REMOVAL OF PERCHLORATE (ClO₄) FROM WATER USING PULSED ARC ELECTROHYDRAULIC DISCHARGE (PAED)

REMOVAL OF PERCHLORATE (CIO₄) FROM WATER USING PULSED ARC ELECTROHYDRAULIC DISCHARGE (PAED)

By

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TITLE:	Removal of Perchlorate (ClO_4) from Water Using Pulsed		
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ABSTRACT

Pulsed Arc Electrohydraulic Discharge (PAED) is a direct plasma water treatment technology that can generate physical and chemical reactions in a single unit process to treat a broad range of chemical and biological contaminants. Karpel Vel Leitner et al. (2005) demonstrated that PAED is capable of treating contaminants via the reduction mechanism, as they reduced nitrate to nitrite. Perchlorate is a difficult-to-treat contaminant with significant negative impacts on human health. One treatment approach for perchlorate is to reduce it. Therefore, laboratory experiments were designed and conducted to examine the efficacy of PAED for reduction of perchlorate in a water matrix.

A 3L stainless steel cylindrical reactor with two titanium electrodes connected to a 0.3 kJ/pulse pulsed arc power supply was used for the treatment processes. Three sets of factorial experiments were performed to determine: a) the power supply settings and water matrix properities for optimal ozone and hydrogen peroxide production; b) the efficacy of PAED for the reduction of perchlorate; and c) the power supply settings and water matrix properties for optimal perchlorate reduction.

The results of these experiments indicated that as much as 0.0544 mg/L of ozone was generated, with water conductivity and the presence of dissolved oxygen being the most important factors contributing to ozone generation. Hydrogen peroxide was not generated in detectable amounts under any of the conditions employed in these experiments. Finally, perchlorate was not reduced by detectable concentration in any of the conditions employed in these experiments.

iii

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TABLE OF CONTENTS

TER 1	- INTRODUCTION	1
BACI	KGROUND	1
RESE	ARCH OBJECTIVES	4
THES	SIS OUTLINE	5
TER 2	- REVIEW OF PERCHLORATE CONTAMINATION	6
INTR	ODUCTION	6
SOUI	RCES AND PHYSICO-CHEMICAL PROPERTIES OF PERCHLORATE	8
.2.1	Sources of Perchlorate Contamination	8
.2.2	Chemical and Physical Properties1	0
.2.3	Health Effects 1	2
FATI	E AND TRANSPORT IN GROUNDWATER 1	3
REM	EDIATION TECHNOLOGIES 1	6
.4.1	Ion Exchange 1	7
.4.2	Membrane Processes	8
.4.3	Chemical REDOX Technologies1	9
.4.4	In-Situ Biological and Biochemical Processes 1	9
.4.5	Ex-Situ Bioreactors	3
	TER 1 BACI RESE THES TER 2 INTR SOUI 2.1 2.2 2.3 FATI REM .4.1 .4.2 .4.3 .4.4 .4.5	TER 1 – INTRODUCTION BACKGROUND BACKGROUND RESEARCH OBJECTIVES THESIS OUTLINE THESIS OUTLINE TER 2 – REVIEW OF PERCHLORATE CONTAMINATION INTRODUCTION SOURCES AND PHYSICO-CHEMICAL PROPERTIES OF PERCHLORATE 2.1 Sources of Perchlorate Contamination 2.2 Chemical and Physical Properties 2.3 Health Effects 1 FATE AND TRANSPORT IN GROUNDWATER 1 REMEDIATION TECHNOLOGIES 1 4.1 4.2 Membrane Processes 1 4.3 4.4 In-Situ Biological and Biochemical Processes 1 4.5 2.5 Ex-Situ Bioreactors

_.

ł

2.4	.6	Summary	24
2.5	PUI	LSED-ARC ELECTROHYDRAULIC DISCHARGE (PAED)	25
2.6	SUI	MMARY	
CHAPT	'ER 3	3 – MATERIALS AND METHODS	
3.1	INT	TRODUCTION	
3.2	MA	TERIALS	
3.2	.1	PAED Power Supply	
3.2	.2	PAED Reactor	
3.2	.3	Perchlorate	
3.2	2.4	Reagents	
3.3	EX	PERIMENTAL METHODS	
3.3	5.1	Experimental Setup	
3.3	3.2	Experimental Design for O3 and H2O2 Generation Experiments	
3.3	3.3	Perchlorate Reduction Experimental Design	41
3.4	ΕX	PERIMENTAL PROCEDURES	54
3.4	I .1	PAED Operating Procedures	54
3.5	AN	ALYTICAL TECHNIQUES	57
3.5	5.1	Perchlorate (ClO ₄) Quantification	57
3.5	5.2	Nitrate Quantification	58
3.5	5.3	Ozone (O ₃) Quantification	60
3.5	5.4	Hydrogen Peroxide (H ₂ O ₂) Quantification	62
CHAPT	ſER	4 – RESULTS AND DISCUSSION	64
4.1	ΟZ	ONE GENERATION EXPERIMENTS	64
4.2	ΗY	GRODEN PEROXIDE GENERATION EXPERIMENTS	72
4.3	BA	TCH PERCHLORATE EXPERIMENTS	73
4.4	FL	OW-THROUGH REACTOR PERCHLORATE EXPERIMENTS	
CHAPT	ΓER	5 – CONCLUSIONS & RECOMMENDATIONS	
5.1.	CC	DNCLUSIONS	86
5.2.	RE	COMMENDATIONS	87
REFER	ENG	CES	
APPEN CALCU	IDIX JLA	K 1 – EXPERIMENTAL PROCEDURES AND STANDARD TIONS	CURVES

-

_

ł

A1.1	OPER	ATING PROCEDURES	92
A1	.1.1	Ion Chromatography Equipments Operating Procedures	92
A1	.1.2	Dissolved Oxygen (YSI MODEL 57 OPERATING PROCEDURES)	94
A1.2	REAG	ENT PREPARATION	97
A1	.2.1	Ozone Test Reagents	97
A1	.2.2	Hydrogen Peroxide Test Reagents	97
A1.3	STAN	DARD CURVES	98
A1	.3.1	Method Detection Limit (MDL)	98
APPEN	DIX 2 -	– EXPERIMENTAL RESULTS 1	.02
A2.1	OZON	VE TEST RESULTS 1	.02
A2.2	BATC	TH PERCHLORATE TEST RESULTS 1	06
A2.3	FLOW	/-THROUGH PERCHLORATE TEST RESULTS 1	.07

LIST OF TABLES

TABLE 2.1 Summary of reported perchlorate concentrations in water sources	. 9
TABLE 2.2 Physicochemical properties of various perchlorate compounds	11
TABLE 3.1 Exterior components of the PAED power supply and their functions	29
TABLE 3.2 Interior components of the PAED power supply	31
TABLE 3.3 Reagents employed in the quantification of O3.	34
TABLE 3.4 Reagents employed for the quantification of H_2O_2	35
TABLE 3.5 Reagents employed for the quantification of perchlorate.	35
TABLE 3.6 Recipe for phosphate buffered saline (PBS) solution.	36
TABLE 3.7 Experimental factors for O_3 and H_2O_2 measurement	38
TABLE 3.8 Factorial design for O ₃ and H ₂ O ₂ measurement	39
TABLE 3.9 O ₃ and H ₂ O ₂ experiment scheme	40
TABLE 3.10 Experimental factors for the perchlorate reduction experiments	42
TABLE 3.11 Fractional factorial experimental design for the batch perchlorate reduction experiments.	m 44

TABLE 3.12 Factor levels with corresponding physical measurements for the batch perchlorate reduction experiments.	. 44
TABLE 3.13 Fractional factorial experimental design for the flow-through perchlorate reduction experiments.	. 50
TABLE 3.14 Factor levels with corresponding physical measurements for the flow- through perchlorate reduction experiments	. 50
TABLE 3.15 HPLC modules	. 59
TABLE 3.16 HPLC operating conditions	. 60
TABLE 4.1 Experimental conditions for O ₃ and H ₂ O ₂ production experiments	. 64
TABLE 4.2 Water matrix conditions for O_3 and H_2O_2 production experiments	. 65
TABLE 4.3 O ₃ Generation results.	. 65
TABLE 4.4 O ₃ Generation experimental model fits	. 68
TABLE 4.5 Effects of factors on ozone generation	. 70
TABLE 4.6 Results of the H ₂ O ₂ Generation Experiments	. 73
TABLE 4.7 Experimental conditions: batch tests	. 75
TABLE 4.8 Factorial design and results for the batch perchlorate experiments	. 76
TABLE 4.9 Main and interaction effects calculated from the batch perchlorate reduction experiments.	on . 77
TABLE 4.10 Experimental conditions for flow-through perchlorate reduction experiments.	. 82
TABLE 4.11 Factorial design and results of the flow-through factorial perchlorate reduction experiments.	82
TABLE 4.12 Calculated effects for the factorial model of the flow-through perchlorate reduction experiments.	e 84
TABLE A1.1 Solubility of oxygen in water exposed to water saturated air at 760 mm pressure	Hg 95
TABLE A1.2 Calibration values for various atmospheric pressures & altitudes	. 96
TABLE A1.3 Determination of MDL for perchlorate in tap water	. 99
TABLE A1.4 Standard calibration model for batch perchlroate experiments $(1-3)$	100
TABLE A1.5 Standard calibration model for batch perchlroate experiments $(4-21)$	100
TABLE A1.6 Standard calibration model for flow-through perchlorate experiments	100
TABLE A1.7 Standard calibration model for batch nitrate experiments	101
TABLE A2.1 O3 test sample calculation	102
TABLE A2.2 Ozone test 1	103

_.

ł

TABLE A2.3 Ozone test 2	
TABLE A2.4 Ozone test 3	
TABLE A2.5 Ozone test 4	
TABLE A2.6 Ozone test 5	104
TABLE A2.7 Ozone test 6	
TABLE A2.8 Ozone test 7	
TABLE A2.9 Ozone test 8	
TABLE A2.10 Ozone test 9	
TABLE A2.11 Ozone test 10	
TABLE A2.12 Ozone test 11	
TABLE A2.13 Ozone test 12	
TABLE A2.14 Batch perchlorate experiment 1 – 3	
TABLE A2.15 Batch perchlorate experiment 4 – 12	
TABLE A2.16 Batch perchlorate experiment 13 – 21	
TABLE A2.17 Flow-through perchlorate experiment 1 – 9	
TABLE A2.18 Flow-through perchlorate experiment 10 – 18	

į

LIST OF FIGURES

i

FIGURE 2.1 Structure of the perchlorate compound 10
FIGURE 2.2 Schematic diagram of the anion-exchange processes to remove perchlorate (with a selective anion-exchange resin)
FIGURE 2.3 GEDIT biodegradation of a soil contaminant 22
FIGURE 3.1 Exterior layout of the PAED power supply
FIGURE 3.2 Schematic diagram of the PAED reactor
FIGURE 3.3 Stainless steel cylindrical PAED reactor
FIGURE 3.4 Batch mode setup for O ₃ , H ₂ O ₂ and perchlorate experiments
FIGURE 3.5 Flow-through mode setup for perchlorate experiments
FIGURE 3.6 Factorial design of the O_3 and H_2O_2 quantification experiments (tap water)
FIGURE 3.7 Factorial design of the O ₃ and H ₂ O ₂ quantification experiments (MilliQ Water)
FIGURE 3.8 Factorial design, batch experiment ($d = 1 \text{ mm}$)
FIGURE 3.9 Schematic diagram of the factorial model, from the batch experiments, for water conductivity (σ) and its interaction ($\sigma \times C$) with the radical scavenger concentration.

