7</td>
<td>Cast iron (45 mA) -- Cu foam (45 mA)</td>
<td>34.8</td>
<td>7.1-6.8</td>
<td>3.79 ± 0.04</td>
<td>45.4 ± 0.4</td>
<td>0.17</td>
</tr>
<tr>
<td>8</td>
<td>Cast iron (45 mA) -- Cu foam (45 mA)</td>
<td>35.1</td>
<td>5.8-5.5</td>
<td>3.54 ± 0.06</td>
<td>44.1 ± 0.6</td>
<td>0.14</td>
</tr>
<tr>
<td>9</td>
<td>Cast iron (60 mA) -- Cu foam (30 mA)</td>
<td>34.7</td>
<td>8.5-7.8</td>
<td>3.49 ± 0.03</td>
<td>43.7 ± 0.3</td>
<td>0.21</td>
</tr>
<tr>
<td>12</td>
<td>-- Cu foam -- MMO</td>
<td>4.9</td>
<td>11.2-9.9</td>
<td>0.53 ± 0.02</td>
<td>44.8 ± 0.3</td>
<td>1.79</td>
</tr>
<tr>
<td>13</td>
<td>Cast Iron -- Cu foam</td>
<td>4.9</td>
<td>10.8-9.8</td>
<td>0.75 ± 0.03</td>
<td>63.9 ± 0.2</td>
<td>1.24</td>
</tr>
</tbody>
</table>
Figure 4-30 depicts the RE and TC of TCE as a function of foam cathode thickness with the cast iron anode (A-1)-copper foam cathode (C)-MMO anode (A-2) electrode configuration with equal current distribution on the anodes. As seen in Figure 4-30a, higher TCE removal efficiencies were observed for lower flow rates, 2 mL min$^{-1}$ when compared to 4 mL min$^{-1}$, advocating that a longer residence time of the electrolyte improves TCE removal efficiency. In contrast, the treating capacity of TCE was higher for a flow rate of 4 mL min$^{-1}$ (Figure 4-30b), indicating that a higher flow rate enhances the mass transport of TCE. RE reached 85.1 % and 75.6 % at 2.54 cm foam cathode thickness for the flow rates of 2 mL min$^{-1}$ and 4 mL min$^{-1}$, respectively. For the applied flow rates, the RE value increased significantly with increasing thickness of the foam cathode between 0.042 cm and 0.635 cm; after that point, the increase in RE slows down and relatively flattens beyond a 1.9 cm foam cathode. On the other hand, for 4 mL min$^{-1}$, the treating capacity of TCE noticeably increased with increasing foam thickness, reaching a value of 3.58 mg h$^{-1}$ at 2.54 cm foam cathode thickness. For 2 mL min$^{-1}$ flow rate, similar to the RE profiles, the TC profile first increased with respect to foam thickness, and then exhibited a relative plateau after 1.9 cm cathode thickness. The nonlinear relationship between RE and foam thickness may be due to the uneven distribution of current from the surface to the inside of the electrode. In other words, the electrical charge flowed through the shortest way between the electrodes, resulting in a specific electrochemical reaction that mainly occurs on the outmost layer of the electrode. Initially, increasing the thickness of the foam cathode enhanced the electrochemical reaction due to the provision of higher surface area for the electrochemical reaction. However, after a certain point, continued increases in foam
thickness did not promote the electrochemical reaction since the inner side of the foam electrode contributes little to the electrochemical reaction.