FIGURE 3.10 Factorial design for the batch experiments conducted with Tap Water 46
FIGURE 3.11 Schematic diagram of the 3-D factorial model for the main effects of the batch perchlorate reduction experiments
FIGURE 3.12 Schematic diagram of the 3-D factorial model for the batch perchlorate reduction experiments. Two-factor interaction effects
FIGURE 3.13 Schematic diagram of the 3-D factorial model for the batch perchlorate reduction experiments. Three-factor interaction effects
FIGURE 3.14 Schematic diagram of the factorial design for the flow-through perchlorate reduction experiments
FIGURE 3.15 Schematic diagram of the 3-D factorial model for the flow-through perchlorate reduction experiments. Main effects
FIGURE 3.16 Schematic diagram of the 3-D factorial model for the flow-through perchlorate reduction experiments. Two-factor interaction effects
FIGURE 3.17 Schematic diagram of the 3-D factorial model for the flow-through perchlorate reduction experiments. Three-factor interaction effects
FIGURE 3.18 HPLC module configuration
FIGURE 3.19 Sampling procedure for the O ₃ experiments
FIGURE 4.1 O ₃ Concentration vs. cumulative input energy for all O ₃ generation experiments
FIGURE 4.2 O_3 Concentration vs. cumulative input energy for O_3 generation experiments $1-4$
FIGURE 4.3 O_3 Concentration vs. cumulative input energy for O_3 generation experiments $5-8$
FIGURE 4.4 O_3 Concentration vs. cumulative input energy for O_3 generation experiments $9-12$
FIGURE 4.5 Nitrate Concentration vs. Cumulative Input Energy for Nitrate Reduction Experiment
FIGURE 4.6 Change in water temperature with cumulative input energy75
FIGURE 4.7 Schematic diagram of the factorial model for the $d \times C$ interaction effect of the batch perchlorate experiment
FIGURE 4.8 Perchlorate concentration versus cumulative input energy for batch tests in PBS and a water electrode gap (d) of 1 mm
FIGURE 4.9 Perchlorate concentration versus cumulative input energy for batch tests conducted with tap water and a water electrode gap (d) of 1 mm
FIGURE 4.10 Perchlorate concentration versus cumulative input energy for batch tests conducted with tap water and a water electrode gap (d) of 1.5 mm

ŧ

FIGURE 4.11 Perchlorate concentration versus cumulative input energy for the flow-	
through perchlorate reduction experiments.	85
FIGURE A1.1 Perchlorate MDL calibration curve	99
FIGURE A1.2 Standard calibration curve for batch nitrate reduction experiment 1	101

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CHAPTER 1 – INTRODUCTION

1.1 BACKGROUND

Water is an essential natural resource; it sustains the structure and composition of all living species. Since the industrial revolution, water pollution has been a serious environmental concern due to ever increasing industrial activities resulting in the release of toxic substances to the environment. Groundwater and surface water are the main sources of the world's potable water supply; hence, the contamination of these water systems has raised serious health issues, both human and environmental. The necessity for high-quality drinking water has led to the development and advancement of water treatment technologies. The water purification processes aims to remove all contaminants from raw water to produce water safe for human consumption.

Among the many toxic chemicals released into the environment, perchlorate has been identified as one that is particularly difficult to treat, as it is strongly oxidative and very stable. Perchlorate has adverse impacts on human health, including the disruption of metabolism and thyroid hormone production. Thyroid disorder can significantly impact fetal and infant brain development. A recent study from the Centers for Disease Control (CDC) in the United States found traces of perchlorate in powdered baby formula derived from cow's milk (Schier *et al.*, 2009). The most likely route for this contamination is contaminated water, ingested by the cows and then transferred to the formula through their milk.

The majority of perchlorate contamination is tied to defense and aerospace sites (Urbansky, 1998). Despite widespread perchlorate contamination, however, there are no federal regulation governing perchlorate concentrations in drinking water in either Canada or the United States. While individual states have their own maximum contaminant level (MCL) guidelines ranging from 1 to $18\mu g/L$. In January 2009, the US Environmental Protection Agency (EPA) issued an interim health advisory report suggesting that no adverse health effects occur from long-term exposure to perchlorate under $15\mu g/L$. Perchlorate concentrations above $6\mu g/L$ have not been reported to date in Canada.

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The tetrahedral configuration of the perchlorate compound creates a well protected shell for the central high oxidation state chlorine atom. Thus, even though the compound is a strong oxidant, it reacts very slowly unless heated. One approach to treating perchlorate is a reduction reaction to convert it to the innocuous chloride ion. Because of the stable structure, however, traditional water treatment technologies have proven ineffective in decomposing this compound when present in water matrices. Few advanced treatment technologies exist, and no cost-effective techniques have been proven to remove perchlorate from large volumes of water.

Pulsed Arc Electrohydraulic Discharge (PAED) is categorized as a direct plasma water treatment technology. This means that, the treatment mechanisms are generated within the water to be treated. The treatment mechanisms are generated via electrical arcs, which are discharged in pulses between two submerged electrodes. The high-current and high-voltage electrical discharges inject energy directly into the aqueous solution forming a plasma channel. The strong pressure waves generated by the arc discharge result in the generation of a cavitation zone, plasma bubbles and shock and expansion waves. The arc discharge also generates photochemical processes leading to UV photolysis, and the formation of radicals (e.g., H• and •OH), ozone and hydrogen peroxide. (Chang *et al.*, 2001; Karpel Vel Leitner *et al.*, 2005)

PAED systems have been proven to be effective in treating chemicals (e.g., VOCs) and inactivating microorganisms (Chang, 2001) in aqueous solution. Research by Karpel Vel Leitner *et al.* (2005) demonstrated reduction via PAED when they converted nitrate

ions to nitrite. Based on Karpel Vel Leitner *et al.*'s (2005) conclusions, it was postulated that PAED may have the potential to reduce perchlorate to innocuous ions. Although the PAED research conducted to date indicates that it has the potential to treat a broad range of contaminants effectively and efficiently, no experiments have been conducted to evaluate its ability to reduce aqueous perchlorate.

1.2 RESEARCH OBJECTIVES

Therefore, the goal of this research is to evaluate the efficacy of PAED for the reduction of aqueous perchlorate. The specific objectives designed to achieve this goal are to:

- a) Develop an analytical method to quantify perchlorate using high performance liquid chromatography (HPLC);
- b) Optimize the power supply settings and water matrix properties for maximum ozone and hydrogen peroxide production;
- c) Determine the efficacy of PAED for the reduction of aqueous perchlorate; and
- d) Establish the power supply setting and water matrix properties for optimal perchlorate reduction.

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1.3 THESIS OUTLINE

This thesis contains four additional chapters.

Chapter 2 provides a background review of perchlorate contamination in the environment, related health issues, and available treatment options. Chapter 3 outlines all of the experimental materials, apparatus and methods used in this research. The experimental observations, results and discussions are provided in Chapter 4. Conclusions drawn from this research, together with recommendations for future work, are presented in Chapter 5.

CHAPTER 2 – REVIEW OF PERCHLORATE CONTAMINATION

2.1 INTRODUCTION

Perchlorate (ClO₄) occurs naturally as a negatively charged chemical compound and as a by-product of manufacturing processes. For many years, perchlorate salts have been used extensively in rocket and missile engine solid propellants, pyrotechnics, additives for lubricating oils, tanning, finished leather, dyes, rubber manufacturing, and other chemical industries (Motzer, 2001). Perchlorate has been observed to have an adverse physiological effect on thyroid hormone production by limiting iodide uptake by the thyroid (Urbansky, 1998). Therefore, the use and disposal of perchlorate salts from manufacturing sites creates environmental concerns in terms of both surface and groundwater systems. Improper disposal and accidental discharges of perchlorate salts by manufacturing facilities may result in its migration to groundwater and surface water. The physical and chemical properties of perchlorate salts and the associated anion make it difficult to delineate perchlorate-contaminated groundwater, and to provide effective and efficient remediation options. For decades, perchlorate pollution in the environment has not received enough attention from the general public and scientific research community. One possible explanation for the lack of effort is that prior to 1997, analytical instruments could not detect perchlorate in groundwater at concentrations below 100µg/L (Motzer, 2001). These low concentrations are of issue, however, as they exceed the 15µg/L for which the USEPA (2008) suggests long-term exposure will likely not cause adverse health effects.

Since the development of ion chromatography with lower detection capability, a significant amount of research concerning perchlorate contamination in the environment has been conducted. The objective of this chapter is to review this research relating specifically to perchlorate contamination and removal technologies. This chapter is divided into the following sections: 1) sources and physico-chemical properties of perchlorate, 2) fate and transport of perchlorate in the environment, 3) removal technologies applicable to perchlorate, and 4) pulsed-arc electrohydraulic discharge.

2.2 SOURCES AND PHYSICO-CHEMICAL PROPERTIES OF PERCHLORATE

2.2.1 Sources of Perchlorate Contamination

Because of its high oxidizing capability, perchlorate is used primarily as an oxidizer in solid rocket propellants, and large quantities are manufactured as ammonium perchlorate. Perchlorate is also found naturally in nitrate deposits in Chile and in fertilizers derived from these deposits (Logan, 2001). The massive production of perchlorate salts, ammonium in particular, began in the 1950s in Henderson, Nevada (Motzer, 2001). Since then, perchlorate contamination resulting from manufacturing discharges has created a growing concern in the surrounding regions. The effluent from industrial facilities containing aqueous perchlorate either infiltrates into the subsurface or is discharged to surrounding surface water bodies. Natural water resources have been seriously contaminated with perchlorate. In the western states, most perchlorate occurrences are located in Nevada, California, and Utah, and are caused by discharge from rocket fuel manufacturing plants or from the demilitarization of weaponry (missiles) (Urbansky, 1998). Because most of the perchlorate production facilities are located in Henderson, Nevada, two nearby surface water bodies, Lake Mead and the Colorado River, are heavily affected by the effluent from these facilities (Urbansky, 2002).

Table 2.1 (after Motzer, 2001) shows various water sources contaminated by perchlorate. The discharges from ammonium perchlorate-manufacturing facilities near Henderson, Nevada are responsible for the contamination in Lake Mead (concentration

ranging from 1,500 to 1,700µg/L). The highest observed perchlorate concentration is located in Placer County ranging from 1,200 to 67,000µg/L (Table 2.1). At the Naval Weapons Industrial Reserve Plant (NWIRP) site in Texas, the level of perchlorate in contaminated soil below the propellant mixing facilities ranges from 0.023mg/kg to 1,800mg/kg (Motzer, 2001). Perchlorate concentrations were measured as high as 5,600µg/L in nearby surface water (Motzer, 2001). Groundwater samples collected in the same area had concentrations ranging from 4.0µg/L to 97,000µg/L. Perchlorate contamination has also been detected in other regions in the U.S., for example, New York and Iowa. There are no large-scale perchlorate manufacturing activities in these areas. The use of fertilizer imported from Chile is believed to be the major source causing perchlorate contaminated groundwater in New York State (Motzer, 2001).