Figure 4-30 (a) TCE removal efficiency vs copper foam cathode thickness for different flow rates. (b) TCE treating capacity vs copper foam cathode thickness for different flow rates. Iron (A-1)-Copper foam (C)-MMO (A-2) electrode configuration and equal current distribution on the two anodes were used (90 mA total, 45 mA for each). Influent TCE concentration was 20 mg L⁻¹. Samples were collected from Port-S4 of Reactor B when steady-state TCE concentration was achieved in the reactor.
The effects of current intensity and influent TCE concentration on the RE of TCE were investigated with four levels of influent TCE concentration (0.5 mg L\(^{-1}\), 5 mg L\(^{-1}\), 20 mg L\(^{-1}\), and 35 mg L\(^{-1}\)) and four levels of current intensity (15 mA, 30 mA, 60 mA, and 90 mA). The calculated RE values are depicted using a contour plot in Figure 4-31. The highest RE values (>82%) were observed when influent TCE concentration was low (0.5-7.5 mg L\(^{-1}\)) and current intensity was high (>45 mA). This indicates that for the low influent TCE concentration, a higher current can be applied to achieve higher TCE removal efficiencies. For the high influent TCE concentration (20-35 mg L\(^{-1}\)), RE increases up to 73% as the applied current increases to 60 mA; yet after this point, the RE of TCE does not increase beyond 73% even as the intensity of the current increases, indicating that 60 mA is the upper limit for the high influent TCE concentration in this experiment. Conversely, for the influent TCE concentration <0.5 gL\(^{-1}\), 75% TCE removal can be obtained when 15 mA current intensity is applied.
Figure 4-31 Contour plots for TCE removal efficiencies with different current density and influent TCE concentration. Iron (A-1)-Copper foam (C)-MMO (A-2) electrode configuration and equal current distribution on the two anodes were used (90 mA total, 45 mA for each). Samples were collected from Port-S4 of Reactor B when steady-state TCE concentration was achieved in the reactor.
CHAPTER 5

5 Summary and Conclusions

5.1 Summary

An experimental program was conducted in three stages to evaluate the performance of iron anode electrolysis for electrochemical remediation of TCE in groundwater.

In the first stage, batch experiments were conducted to evaluate chemical changes in the electrolyte as a result of iron electrolysis. The changes in the electrolyte were monitored with varying operating conditions including electrode materials (inert or iron anode), applied current intensity, and electrolyte composition. Then, TCE dechlorination by three anode materials and six cathode materials were investigated. The electrode couple (iron anode and copper foam cathode) with the best TCE removal performance was selected for further testing. In the second stage, the operating variables were optimized for the best TCE removal efficiency. Operating variables in the second stage included current intensity, ionic conductivity of the electrode, thickness of the foam electrode, and initial TCE concentration.
In the final stage of this study, the performance of iron electrolysis was evaluated under flow. How to regulate pH and ORP under flow to create favorable conditions for TCE removal and what are the potential adverse effects of iron electrolysis on the aquifer were the main research questions in the final stage of this study.

5.2 Conclusions

Based on research results, the following conclusions can be made:

1. Batch Experiments:
   a. When an iron anode is used for electrochemical treatment of groundwater; a highly reducing, basic electrolyte will develop. This environment is critical for the reductive transformation of some contaminants. When a mixed-metal-oxide (inert) anode is used, a relatively oxidizing electrolyte environment and neutral pH is achieved.

   b. Electrolyte composition significantly affects the pH, ORP, iron speciation, and electrolysis efficiency of iron electrolysis. A sulfate solution results in the highest pH and the most reducing ORP compared to bicarbonate and chloride solutions. The bicarbonate electrolytes are more resistant to pH changes compared to sulfate and chloride solutions. The ORP values show similar trends for all three electrolyte composition.
c. Electrolyte composition governs the type precipitation formed during iron electrolysis. Magnetite and iron hydroxide are the main iron based precipitates formed when a sulfate and chloride electrolyte are used. Magnetite formation is ceased in the absence of initial dissolved oxygen in the electrolyte. When a high buffer capacity electrolyte such as bicarbonate is used, lepidocrocite is the main iron oxide formed in the electrochemical cell.

d. The iron anode showed the most significant enhancing effect for cathodic dechlorination efficiency. Furthermore, porous copper cathode showed the best performance compared to other cathode materials.

e. TCE dechlorination rate constants mainly depend on the applied current and the initial TCE concentration. TCE removal rate increases with an increase in applied current. However, current efficiency for TCE dechlorination is less under high currents. Initial TCE concentration affects the TCE dechlorination rate constant inversely.

f. When an iron anode is coupled with a porous cathode in batch experiments, the TCE dechlorination rate increases with an increase in electrolyte ionic conductivity.
When an inert anode (MMO) is used, the TCE dechlorination rate is lower with the presence of NO₃⁻ and Cl⁻ in the electrolyte. When the iron anode is used, the effect of these anions on the TCE degradation rate is negligible.