Location				
State	Country	Type of well or source	No. of wells	Perchlorate concentration range (µg/L)
California:	Los Angeles	Drinking Water	88	1.49 to 159.0
	Orange	Drinking Water	14	5.06 to 10.7
	Placer (near Lincoln)	Monitoring	1	1,200 to 67,000
	Riverside	Drinking Water	23	4.0 to 55.0
	Sacramento	Drinking Water	15	4.0 to 400
	San Benito	Agricultural	1	to 34
	San Benito	Drinking Water	1	to 810
	San Bernardino	Agricultural	24	11.3 to 99.1
	San Bernardino	Drinking Water	31	4.0 to 820
	Santa Clara	Monitoring	?	
	Ventura	Springs	2	6.8 to 11.6
Nevada:	Clark	Lake Mead Inlet (Las Vegas Wash)	-	1,500 to 1,680
	Clark	Lake Mead and the Colorado River	-	4 to 16
	Clark	Lake Mead Outlet at Hoover Dam	-	8
	Clark (Henderson)	Monitoring	1	to 3,700,000

TABLE 2.1 Summary of reported perchlorate concentrations in water sources. After: Motzer, 2001

2.2.2 Chemical and Physical Properties

The perchlorate anion (ClO_4) consists of a tetrahedral array of oxygen atoms around a central chlorine atom (Figure 2.1).



FIGURE 2.1 Structure of the perchlorate compound.

The chlorine atom in the perchlorate molecule is in the +7 oxidation state, thus, perchlorate is a strong oxidizing agent. Because of the high oxidation state of the central chlorine atom, the compound is usually used as an oxidant or an electron acceptor in reduction-oxidation (REDOX) reactions. Common perchlorate salts include ammonium, potassium, and sodium perchlorate. Perchlorate salts are extremely soluble (Table 2.2) and highly reactive as solids. However, once dissolved in water and under standard temperature and pressure conditions, the associated anions are highly mobile, nonreactive, stable, and require decades to degrade (Motzer, 2001).

Compound	Structural Formula	Molecular Mass (g/mol)	Density (g/cm ³) (water = 1)	Aqueous Solubility at 20°C (10^3 mg/L)
Ammonium Perchlorate	NH4ClO4	117.488	1.952	217.0-220.0
Calcium Perchlorate	$Ca(ClO_4)_2$	238.978	2.651	Soluble
Lithium Perchlorate	LiClO ₄	106.3906	2.428-2.429	375.0
Magnesium Perchlorate	$Mg(ClO_4)_2$	223.23	2.21-2.6	496.0
Perchloric Acid	HClO ₄	100.457	1.664-1.764	v.s.; > 50% but not > 72% acid, by mass
Potassium Perchlorate	KClO4	138.547	2,5298	7.5 to 16.80
Sodium Perchlorate	NaClO ₄	122.439	2.02-2.499	2010.0

TABLE 2.2 Physico-chemical properties of various perchlorate compounds. *After: Motzer, 2001*

Although perchlorate compounds contain a highly oxidized central halogen atom, chlorine (+7), the reactivity as an oxidant is relatively low. Four oxygen atoms form a strong shield to protect the central chlorine. Therefore, the structure prevents chlorine from being reduced under normal atmospheric conditions. The unusually low reactivity is a matter of kinetic lability rather than thermodynamic stability (Urbansky, 1998). In the presence of an electron donor, reduction of perchlorate proceeds through the following pathway (Simon & Weber, 2005):

Due to the chemical and physical properties of perchlorate, it is extremely difficult to effectively delineate, and therefore remediate, contaminated groundwater systems. Physically, perchlorate does not sorb well to most surfaces because of the low charge density of the perchlorate anion (Urbansky, 2002). Chemically, common reducing agents, such as hydrogen, do not reduce perchlorate readily, and common cations, such as metal ions, do not precipitate it (Urbansky, 1998).

2.2.3 Health Effects

Perchlorate compounds in the form of dust irritate the skin, eyes and mucous membranes. However, studies show that inhalation by workers in perchlorate manufacturing facilities with airborne exposure resulted in a no-observed-adverse-effect-level (NOAEL). Other studies of long-term exposure to ammonium perchlorate have shown that it may result in the destruction of red blood cells and liver and kidney damage (Motzer, 2001). The perchlorate anion solution does not sorb through skin, and therefore the exposure pathway for aqueous perchlorate is through ingestion of contaminated water. Perchlorate can also disrupt the production of thyroid hormones and thus disrupt the human metabolism (Urbansky, 2002). The perchlorate anion has the same ionic charge and radius as the iodide ion, thus it interferes with the body's iodine uptake, inhibiting

thyroid hormone production (Motzer, 2001). Perchlorate can directly affect organs and tissues in addition to the thyroid gland (Urbansky, 1998). Perchlorate has also been used as a medical treatment for Grave's disease which is an over production of the thyroid hormone (hyperthyroidism) (Logan, 2001). However, the health impact of perchlorate on the human body at low dosages is unclear.

2.3 FATE AND TRANSPORT IN GROUNDWATER

When improperly disposed or accidentally spilled, perchlorate salts will dissolve into precipitation and subsequently infiltrate into the groundwater system or discharge to surface water bodies. Perchlorate reaching the saturated zone in the subsurface is then transported with the groundwater flow. The main solute transport processes in groundwater include advection, diffusion, dispersion, adsorption, and biodegradation (Bedient *et al.*, 1999). The high solubility of perchlorate salts and low sorption coefficient in most soils results in high mobility and rapid transport in groundwater systems (Motzer, 2001). Numerous factors will have a significant impact on the movement of perchlorate in subsurface systems, including: 1) the initial perchlorate concentration, 2) properties of the porous media (i.e., porosity, fraction of organic carbon (f_{oc}), permeability, tortuosity and heterogeneity), 3) hydraulic gradient, 4) temperature, and 5) microbial population present (Tan *et al.*, 2005). Understanding the principles of perchlorate transport in groundwater systems aids with the delineation of contaminated zones in subsurface systems, and ultimately with the development of remedial options. In addition to advection and dispersion, the primary physical mechanisms influencing perchlorate transport in groundwater systems includes density effects, plant uptake, and capillarity. The release of large masses of perchlorate into the environment can result in a dense brine solution due to the high solubility of perchlorate. The movement of these brine solutions in groundwater is controlled primarily by density effects, similar to the density-driven component of dense non-aqueous phase liquid (DNAPL) migration (Motzer, 2001). These brine solutions sink through more permeable zones and form pools upon encountering capillary barriers. The brine pools are then a long term contaminant source.

In unsaturated zones and unconfined aquifers, perchlorate can be taken up by plants through their root systems. Additionally, perchlorate may be held immobile, in the capillary fringe and the vadose zone by capillary forces (Trumpolt *et al.*, 2005).

The two primary chemical processes impacting perchlorate transport in groundwater systems are sorption and precipitation. Sorption is typically measured by the distribution coefficient, K_d . There are three main factors contributing to the distribution coefficient, including: 1) the aqueous solubility; 2) polar-ionic characteristics, and 3) the octanol-water partition coefficient (Bedient *et al.*, 1999). The perchlorate distribution coefficient has been well established by researchers; however, sorption to soil and sediments has not been well characterized and research is still in progress. In very sandy soil, perchlorate sorption is considered to be insignificant (Motzer, 2001). Experiments by Tipton *et al.* (2003) demonstrated no retardation of perchlorate relative to bromide in

14

either organic-rich or poor soils. However, the conditions in the experiments cited here are not exhaustive, and therefore more work is required to fully determine the effects of perchlorate sorption in subsurface systems. Ionic strength and pH both influence sorption capacity, and therefore it is possible that at some ionic strength and pH combination perchlorate will sorb to soil (Motzer, 2001).

Motzer (2001) noted that precipitation may also have a significant impact on perchlorate migration in groundwater. Some perchlorate salts are less soluble than others, causing a "salting-out" effect thereby reducing the migration potential.

The biological mechanism affecting perchlorate transport in groundwater systems is biodegradation, which is a biochemical reaction, mediated by microorganisms. In general, electrons are transferred from electron donors (oxidation) to electron acceptors (reduction) (Bedient *et al.*, 1999). Six conditions are required for biodegradation to take place: 1) appropriate organisms, 2) an energy source (electron donor), 3) a carbon source, 4) an electron acceptor, 5) nutrients, and 6) acceptable environmental conditions.

Tipton *et al.* (2003) performed column experiments to demonstrate that biodegradation has the potential to influence the transport of perchlorate in soils that have not been amended with either nutrients or carbon. These experiments suggested that hydraulic conductivity impacts biodegradation in contaminated zones; lower conductivity zones provide more time for the biodegradation of perchlorate to take place, which also slows down the transport of perchlorate. Tan *et al.* (2004) studied the kinetics of perchlorate biodegradation in sediments and soils. Generally, perchlorate biodegradation

15

rates are affected by the availability of organic substrate, not by nitrate. The results of these experiments indicated that perchlorate degradation follows a first-order kinetic process. However, the degradation constant varied from site to site due to different environmental conditions, such as organic substrate availability. In addition, the lag time (acclimation period without degradation or with less than 5% degradation) of perchlorate degradation increased with lower levels of TVS in the soil. Bio-degradation kinetics also have a significant impact on the transport of perchlorate in groundwater.

In summary, in the absence of remedial efforts, the transport of perchlorate in soil and groundwater systems is controlled primarily through physical mechanisms (i.e., advection and dispersion) rather than chemical (i.e., absorption and adsorption) or biological processes (Adilman *et al.*, 2000). Because perchlorate is present in groundwater systems and it has a negative effect on human and environmental health, effective remedial strategies need to be developed.

2.4 **REMEDIATION TECHNOLOGIES**

Many traditional remedial and treatment techniques do not effectively remove perchlorate from water; therefore, advanced remediation technologies need to be developed to solve the perchlorate problem. The following paragraphs discuss several remediation techniques that have been applied to perchlorate solutions, including ion exchange, membrane processes, REDOX reactions, and various biological and biochemical techniques. The remediation technologies discussed here are examined primarily with respect to perchlorate removal efficacy under various environmental conditions.

2.4.1 Ion Exchange

Ion-exchange has been widely used in the water treatment industry for decades (Gu et al., 2003). In the ion-exchange process, ions in solution are exchanged with more benign ions contained in a resin, while maintaining electroneutrality in both the resin and solution. For example, chloride ions may be substituted for perchlorate ions one for one (Motzer, 2001; Urbansky, 2002). One problem in the conventional ion-exchange system is the unselective removal of all anions in the water. Therefore, because perchlorate concentrations are generally relatively low in comparison with other anions typically present in groundwater (e.g., NO₃⁻, SO₄²⁻, Cl⁻, and HCO₃⁻), the percentage of perchlorate anions removed is relatively low due to competition for sorption sites from these other ions (Figure 2.2) (Gu *et al.*, 2003). Additionally, the reduction potential of perchlorate (E^0 = +1.4V) is relatively high, indicating that it will exchange with the anions on the resin less readily than most other anions present in solution. Therefore, selective anion exchange resins need to be used to intentionally capture perchlorate ions. Gu et al. (2003) used a case study at Edwards Air Force Base (AFB) to demonstrate the treatment efficacy of a selective anion-exchange resin to remove perchlorate from groundwater. The resin was able to treat 40,000 bed volumes of groundwater with an initial perchlorate concentration of 450µg/L before breakthrough was observed.



FIGURE 2.2 Schematic diagram of the anion-exchange processes to remove perchlorate (with a selective anion-exchange resin). Source: Gu et al., 2003

2.4.2 Membrane Processes

Simple salts, including perchlorate salts, can be removed using membrane processes and nanofiltration. However, these processes are not selective and therefore result in demineralization of the water being treated (Urbansky, 2002). Although membrane technologies, like reverse osmosis (RO), can significantly reduce perchlorate concentration in water, they are expensive to operate and will produce concentrated wastes that need further treatment. Given the state of current technology, it is neither practical nor economical to employ membrane processes for large-scale perchlorate removal efforts due to the fouling of membranes and the associated maintenance. Membrane systems are currently more suitable for homeowners and small businesses as a point-of-use device.

2.4.3 Chemical REDOX Technologies

Because of the high oxidation state of the chlorine atom (+7) in its chemical formation, perchlorate compounds are often used as a strong oxidants or electron acceptors in redox reactions. To remove perchlorate from water, however, the chlorine atom must be reduced to its innocuous chloride anion. To reduce the oxidation state of the central chlorine molecule, appropriate electron donors must be presented to facilitate electron transfer between oxidants and reductants. Reduction of the perchlorate anion using the reducing agent Fe^o has been demonstrated. When combined with UV light, significant reduction of perchlorate can occur (Motzer, 2001). However, the REDOX technologies for perchlorate reduction have not been explored extensively.

2.4.4 In-Situ Biological and Biochemical Processes

Bioaugmentation and bioremediation techniques, which promote biological and biochemical treatment, may be effective approaches to solve the perchlorate contamination problem. Several bacteria containing nitrate reductases have the ability to reduce the perchlorate compound (Urbansky, 1998). Urbansky (2002) noted that biological remediation appears to hold the most promise in dealing with contaminated sites. Simon and Weber (2006) demonstrated that perchlorate present in river sediment can be reduced by naturally occurring microbes that have not been previously exposed to

19

perchlorate. Urbansky (1998) also noted that researchers have reported that perchlorate and chlorate can be reduced to chloride by *Proteobacteria* with acetate as an energy source (reductant) at a neutral pH.

Gaseous electron donor injection technology (GEDIT), which is an anaerobic variation of petroleum hydrocarbon bioventing, was applied to perchlorate-contaminated groundwater by Evans and Trute (2006). This technology involves injecting a gaseous electron donor, such as hydrogen or ethyl acetate, into the contaminated zone to promote biodegradation and reduction (Figure 2.3). Evans and Trute (2006) employed GEDIT to evaluate its potential for the *in-situ* bioremediation of nitrate and perchlorate in the vadose zone. Their experiment employed two studies to evaluate the GEDIT performance under various conditions. The first study involved two soil microcosms to examine the effects of different electron donors (i.e., hydrogen and ethanol) on nitrate and perchlorate biodegradation under various moisture and nutrient conditions. This first study showed that moisture had a positive effect on nitrate and perchlorate reduction with hydrogen and ethanol as electron donors in the microcosms. With only moisture supplementation, ethanol promoted complete perchlorate reduction, and hydrogen promoted only partial reduction, ranging from 10% to 40%. Nutrient supplementation did not promote significant nitrate or perchlorate reduction. The second study, in which electron donor concentrations were varied, showed that both sufficient time (i.e., 105 days) and electron donor (i.e., 400% stoichiometric ethanol or 2,000% stoichiometric hydrogen) must be provided to achieve complete nitrate and perchlorate reduction.

Evans and Trute (2006) subsequently performed column studies to investigate electron donor transport and biodegradation of nitrate and perchlorate in columns of contaminated soil. The soil samples were homogenized, and argon was used as the carrier gas to carry the liquid electron donor into the column inlet. The influent liquid electron donor (i.e., ethanol, ethyl acetate, butyl acetate, and butyraldehyde) flow rate was kept constant at 0.5µL/min, and carrier gas flowrate was set to 42mL/min for the duration of the experiment. Various electron donors were used to compare their efficiencies, and effluent samples were analyzed after 34 days. The results showed that, at a given time, ethyl acetate and butyraldehyde travelled longer distances than either ethanol or butyl acetate in the soil column. The electron donor transport was affected not only by the mass injected, but also by its ability to partition from the gaseous phase to the soil and soil moisture phases. Several factors were considered to have an impact on the electron donor transport, including soil moisture, Henry's Law constant and the organic carbon-water partitioning coefficient (K_{OC}). Because of the poor electron donor transport properties (i.e., incomplete mixing throughout the column), complete perchlorate reduction was not observed in any of the column experiments. However, the ethyl acetate was transported more quickly and mixed better throughout the column, resulting in consistent and significant nitrate reduction throughout the column. The differing transport properties of the electron donors resulted in nitrate reduction occurring prior to perchlorate reduction. It was therefore concluded that electron donors for GEDIT must satisfy following conditions: 1) ability to facilitate anaerobic biodegradation of nitrate or perchlorate, 2) capable of being transported through moist soil, 3) sufficient mass can be added to

promote anaerobic reduction, and 4) possess properties that minimize gas volume being injected to meet the stoichiometric demand (400%).



FIGURE 2.3 GEDIT biodegradation of a soil contaminant Source: Evans and Trute (2006)

Hunter (2002) performed an experiment with permeable barriers containing vegetable oil in soil columns to investigate the removal of chlorate and perchlorate from groundwater. The goal was to provide an appropriate electron donor to enable native microorganisms to reduce the chlorate and perchlorate ions to chloride as water flowed through the permeable barrier. Vegetable oils are a unique electron donor; they can be injected into the groundwater to form *in situ*, biologically active permeable barriers that separate clean water from the contaminant front due to their immiscible nature. The soil samples employed in Hunter's (2002) columns were packed to a uniform bulk density and received a fixed mass of soybean oil emulsion. Water containing perchlorate was pumped through the columns for a period of 20 weeks. Separate microcosm studies and
soil surveys were also performed to evaluate the perchlorate reducing ability of the soil in the presence of soybean oil.

In the column study, more than 99% of the perchlorate in the influent water was reduced to chloride within the columns. The soil survey study with soil samples collected from various sites (e.g., sewage sludge and agricultural irrigation ditch) showed microorganisms in the samples were capable of reducing perchlorate in the presence of soybean oil. This study also showed that perchlorate-reducing microorganisms are ubiquitous in surface soils. The soybean oil barrier stimulated these microorganisms in the soil to reduce perchlorate to chloride, confirming that vegetable oils may be effective *in situ* permeable biobarriers for perchlorate removal.

2.4.5 Ex-Situ Bioreactors

Min *et al.* (2004) conducted pilot-scale experiments to test the perchlorate removal efficiency of both sand and plastic media-based packed bed bioreactors (PBR). The objective of the experiments was to demonstrate the efficacy of a PBR system for complete perchlorate degradation. Two pilot-scale bioreactors were operated side-by-side to treat perchlorate-contaminated groundwater at a site in Redlands, California. One was packed with sand and the other one was packed with plastic media. Both reactors were bioaugmented with the perchlorate-respiring bacterium. In both PBRs, the effluent perchlorate concentrations (between 95% and 48% removal, reported as non-detect when $< 4\mu g/L$) were a function of the hydraulic loading rate and backwashing frequency. In the

plastic media reactor, consistent and complete perchlorate removal was achieved with a hydraulic loading rate of 0.34 L·m⁻²·s⁻¹ in the first month of operation. After approximately one month, a higher loading rate, of $0.68L \cdot m^{-2} \cdot s^{-1}$, was employed but the perchlorate removal efficiency became inconsistent. The results also showed that regular backwashing was critical for complete and consistent perchlorate removal, as it ensured efficient reactor operation and prevented channelling or short-circuiting of flow inside the PBR. The detention time required in the plastic media PBR was longer than that required in the sand-based operation (i.e., 70min for plastic media PBR and 30min for sand media PBR) due to the specific surface area differences between the two media ($A_{plastic} = 230 \text{ m}^{-1}$, $A_{sand} = 6000 \text{ m}^{-1}$). Even so, the plastic media PBR was preferred over the sand media PBR due to the fact that 1) the sand media PBR was more difficult to backwash than the plastic media as channelling and short-circuiting problems occurred in the lower porosity sand, and 2) the sand medium reactor produced higher back pressures (i.e., $50 \pm 11 \text{ kPa}$ versus $32 \pm 11 \text{ kPa}$ in plastic media), which resulted in higher operating costs.

2.4.6 Summary

It has been shown that aqueous perchlorate can be partially removed or eliminated from water by various remediation technologies. Selective ion exchange was able to remove perchlorate from as much as 40, 000 bed volumes of contaminated water. Membrane technologies are neither practical nor economical for large-scale perchlorate removal. Depending on soil conditions and electron donors used in the process, bioremediation techniques have been demonstrated to have potential for perchlorate removal in the vadose zone. Biological and biochemical processes were successful in removing more than 99% of perchlorate present in soil. Furthermore, packed bed bioreactors were capable of removing perchlorate from water to below the detection limit $(4\mu g/L)$ with constant hydraulic loading and frequent backwashing

2.5 PULSED-ARC ELECTROHYDRAULIC DISCHARGE (PAED)

There are three types of plasma technologies available for the treatment of water, including: remote (plasma generation away from the medium to be treated e.g., ozone), indirect (near to, but not directly within the medium to be treated, e.g., UV), and direct (within the medium to be treated, e.g., electrohydraulic discharge) (Chang *et al.*, 2008).

Pulsed-Arc Electrohydraulic Discharge (PAED) was developed as a direct plasma water treatment technology for the removal of physical, chemical and microbial contaminants (Chang *et al.*, 2000, 2001, 2004; Karpel Vel Leitner *et al.*, 2005; Sato *et al.*, 1996). PAED treatment systems incorporate two components, including a reactor equipped with electrodes and a spark-gap-type power supply. PAED systems generate a rapid discharge of stored electrical charge across the submerged electrodes (in the reactor) to form a local plasma region within the water matrix. Several physical and chemical treatment mechanisms are produced, including: high electric fields, UV radiation, pressure waves, radicals, heat, electrons and ions, and electromagnetic pulses. Research has shown that PAED has the ability to effectively treat a wide range of contaminants, including both chemical and biological (Chang et al., 2008), together in a single unit process.

Karpel Vel Leitner *et al.* (2004) observed the reduction of nitrate to nitrite using a PAED treatment system. Perchlorate and nitrate both require a similar reduction mechanism, and it was therefore postulated that PAED may provide sufficient electron donors and thermal energy to initiate the reduction of perchlorate to chloride. Therefore, this research was designed to examine the potential application of PAED to aqueous perchlorate reduction.

2.6 SUMMARY

The development of better analytical instruments has significantly improved the capability for detecting perchlorate contamination at low concentrations, which has provided a platform for further research on the perchlorate contamination problem. To date, much of the research conducted on perchlorate contamination in the environment and potential perchlorate remediation technologies has shown promising results. However, much work remains to be done in order to successfully eliminate the problem: 1) the factors concerning the fate and transport of perchlorate in groundwater systems have not yet been studied in full detail, and 2) more effective and economical *in-situ* and *ex-situ* technologies for the remediation of perchlorate-contaminated water still need to be developed.

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Although advanced treatment technologies exist to remove perchlorate from water, there is no proven cost-effective treatment process that can remove perchlorate from large volumes of water. Karpel Vel Leitner *et al.* (2004) demonstrated the reduction of nitrate to nitrite using a PAED system, which suggests that this system may also be capable of reducing perchlorate to the innocuous chloride ion.