2. Optimization Experiments:
   
a. Optimization experiments show that applied current is the most influential factor on final TCE removal. For specific energy consumption of electrolysis, ionic conductivity of the electrolyte and applied current are the most dominant operating variables.

b. Under constant-charge but different current intensity, final TCE elimination efficiency drops with an increase in the applied current, indicating that current efficiency decreases with increasing current intensity. Parallel to that, specific energy consumption of electrolysis increases with increasing applied current.

c. Higher final TCE elimination efficiency is observed with increasing ionic conductivity of the electrolyte because higher ionic conductivity ensures more homogeneous charge transfer over potential through the layers of the foam electrode. For specific energy consumption, an increase in ionic conductivity causes a drop in the cell voltage, meaning lower specific energy consumption values.

d. Thickness of the foam electrode has no effect on specific energy consumption for TCE since it has no effect on cell voltage. Unlike specific
energy consumption, foam thickness significantly increases TCE elimination efficiency as a result of larger surface area for the electrochemical dechlorination of TCE. However, TCE final elimination efficiency does not linearly increase with electrode thickness, suggesting that the TCE dechlorination rate is not homogeneous through the layers of the foam electrode.

e. Initial TCE concentration has limited effect on both TCE specific energy consumption and final elimination efficiency. A positive impact on FEE and a negative impact on SEC were observed.

3. When an inert anode (MMO) is used, the TCE dechlorination rate is lower in the presence of NO3- and Cl- in the electrolyte. When an iron anode is used, the effect of these anions on TCE degradation rate is negligible.

4. Flow-through Column Experiments:
   a. Flow rate significantly affects the distribution of pH and ORP in the column during the early stage of electrolysis. However, the pH and ORP values stabilize at a specific time and the effect of flow rate becomes negligible.

   b. Iron electrolysis may induce a decrease in hydraulic conductivity. This decrease highly depends on the applied current and electrolysis duration. Since the amount of produced iron precipitates is
negligible compared to the amount of generated gas, the decrease in hydraulic conductivity is primarily due to the entrapment of electrochemically-generated gases in the column.

c. A slight decrease is observed in the effluent pH when an MMO anode-copper cathode is used. For ORP, the effluent ORP significantly increases when an MMO anode is used.

d. The effluent pH and ORP can be regulated to achieve for a suitable environment for TCE dechlorination by adopting a three-electrode system (the sequence of iron anode-copper cathode-MMO anode). Unlike pH, effluent ORP decreases and stabilizes at a lower value than the influent ORP value under electrolysis with three-electrode system.

e. Comparing various electrode configurations, the three-electrode system with an iron anode-copper foam cathode-MMO anode sequence shows the highest degradation efficiency. Deoxygenated influent with copper foam and the MMO anode configuration shows comparative results suggesting that the improved TCE dechlorination with iron electrolysis is due to the consumption of oxygen in the influent by iron based species generated at the iron anode.
f. Higher TCE removal efficiencies are reached at a lower flow rate, supporting the conclusion that a longer residence time of the electrolyte improves TCE removal efficiency. Conversely, the treating capacity of TCE is higher for a higher flow rate, indicating that a higher flow rate enhances the mass transport of TCE.

g. Under flow conditions, using thicker foam cathode results in an increase in TCE removal efficiency. However, the relationship between TCE removal efficiency and cathode thicknesses is not linear.

5.3 Recommended Future Research

Using iron electrolysis for the treatment of chlorinated compounds requires additional research. The following possible future research topics are recommended:

- Ferrous species produced at the iron anode can be used as an activator for other technologies, such as iron-activated persulfate and Fenton’s reagent. The potential applicability of iron electrolysis to provide an in situ activator for other remediation systems should be evaluated. Also, an alkaline condition created by iron electrolysis can be used to activate persulfate for chemical oxidation of a variety of contaminants.
• The accumulation of iron oxides on the iron anode surface may passivate the electrode, therefore the long-term performance of the technology should be evaluated before applying in the field. Operating variables should be optimized and engineered to extend the performance of the technology.

• The performance of iron electrolysis for the removal of other commonly found contaminants should be evaluated to extend the applicability of this technology.
REFERENCES

6 References


13. USEPA Search Superfund Site Information.

http://cumulis.epa.gov/supercpad/Cursites/srchsites.cfm (November 14, 2015),


75. ITRC *Permeable Reactive Barrier: Technology Update*; Washington DC, 2011.


*Electrochim Acta* 2015, 181, 118-122.