CHAPTER 3 – MATERIALS AND METHODS

3.1 INTRODUCTION

The purpose of this research is twofold: 1) to quantify ozone and hydrogen peroxide production by PAED under various experimental conditions, and 2) to examine the efficacy of PAED for the reduction of aqueous perchlorate. A series of laboratory experiments were designed and conducted to fulfill these objectives. This chapter describes the materials, apparatus and methods employed for these experiments.

3.2 MATERIALS

3.2.1 PAED Power Supply

A custom spark-gap-type power supply (Dajere Technology Inc., Model MD 03) was employed in this research. The power supply consists of three major components: a constant current charger, a high voltage switch, and two capacitors. The exterior layout of the power supply is shown in Figure 3.1; the components and their functions are listed in Table 3.1. The power supply is driven by a 120V source and has the ability to supply 0.3 kJ per electrical pulse. Once the current charges the capacitor to 0.3 kJ, a high voltage is imposed between two air-gap electrodes through a mechanical switch and the gap is closed by pulsed electrical discharges. The current that has been stored in the capacitor then flows into the water electrode gap and generates an arc discharge channel (Chang *et al.*, 2004).

COMPONENT	FUNCTION		
Air Gap Adjustor	Adjusts the air gap distance inside the power supply within $1\mu m$.		
Door Lock Pin	Locks the power supply door for safety purposes		
Fan	Cools the electrical components		
Ground Stick	Ensure complete discharge of the electrical current the reactor after the power supply is shut down		
High Voltage Adjustor	Enables the voltage input to be adjusted		
High Voltage Output Cable	Connects the power supply to the reactor		
Pilot Lamp	Indicates when the power supply is turned on		
Power Cord	Plugs into a 120V outlet to provide energy for the		
(Canadian Plug AC125V, 15A)	power supply		
Power Switch	Turns the power supply on and off		

TABLE 3.1 Exterior components of the PAED power supply and their functionsCOMPONENTFUNCTION

TABLE 3.1 Exterior components of the PAED power supply and their functions

Safety Switch	Shuts down the power supply immediately in
	emergency situations.

Voltage Meter	Indicates the charging voltage externally.
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FIGURE 3.1 Exterior layout of the PAED power supply.

The interior components of the PAED power supply are proprietary (Dajere Technologies Inc.); however, the components and their functions are listed in Table 3.2.

COMPONENT	FUNCTION/SPECIFICATIONS
Air Gap	two Ti electrodes separated by a gap (adjustable via the air gap adjustor)
Capacitors	store electrical energy (0.95 <i>u</i> F, 2200VAC)
Charging Voltage Capacitor	stores electrical energy $(4uF)$
Diodes	unidirectional electric current flow
Fan	cools electrical components
Gap Adjustor	adjusts the air gap distance
Ground Point	connects to ground
High Voltage Resistor	100k, 1/4W
Nichrome Wire	0.051 inch
Output Cable	Transfers energy to the reactor electrodes (water gap)
Safety Switch	disconnects power when the access door is open
Transformer	transfers electrical energy from the input to the air gap discharge (input 120V, 60Hz; output 2500V, 0.6A)
Variac	variable autotransformer, regulates the voltage input to the system (input 120V AC, output 0-115VAC, 60Hz)
Voltage Meter	displays the charging voltage
Voltage Resistors	$40k\Omega$, 10W, 5 in series

TABLE 3.2 Interior components of the PAED power supply

3.2.2 PAED Reactor

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A 3-Litre stainless steel cylindrical reactor with a length to width ratio of 3:1 was used in these experiments. A schematic diagram and photograph of the reactor are shown in Figures 3.3 and 3.4 respectively. Two 0.635cm diameter titanium electrodes were installed off-centre (eccentrically), 1.865cm above bottom of the reactor wall, end-to-end in the reactor so that the reflected pressure waves would not cancel out new pressure waves as they are generated. The electrodes were insulated from the reactor body using Teflon fittings. Two Teflon supports were placed in the middle of the reactor to stabilize the electrodes during discharges. Stainless steel male connectors (Swagelok SS-400-1-4) were used at each end of the reactor to provide additional support for the electrodes and facilitate the adjustment of the water electrode gap. A circular opening near the middle of the reactor body provides viewing of the water electrode gap and enables the extraction of water samples. Withdrawal ports are located on the upstream and downstream ends of the reactor for sampling purposes during the flow-through experiments. A plastic and wood stand provides further stability for the reactor during the PAED treatment process.



FIGURE 3.2 Schematic diagram of the PAED reactor.



FIGURE 3.3 Stainless steel cylindrical PAED reactor.

3.2.3 Perchlorate

Potassium perchlorate (KClO₄) (90-100%, CAS#:7778-74-7, J.T.Baker) was used for the preparation of perchlorate solutions at various concentrations. The salt has an aqueous solubility of 15g/L and a density of 2.52 g/cm³. Stock and standard solutions were prepared for ion chromatography calibration and experimental treatment solutions according to the method prescribed by Standard Methods (Method 4110B, APHA-AWWA-WEF, 2000).

3.2.4 Reagents

Various reagents were prepared and employed for the quantification of ozone (O_3) , hydrogen peroxide (H_2O_2) and perchlorate. The recipes for these reagents are given in Tables 3.3, 3.4, and 3.5 respectively. Two water matrices were employed in the perchlorate reduction experiments: tap water and a phosphate buffered saline solution (PBS). The recipe for the PBS solution is given in Table 3.6. Appendix 1.2 provides detailed procedures for the preparation of these reagents.

DEACENTS	RECIPE		
KEAGENIS	Chemicals	Quantity	
Indigo Stock Solution	MilliQ water (Barnstead, Nano Pure Diamond)	500 mL	
	Phosphoric acid-85% (Fisher Scientific)	1 mL	
	Potassium indigo trisulfonate – $C_{16}H_7N_2O_{11}S_3K_3$ (Sigma-Aldrich Canada)	770 mg	
Indigo Reagent I	MilliQ water	1000 mL	
	Phosphoric acid-85%	7 mL	
	Sodium dihydrogen phosphate – NaH ₂ PO ₄ <i>(EMD Chemicals)</i>	10 g	
	Indigo stock solution	20 mL	

TABLE 3.3 Reagents employed in the quantification of O_{3.}

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DEACENTS	RECIPE		
KEAGENIS	Chemicals	Quantity	
Potassium iodide solution (1% w/v)	Potassium Iodide – KI <i>(Sigma-Aldrich Canada)</i>	1.0 g	
	MilliQ water	100 mL	
Ammonium molybdate solution	Ammonium Molybdate (MP Biochemicals LLC)	9 g	
	6N NH₄OH	10 mL	
	NH ₄ NO ₃	24 g	
Sulphuric acid solution	$H_2SO_4 - 93\%$ (Mallinckrodt Chemical)	1 part	
	MilliQ water	4 parts	
Starch indicator	Starch – 1%w/v (VWR International)	varies	
Sodium thiosulfate solution (0.1N)	Na ₂ S ₂ O ₃ (VWR International)	varies	

TABLE 3.4 Reagents employed for the quantification of H₂O_{2.}

TABLE 3.5 Reagents employed for the quantification of perchlorate.

	RECIPE		
KEAGEN15	Chemicals	Quantity	
Water	MilliQ water, 18.0 M Ω -cm resistance	varies	
Eluent	NaOH (50% w/w, VWR International)	50 mM	
Regenerant	H ₂ SO ₄	50 mN	
Standard Anion Solutions	Perchlorate Standards	1mg/L, 5mg/L, and 10 mg/L	
Gas	Helium Gas (<i>VitalAire, Medical Grade</i>)	varies	

DEACENTE	RECIPE		
KEAGEN15	Chemicals	Quantity	
1X PBS solution	Sodium Chloride – NaCl (EMD Chemicals)	8 g	
	Potassium Chloride – KCl (EMD Chemicals)	0.27 g	
	Sodium Phosphate – Na ₂ HPO ₄ (EMD Chemicals)	1.44 g	
	Potassium Phosphate – KH ₂ PO ₄ (EMD Chemicals)	0.2 g	
	MilliQ water	~1 L	

TABLE 3.6	Recipe f	for phosp	hate buf	fered saline	(PBS)) solution.
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3.3 EXPERIMENTAL METHODS

3.3.1 Experimental Setup

A series of batch experiments was conducted to quantify both O_3 and H_2O_2 production and perchlorate reduction by the PAED system. Flow-through experiments were then conducted to further investigate perchlorate reduction by PAED. This section describes the apparatus and methodology used for both the batch and flow-through experiments.

Schematic diagrams of the apparatus for the batch and flow-through experiments are shown in Figures 3.4 and 3.5 respectively. For the flow-through experiments, an 8L reservoir was used to store the perchlorate-contaminated water that was continuously pumped through the system. Tubing (Tygon[®]R-3603 ID-0.9525cm) and a peristaltic pump (Masterflex[®]L/S, Model 7523-60) were used to connect the reservoir and the

36

reactor to form a flow-through loop. The system effluent was directed to the storage reservoir and pumped back into circulation.



FIGURE 3.4 Batch mode setup for O₃, H₂O₂ and perchlorate experiments.



FIGURE 3.5 Flow-through mode setup for perchlorate experiments.

3.3.2 Experimental Design for O₃ and H₂O₂ Generation Experiments

A literature review was conducted to determine which factors likely have the largest effect on the generation of O_3 and H_2O_2 . With the goal of maximizing the concentrations of these constituents produced by PAED, the review indicated that the water matrix composition, dissolved oxygen concentration, and water electrode gap should be investigated. Table 3.7 lists the rational for choosing each of these operating parameters. An initial fractional factorial experiment was then designed to determine exactly which factor(s) required further investigation. A well-constructed experimental design procedure such as this provides the most effective and economical approach towards optimizing any system.

PARAMETER		RATIONALE
1. Water matrix		MilliQ water (~0.04 mS/cm) is devoid of ions, and therefore
(Distilled water and		results in minimal interference when conducting analyses;
Sodium Phosphate)	-	DI water alone is not conductive enough to facilitate arc
		discharges;
	-	Tap water (~0.33mS/cm) can facilitate discharges, but oxidants
		(e.g. chlorine) may cause interference with the indigo ozone
		quantification technique;
	_	The addition of sodium phosphate (Na ₂ HPO ₄) to MilliQ water
		increases the conductivity while limiting potential interference
		for O_3 and H_2O_2 quantification techniques.

TABLE 3.7 Experimental factors for O₃ and H₂O₂ measurement

I ADDE 507 Experin	none	an factors for O3 and 11202 measurement
2. Dissolved	_	Oxygen molecules are essential in the production of O_3 by
Oxygen (DO) concentration		PAED;
	_	The concentration of DO in the water matrix affects the
		amount of oxygen available for O_3 formation by PAED.
3. Water Electrode	_	Previous research suggests that the water electrode gap affects
Gap		the characteristics of the arc discharge.

TABLE 3.7 Experimental fa	ctors for O3 and H	₂ O ₂ measurement
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Table 3.8 shows the actual value for each factor level investigated in these experiments. The factorial experimental scheme is given in Table 3.9. A total of 12 experiments were conducted in which the specific operating conditions (factors) were varied, and the resulting O_3 and H_2O_2 concentrations generated were analyzed in samples collected from the batch reactor. The geometric configurations of the factorial models for the O_3 and H_2O_2 generation experiments are presented in Figures 3.6 and 3.7.

TABLE 5.6 Factorial design for 63 and 11202 measurement						
FACTOR	UNIT	-1	0	+1		
1. Sodium Phosphate (Na ₂ HPO ₄)	mg/L	1000	4000	8000		
2. Dissolved Oxygen (DO)	mg/L	None	-	Saturated (8.3 mg/L)		
3. Water Electrode Gap	mm	1	-	1.5		

TABLE 3.8 Factorial design for O₃ and H₂O₂ measurement

Run	Water Matrix	Na2HPO4 (mg/L)	Electrode Gap (mm)	Dissolved Oxygen (mg/L)
1	Тар	0	1	Saturated
2		1000	1	Saturated
3	MilliQ	4000	1	Saturated
4		8000	1	Saturated
5	Тар	0	1	0
6		1000	1	0
7	MilliQ	4000	1	0
8		8000	1	0
9	Тар	0	1.5	Saturated
10		1000	1.5	Saturated
11	MilliQ	4000	1.5	Saturated
12		8000	1.5	Saturated

TABLE 3.9	O ₃ and	H_2O_2	experiment	scheme
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FIGURE 3.7 Factorial design of the O_3 and H_2O_2 quantification experiments (MilliQ Water)

For experiments 1 through 4, samples were collected every 5 minutes for a total of 6 samples per test. For the remaining experiments, samples were collected every 10 minutes for a total of 3 samples per experiment. All samples were analyzed for O_3 concentration, while only the 30-min sample from each test was analyzed for H_2O_2 concentration.

3.3.3 Perchlorate Reduction Experimental Design

The objective of these experiments was to determine the optimal operating parameters for perchlorate reduction by PAED. According to the literature, a number of factors have the potential to affect the reduction of perchlorate by PAED, including: the radical scavenger concentrations, the conductivity of the water matrix, the water electrode gap, and the cumulative input energy. Table 3.10 lists the factors chosen for investigation in these experiments, together with the rational for each one.

The extent of the influence of each factor was unknown prior to these experiments. Therefore, similar to the O_3 and H_2O_2 production experiments, an initial set of fractional factorial experiments was conducted to determine the influence of each factor and determine the most appropriate direction for further experiments.

PARAMETER		RATIONALE				
1. Cumulative Input	_	Associated with the residence time of the water being treated				
Energy (E)		inside the PAED reactor				
	-	Since perchlorate does not react rapidly under normal				
		atmospheric conditions, more energy is needed to initiate the				
		reduction process				
	-	This factor must be optimized from an economic perspective				
2. Radical	-	PAED systems produce highly oxidative radicals, such as •OH				
Scavenger Concentration (C)		and •H				
(HCO ₃)	-	Perchlorate requires reducing species to initiate reduction				
	-	The activity of the oxidative species produced by PAED must				
		be suppressed in order to promote the reduction reaction				
	_	Bicarbonate (HCO ₃) is known as a \cdot OH radical scavenger				
		$(k_{OH/HCO_3} = 8.5 \times 10^6 Lmol^{-1} s^{-1}; Buxton et al., 1988)$				
	-	In the experiments performed by Karpel Vel Leitner et al.				
		(2005), the presence of the •OH radical scavenger (HCO ₃) was				
		found to inhibit atrazine removal (an oxidation process)				

 TABLE 3.10 Experimental factors for the perchlorate reduction experiments.

 PADAMETER

TADLE 5.10 Experime	<u>un</u>	tar ractors for the peremorate reduction experiments.
-	_	Bicarbonate was selected as the radical scavenger in these
		experiments to test its effect on promoting reduction potential
3. Water Electrode -	_	Previous research has suggested that the gap distance between
Gap (a)		the water electrodes has a significant impact on the discharge
		characteristics as well as the water treatment mechanisms
		generated
-	_	It is unclear what gap distance will generate an optimal
		treatment environment for perchlorate reduction
4. Water		The electrical discharges across the submerged electrodes are
Conductivity (σ)		controlled, in part, by the electrical conductivity of the
		medium
-	_	Different conductivities have impacts on the physical and
		chemical properties generated by arc discharges
-	_	Higher conductivities lead to higher ion concentrations,
		thereby increasing the ionic reactions initiated by the PAED
		system
-	—	Tap water and phosphate buffered saline (PBS) are the water

 TABLE 3.10 Experimental factors for the perchlorate reduction experiments.

A total of 18 batch perchlorate reduction experiments were conducted; Table 3.11 shows the fractional factorial experimental design for the batch perchlorate reduction experiments. Table 3.12 shows the physical measurements corresponding to factor levels investigated in these experiments. For the first six tests, samples were collected at 5-minute intervals for the first half hour and at 10-minute intervals for the remainder of the test. For tests 7 through 18, all samples were collected at 30-minute intervals.

		FAC			
Test #	Cum. Input Energy	Radical Scavenger	Electrode Gap	Water Conductivity	
	<u>(KJ)</u>	(mg/L)	(mm)		
1	360	2000	I	PBS	
2	360	4000	1	PBS	
3	360	8000	1	PBS	
4	360	2000	1	ТАР	
5	720	2000	1	ТАР	
6	1080	2000	1	TAP	
7	360	4000	1	TAP	
8	720	4000	1	ТАР	
9	1080	4000	1	ТАР	
10	360	8000	1	ТАР	
11	720	8000	1	TAP	
12	1080	8000	1	TAP	
13	360	2000	1.5	TAP	
14	720	2000	1.5	TAP	
15	1080	2000	1.5	TAP	
16	360	4000	1.5	TAP	
17	720	4000	1.5	TAP	
18	1080	4000	1.5	TAP	
19	360	8000	1.5	TAP	
20	720	8000	1.5	TAP	
21	1080	8000	1.5	TAP	

TABLE 3.11 Fractional factorial experimental design for the batch perchlorate reduction experiments.

TABLE 3.12 Factor levels with corresponding physical measurements for the batch perchlorate reduction experiments.

FACTOR	UNIT	-1	0	+1
1. Cumulative Input Energy (E)	kJ	360	720	1080
2. Radical Scavenger HCO_3^- concentration (<i>C</i>)	mg/L	2000	4000	8000
3. Water Electrode Gap (<i>d</i>)	mm	1	-	1.5
4. Water Conductivity (σ)	mS/cm	Tap	-	PBS

The geometric configurations of the batch perchlorate reduction experiments, conducted with both PBS and tap water matrices, are shown in Figures 3.8 and 3.10 respectively. The factorial model employed to determine the effect of water conductivity and its interaction with the radical scavenger concentration is shown in Figure 3.9. The two- and three-factor-interaction effect models are shown in Figures 3.12 and 3.13 respectively.



FIGURE 3.8 Factorial design, batch experiment (d = 1 mm).



FIGURE 3.9 Schematic diagram of the factorial model, from the batch experiments, for water conductivity (σ) and its interaction ($\sigma \times C$) with the radical scavenger concentration.

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FIGURE 3.10 Factorial design for the batch experiments conducted with Tap Water.

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FIGURE 3.11 Schematic diagram of the 3-D factorial model for the main effects of the batch perchlorate reduction experiments.



FIGURE 3.12 Schematic diagram of the 3-D factorial model for the batch perchlorate reduction experiments. Two-factor interaction effects.



FIGURE 3.13 Schematic diagram of the 3-D factorial model for the batch perchlorate reduction experiments. Three-factor interaction effects.

Flow-through experiments were then performed using the optimal operating conditions determined from the batch tests. A total of 18 flow-through experiments were conducted; Table 3.13 shows the fractional factorial experimental design for the flow-through perchlorate reduction experiments. Table 3.14 shows the physical measurements corresponding to the factor levels investigated in these experiments. The geometric configuration of the flow-through perchlorate reduction experimenter reduction experiments is shown in Figure 3.14.

		FACTOR	
Test #	Retention Time	Cum. Input Energy	Radical Scavenger
	(min)	(kJ)	(mg/L)
1	5	720	0
2	5	1080	0
3	5	1440	0
4	30	720	0
5	30	1080	0
6	30	1440	0
7	60	720	0
8	60	1080	0
9	60	1440	0
10	5	720	8000
11	5	1080	8000
12	5	1440	8000
13	30	720	8000
14	30	1080	8000
15	30	1440	8000
16	60	720	8000
17	60	1080	8000
18	60	1440	8000

TABLE 3.13 Fractional factorial experimental design for the flow-through perchlorate reduction experiments.

 TABLE 3.14 Factor Levels with Corresponding Physical Measurements for the

 Flow-Through Perchlorate Reduction Experiments

FACTOR	UNIT	-1	0	+1
1. Retention Time	min	5	30	60
2. Cum. Input Energy	kJ	720	1080	1440
3. Radical Scavenger (HCO $_3$) concentration	mg/L	0	-	8000



FIGURE 3.14 Schematic diagram of the factorial design for the flow-through perchlorate reduction experiments.

Similar to the batch perchlorate experiments, the factorial model for main effects from the flow-through experiments is shown in Figure 3.15, and the two- and three-factor-interaction effects models are shown in Figures 3.16 and 3.17 respectively.

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FIGURE 3.15 Schematic diagram of the 3-D factorial model for the flow-through perchlorate reduction experiments. Main effects.

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FIGURE 3.16 Schematic diagram of the 3-D factorial model for the flow-through perchlorate reduction experiments. Two-factor interaction effects.



FIGURE 3.17 Schematic diagram of the 3-D factorial model for the flow-through perchlorate reduction experiments. Three-factor interaction effects.

3.4 EXPERIMENTAL PROCEDURES

3.4.1 PAED Operating Procedures

The operating procedure for the batch experiments conducted with the PAED system is as follows:

- 1. Fill the reactor with the specified water matrix, and measure the temperature, conductivity and pH of the water matrix;
- 2. For the O_3 generation experiments only, purge the water matrix with air to saturate it with DO, or purge with helium to devoid the water matrix of DO;

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- 3. Adjust the water electrode gap distance using a micrometer and tighten the Swagelock fitting;
- 4. Close the reactor and connect the water electrodes to the power supply;
- 5. Adjust air gap distance and turn the high voltage adjustor clockwise to the maximum;
- 6. Plug in the power cord, turn on the power supply, and record the pulse rate;
- 7. Sample as required throughout the experiment;
- 8. Turn off the power supply and use the ground stick to discharge any remaining current upon the completion of the experiment.

The operating procedure for the flow-through experiments conducted with the PAED system is as follows:

- 1. Fill the reactor with the specified water matrix, and measure the temperature, conductivity and pH of the water matrix;
- 2. Adjust the water electrode gap using a micrometer and tighten the Swagelock fitting;
- 3. Close the reactor and connect the water electrode to the power supply;
- 4. Turn on the peristaltic pump to circulate the water matrix through the loop (reservoir, reactor and connecting tubing) until the concentration of all constituents reaches a steady-state within the system;

- 5. Adjust air gap distance and turn the high voltage adjustor clockwise to the maximum;
- 6. Plug in the power cord, turn on the power supply, and record the pulse rate;
- 7. Collect samples as required throughout the experiment;

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- 8. Turn off the power supply and use the ground stick to discharge any remaining current upon the completion of the experiment;
- 9. Turn off the peristaltic pump, re-circulating the water;

The sampling procedure for all experiments is as follows:

- Stop the power supply and discharge any remaining electricity from the reactor with the ground stick;
- Collect the sample, from the top sampling port or the downstream sampling port for the batch and flow-through experiments respectively, using a 1.5mL glass vial (Chromatographic Specialties Inc. Part No. C223700C).
- 3. Turn the power supply back on and resume the experiment.

3.5 ANALYTICAL TECHNIQUES

3.5.1 Perchlorate (ClO₄) Quantification

A high performance liquid chromatograph (HPLC) was employed in combination with a conductivity detector to quantify aqueous perchlorate in these experiments. This instrument is an accurate tool for measuring specific anions and cations in dilute solutions. The anions and cations are separated by differences in the rate at which they pass through a column packed with either anion- or cation-exchange particles (Fritz, S.J. and Douglas T. G., 2009).

Perchlorate standards and experimental samples were transferred into 1.5 mL glass vials (Chromatographic Specialties Inc. Part No. C223700C), capped with black hole tops (Chromatographic Specialties Inc. Part No. C223710C) and sealed with PTFE-backed septa (Chromatographic Specialties Inc. Part No. C242C). The samples were placed into the HPLC autosampler (Varian Inc. Prostar 410 Autosampler) for analysis. The specific HPLC modules employed in this work are listed in Table 3.15, and the configuration is shown in Figure 3.18. EPA method 314.0 (Hautman *et al.*, 1999) was employed to quantify perchlorate, with minor modifications to accommodate the specific conditions in the laboratory (i.e., system back pressure and external regenerant). Table 3.16 shows the HPLC method employed. An AS16A column (Dionex Ionpac[®], 4×250mm) fitted with a guard column (Dionex Ionpac[®] Guard Column AS16A 4×250mm) and an anion suppressor (Dionex Suppressor AMMS III 4mm) was used with a 50 mM NaOH eluent and a 50 mN H₂SO₄ regenerant. A 1000µL sample loop and a

flow rate of 1.5mL/min were used for injections. The method detection limit (MDL) [Method 1030C, APHA-AWWA-WEF, 1998] was determined to be 0.35µg/L. Perchlorate standards were prepared for calibration purposes [Method 4110B, APHA-AWWA-WEF, 2000]. Typical calibration models are illustrated in Tables A1.4, A1.5 and A1.6. Additionally, perchlorate standards and blanks were analyzed periodically throughout each HPLC run for quality assurance (QA) and quality control (QC) purposes [Method 4020A, B, APHA-AWWA-WEF, 2000].

3.5.2 Nitrate Quantification

Samples from the nitrate reduction experiments were collected and placed into HPLC autosampler following the same procedures as perchlorate, described in Section 3.5.1. Standard Method 4110B [APHA-AWWA-WEF, 2000] was employed to quantify the nitrate in solution. An AS12A column (Dionex Ionpac[®], 4×250mm) fitted with a guard column (Dionex Ionpac[®] Guard Column AS12A 4×250mm), and an anion suppressor (Dionex Suppressor AMMS III 4mm). The eluent was a 1.7mM sodium bicarbonate and 1.8mM sodium carbonate solution, and the regenerant was a 50 mN H₂SO₄ solution. A 10µL sample loop and a flow rate of 1.5mL/min were employed for injections.

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TABLE 3.15 HE	TABLE 3.15 HPLC modules.						
SUPPLIER	MODULE						
Varian Inc.	Prostar 410 HPLC Autosampler with 1000µL sample loop						
	Prostar 230 Ternary HPLC Solvent Delivery Method (SDM)						
	Star 800 Module Interface						
	Star Workstation software						
DIONEX	CD25 Conductivity Detector						
	Dionex Ionpac [®] Analytical Column AS16A 4x250mm						
	Dionex Ionpac [®] Guard Column AS16A 4x250mm						
	Dionex Suppressor AMMS III 4mm						



FIGURE 3.18 HPLC module configuration.

Component	Specifications/Operating Conditions
Columns	IonPac [®] AS16A Analytical 4x250mm
	IonPac® AS16A Guard 4x250mm
Sample Loop	Full loop – 1000 μL
Eluent	50 mM Sodium Hydroxide (NaOH)
Regenerant	50 mN Sulphuric Acid (H ₂ SO ₄)
Flow Rate	1.5 mL/min
Pump Pressure	Approx. 175 atm
Temperature	Room Temperature, Approx. 24 °C
Detection	Suppressed conductivity, AMMS III (4mm)
	Chemical regeneration mode with 50 mN sulphuric acid
Background Conductance	15 ~ 18 μS, Range: 100 μS
Run Time	12 min

TABLE 3.16 HPLC operating conditions.

3.5.3 Ozone (O₃) Quantification

Water samples collected from the PAED reactor were analyzed for O₃ concentration using the indigo colorimetric method (Standard Method 4500. APHA-AWWA-WEF, 2000). Small modifications were made to the analytical sample volume to accommodate the experimental conditions; 25mL sample volumes were used in these experiments.

The principle behind the indigo colorimetric method is that residual O_3 rapidly decolourizes indigo present in an acidic solution. The absorbance of the indigo solution at 600 ± 10 nm is inversely proportional to the ozone concentration. Other oxidants, such as H_2O_2 and organic peroxides, also decolourize the indigo reagent but at a much slower rate.

Bromine and chlorine concentrations exceeding 0.1 mg/L also interfere with O_3 measurements. Chlorine concentrations under 0.1 mg/L can be masked by malonic acid.

25mL samples collected from the PAED experiments were immediately put into an indigo reagent to prevent decay. The samples were then filtered through 0.45μ m paper to remove particulate matter, and inserted into the spectrophotometer for UV absorbance analysis. A spectrophotometric method (volumetric) was used to determine the O₃ concentrations in the experimental samples:

$$\operatorname{mg} O_3/L = \frac{100 \times \Delta A}{f \times b \times V}$$
 Eq 3.1

Where ΔA represents difference in absorbance between sample and the blank, f is a constant set to 0.42, b is the path length of cell (cm), and V is the volume of sample (mL).

Figure 3.19 shows the technique employed for drawing the O_3 samples from the PAED reactor and place into spectrophotometer for analysis.



FIGURE 3.19 Sampling procedure for the O₃ experiments

3.5.4 Hydrogen Peroxide (H₂O₂) Quantification

25mL water samples collected from the PAED experiments were analyzed for H_2O_2 concentration in accordance with the iodometric titration method (H2O2.com, http://www.h2o2.com/intro/iodometric.html, US Peroxide's Commercial Office, accessed 1 June, 2009).

The principle behind this method is that H_2O_2 oxidizes iodide to iodine in the presence of acid and molybdate catalysts. The iodine formed is titrated with a thiosulfate solution with a starch indicator. This particular method is less susceptible to interferences by organics due to the catalysts, and suitable for H_2O_2 concentrations in the ppm range. The specific reactions are as follows.

$$H_2O_2 + 2KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2H_2O \qquad \text{Eq 3.2}$$

$$l_2+2Na_2S_2O_3 \rightarrow Na_2S_4O_6+2NaI$$
 Eq 3.3

Samples collected were immediately mixed with the iodide reagent to prevent decay. Results were calculated as follows.

Weight%
$$H_2O_2 = (A - B) \times (Normality of Na_2S_2O_3) \times 1.7$$
 Eq 3.4

Where sample weight in grams, A is the volume of $Na_2S_2O_3$ for sample (mL), and B is the volume of $Na_2S_2O_3$ for blank (mL).

25mL samples were collected from the reactor in a graduated cylinder by opening a sampling port. The samples were then transferred to an Erlenmeyer flask. 25mL of MilliQ water, 10mL of sulfuric acid solution (1 part 93% - H₂SO₄ to 4 part water), 1015mL of KI solution (1% w/v), and two drops ammonium molybdate solution were added to the sample. This solution was titrated with 0.1 N Na₂S₂O₃ to a faint yellow or straw color. At this point, approximately 2mL of starch indicator was added, turning the solution blue, and the titration was continued until the blue color disappeared resulting in a clean, colourless solution. This procedure was repeated on a 25mL sample of MilliQ water.

CHAPTER 4 – RESULTS AND DISCUSSION

4.1 **OZONE GENERATION EXPERIMENTS**

Experiments directed at measuring the concentrations of ozone (O₃) and hydrogen peroxide (H₂O₂) generated by the PAED system were conducted according to the methods described in Chapter 3. The PAED system operating conditions and the water matrix conditions employed in these experiments are listed in Tables 4.1 and 4.2 respectively.

TABLE 4.1 Experimental conditions for O ₃ and H ₂ O ₂ production experiments.								
Reactor Volume	3 L	Sampling Duration	30 min					
Temperature	24 °C	Sampling Interval	5 & 10 mins					
Pulse Rate	0.33 pulse/s							

TABLE 4.2 Water matrix conditions for O_3 and H_2O_2 production experiments.										
Water Matrix	Na ₂ HPO ₄	\mathbf{pH}	Conductivity							
Тар	0	7.33	0.41 mS/cm							
	1000 mg/L	7.84	1.41 mS/cm							
MilliQ	4000 mg/L	8.78	4.36 mS/cm							
	8000 mg/L	8.95	7.80 mS/cm							

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The results obtained from the O₃ and H₂O₂ production experiments are presented in Table 4.3. The concentration of O₃ produced as a function of cumulative input energy is shown in Figures 4.1 through 4.4. Raw experimental data and sample calculations are given in Appendix 2.1.

Test #	Water Matrix	Na ₂ HPO ₄ Level	Water Electrode Gap Level	Dissolved Oxygen Level	O ₃ Concentration (mg/L)
1	Tap	N/A	-1 ²	13	0.1029
2		-11	-1	1	0.0743
3	MilliQ	0^1	-1	1	0.0886
4		1^{1}	-1	1	0.0867
5	Тар	N/A	-1	-1 ³	0.0533
6		-1	-1	-1	0.0429
7	MilliQ	0	-1	-1	0.0438
8		1	-1	-1	0.0486
9	Тар	N/A	12	1	0.0314
10		-1	1	1	0.0248
11	MilliQ	0	1	1	0.0267
12		1	1	1	0.0286

TABLE	4.3	O ₃	Generation	results.
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Note: factorial levels

¹ Na₂HPO₄: -1 - 1000 mg/L; 0 - 4000 mg/L; +1 - 8000 mg/L.

²Water electrode gap: -1 - 1 mm; +1 - 1.5 mm.

³Dissolved oxygen: -1 - zero; +1 - saturated.



FIGURE 4.1 O_3 Concentration vs. cumulative input energy for all O_3 generation experiments.



FIGURE 4.2 O_3 Concentration vs. cumulative input energy for O_3 generation experiments 1-4.



FIGURE 4.3 O_3 Concentration vs. cumulative input energy for O_3 generation experiments 5-8.



FIGURE 4.4 O_3 Concentration vs. cumulative input energy for O_3 generation experiments 9 - 12.

v v	TA	BLE	4.4	O ₃	Generation	1 experi	imental	model	fits.
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Test #	Model Fit	R ²
1	$y = 9E-7x^2 + 2E-4x - 2E-3$	0.99
2	$y = 5E-7x^2 + 2E-4x - 4E-3$	0.96
3	$y = 6E-7x^2 + 2E-4x - 4E-3$	0.97
4	$y = 2E-6x^2 - 2E-4x + 4E-3$	0.98
5	$y = 9E-7x^2 - 5E-5x + 7E-4$	0.99
6	$y = 8E-7x^2 - 6E-5x - 2E-17$	1.00
7	$y = 8E-7x^2 - 6E-5x - 5E-4$	1.00
8	$y = 1E-6x^2 - 1E-4x - 1E-3$	0.98
9	$y = 3E-7x^2 + 5E-5x - 1E-4$	1.00
10	$y = -9E-8x^2 + 1E-4x - 2E-3$	0.91
11	$y = 3E-8x^2 + 1E-4x - 8E-4$	0.97
12	$y = 9E-8x^2 + 9E-5x - 1E-3$	0.94

As shown in Figures 4.2, 4.3 and 4.4, the pattern of increasing ozone concentration with respect to cumulative input energy was observed in all experiments. The models describing the relationship between O_3 production and cumulative input energy are given in Table 4.4, together with their respective coefficients of determination (R^2).

The first group of experiments (see Figure 4.2) with the water electrode gap distance at 1 mm and saturated dissolved oxygen concentrations, resulted in the largest amounts of O_3 production. Figures 4.2 through 4.4 show that the conductivity of the water matrix has no significant impact on O_3 production by the PAED system. The second group of tests (see Figure 4.3) was performed with no dissolved oxygen in the water matrix. Significantly lower O_3 production was observed in this group of tests (see Figure 4.3) with all other factors held constant. The third group of tests (see Figure 4.4) was performed with a water electrode gap distance of 1.5 mm under saturated dissolved oxygen conditions. A comparison of the third group of tests to the first group shows that the larger water electrode gap significantly decreased the O_3 production.

The factorial experimental design presented in Chapter 3 was used to further investigate the effects of each factor on O_3 production. The estimated effects (main and interaction) of each factor are given in Table 4.5. The main effect for each variable and the interaction effects between variables are estimated as the difference between the

69

average values from the positive and negative levels (see section 3.3.2: Figures 3.6 and 3.7):

Main Effect (or Interaction Effect) =
$$\overline{X}_{+1} - \overline{X}_{-1}$$
 Eq. 4.1

Where \overline{X}_{+1} is the average test results on the positive plane on the 3-D factorial model, and \overline{X}_{-1} is the average test results on the negative plane on the 3-D factorial model

ESTIMATE (mg/L)
0.0544 ± 0.0153
-0.0565
0.0381
0.0073

TABLE 4.5 Effects of factors on ozone generation.

The estimated effects presented in Table 4.5 show that all parameters, except the water electrode gap, are positively correlated with ozone production. The water electrode gap is negatively correlated with O_3 production, meaning that a decrease in this gap size leads to an increase in O_3 production within the ranges investigated in this work. These results lead to the following conclusions:

- 1. The average O_3 concentration of 0.05 mg/L generated in these experiments indicates that the PAED system generates detectable concentrations of O_3 under these operating conditions.
- 2. The tap water samples resulted in the highest O_3 production of all three test groups. This effect, however, may actually be a result of interferences caused

by other possible oxidants, such as chlorine, commonly present in tap water. Standard Method 4020 (Quality Control) suggests that the presence of chlorine in excess of 0.1 mg/L may lead to inaccurate measurement of O_3 due to its reaction with the indigo reagent. Typical chlorine levels in tap water are in the range of 1.9 to 2.3 mg/L (Drinking water report tables, City of Hamilton, 2009). This reaction results in reduced sample absorbance, ultimately ensuing falsely elevated O_3 concentrations. Although the chlorine present in tap water can be removed or measured, and therefore easily accounted for, there are many other oxidants that may be present in tap water. Therefore, the samples containing MilliQ water and sodium phosphate, with no other oxidants present, provides a better estimate of O_3 generation by the PAED system.

- 3. Increasing the water electrode gap to 1.5 mm reduced the O₃ production by approximately 0.06 mg/L. A water electrode gap of 1.0 mm provided the optimal O₃ production within the range of water electrode gaps investigated here.
- 4. Of all the factors considered in these experiments, the dissolved oxygen concentration had the most impact on the O₃ production. However, even in the second test group, which was theoretically devoid of dissolved oxygen, a measurable O₃ concentration was produced, and it increased with the cumulative input energy. It is possible that experimental error resulted in incomplete removal of dissolved oxygen, enabling the residual to contribute to the discharge process. More likely, however, the ozone was generated entirely

from oxygen molecules released from water molecules, by arc discharges, when the solution was void of dissolved oxygen.

4.2 HYGEODEN PEROXIDE GENERATION EXPERIMENTS

The hydrogen peroxide (H_2O_2) concentration in the water samples collected throughout the PAED experiments were quantified using the iodometric titration method described in Section 3.5.3. Similar to the O₃ generation experiments, factorial experiments were employed to analyze the effects of each factor on H₂O₂ production. The results of the H₂O₂ generation experiments are given in Table 4.6. No detectable level of H₂O₂ was observed in any of these experiments. The H₂O₂ produced by the PAED processes either degraded before it could be quantified through the titration technique, or it was never generated in detectable quantities.

The electrical discharge from the PAED system causes water molecules to break into H• and •OH radicals. The •OH radicals then recombine to form H₂O₂. However, since the discharge occurs in pulses, any H₂O₂ formed likely breaks into OH⁻, •OH and other anions and radicals in subsequent arc pulses. The dissociation rate constant of H₂O₂ (e⁻ + H₂O₂ \rightarrow OH⁻ + •OH, $k = 1.1 \times 10^{10} \text{ L} \cdot \text{mol}^{-}1 \cdot \text{s}^{-1}$) is greater than the formation constant (OH• + •OH \rightarrow H₂O₂, $k = 5.5 \times 10^9 \text{ L} \cdot \text{mol}^{-}1 \cdot \text{s}^{-1}$, Buxon *et al.*, 1998). Therefore, it is likely that H₂O₂ is never generated in detectable concentrations of 0.1 weight%, as it degrades and forms simultaneously. In the experiments performed by Sato *et al.*, 1996, the maximum concentration of H_2O_2 detected was 0.035 weight%, which is below the detection limit of the indigo method employed in the current research.

	0.1N N	$a_2S_2O_3$	Waight%		0.1N N	Woight ⁰ /		
TEST	Sample (A-mL)	Blank (B-mL)	H_2O_2	TEST	Sample (A-mL)	Blank (B-mL)	H ₂ O ₂	
1	ND*	0	ND	7	ND	0	ND	
2	ND	0	ND	8	ND	0	ND	
3	ND	0	ND	9	ND	0	ND	
4	ND	0	ND	10	ND	0	ND	
5	ND	0	ND	11	ND	0	ND	
6	ND	0	ND	12	ND	0	ND	

TABLE 4.6 Results of the H₂O₂ Generation Experiments.

*ND refers to non detect

4.3 BATCH PERCHLORATE EXPERIMENTS

Prior to the perchlorate reduction experiments, batch nitrate reduction experiments were conducted to ensure that the reduction phenomenon observed by Karpel Vel Leitner *et al.* (2005) could be reproduced. Karpel Vel Leitner *et al.* (2005) performed a nitrate reduction experiment to examine the reducing species produced by the PAED system. The results showed nitrate degradation of 0.36µmol/L with 100 kJ/L of input energy. The initial nitrate concentration in their experiments was 500µmol/L, and therefore 7.2% of that was converted to nitrite. The standard calibration curve for nitrate is shown in Figure A1.2. The experimental results of the nitrate reduction experiments are given in Figure 4.5. These experiments achieved a total nitrate reduction of 1.73% with 720 kJ of cumulative input energy. These experiments showed that nitrate ions were reduced during the PAED reaction, confirming the observations of Karpel Vel Leitner *et al.* (2005).



FIGURE 4.5 Nitrate Concentration vs. Cumulative Input Energy for Nitrate Reduction Experiment

Upon confirmation of the ability of the PAED system to initiate reduction reactions, batch tests were performed to evaluate the potential of the PAED system for perchlorate reduction. From a thermodynamic standpoint, perchlorate reduction to chloride is a spontaneous reaction ($\Delta G = -1071.3$) (Urbansky, 1998). Nine sets of experiments were conducted and 21 groups of removal data were obtained from these experiments. The PAED system operating conditions for these experiments are listed in Table 4.7.

TABLE 4./ Experimental co	TABLE 4./ Experimental conditions: batch tests.						
Reactor Volume	3 L						
Water Matrix	PBS & Tap water						
Initial Water Temperature	24 °C						
Pulse Rate	0.33 pulse/s						
Sampling Interval	10 & 30 mins						
Total Input Energy	1080 kJ						
Radical Scavenger	NaHCO ₃						

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The water temperature rose significantly and consistently during each experiment due to the electrical current passing through the submerged electrodes. The cumulative temperature change versus cumulative input energy is summarized in Figure 4.6. The change in temperature (y) versus cumulative input energy (x) data were fit with the following equation:

$$y = 0.02x + 0.75 (R^2 = 0.98)$$
 Eq. 4.2





The results obtained from the perchlorate reduction experiments are presented in Table 4.8. The HPLC quantification results of the experimental samples are listed in Appendix 2.2. The percentage removal is calculated by the difference between the initial and final perchlorate concentrations from each experiment. Two initial perchlorate concentrations were used, one for the experiments conducted with the PBS water matrix, and the other for those conducted with the tap water matrix.

]	FACT	'OR		UNIT	-1	0	+1	
	1.C	um. In	put Er	nergy		kJ	360	720	1080)
	2. R	adical	- Scave	nger (F	$\frac{1}{100}$	mg/L	2000	4000	8000)
	3. W	later E	lectro	de Gan	1003)	mm	1		15	
	4. W	later C	onduc	tivity		mS/cm	ТАР		PBS	3
										-
		· · · · · · · · · · · · · · · · · · ·			Initial		Final	Ave		
Test #	1	2	3	4	Conc.		Conc.	ΔCo	nc.	% Removal
1	-1	-1	-1	1	8.8		8.8	$0.00 \pm$	0.08	0.1%
2	-1	0	-1	1	9.5		9.4	-0.01 ±	0.01	0.5%
3	-1	1	-1	1	8.7		8.8	$0.01 \pm$	0.03	-0.5%
4	-1	-1	-1	-1			9.6			0.6%
5	0	-1	-1	-1	9.7		9.6	$0.00 \pm$	0.04	0.6%
6	1	-1	-1	-1			9.7			0.3%
7	-1	0	-1	-1			9.8			1.4%
8	0	0	-1	-1	9.9		9.8	-0.04 ±	0.10	1.8%
9	1	0	-1	-1			9.7			2.5%
10	-1	1	-1	-1			9.8			2.5%
11	0	1	-1	-1	10.1		9.9	-0.04 ±	0.09	1.8%
12	1	1	-1	-1			9.9			2.2%
13	-1	-1	1	-1			1.0			0.2%
14	0	-1	1	-1	10.0		9.9	$-0.02 \pm$	0.02	0.7%
15	1	-1	1	-1			9.9			1.0%
16	-1	0	1	-1			9.7			0.2%
17	0	0	1	-1	9.8		9.7	$0.00 \pm$	0.04	0.3%
18	1	0	1	-1			9.8			0.02%
19	-1	1	1	-1			9.6			0.3%
20	0	1	1	-1	9.6		9.6	-0.01 ±	0.04	-0.5%
21	1	1	1	- <u>1</u>			9.5			0.8%

 TABLE 4.8 Factorial design and results for the batch perchlorate experiments.

The average perchlorate removal for all 21 tests was 0.8%. The lowest removal observed was -0.5%, and the highest removal was 2.5%. The average concentration change column does not show a clear pattern of perchlorate reduction during the treatment process. Confidence interval estimates are also given in Table 4.8. The fact that these confidence intervals cross zero (i.e., possibly 0% reduction) indicates that no significant reduction of perchlorate was achieved during these experiments.

A three-dimensional (3-D) factorial model was used to analyze the effects of each factor, and the interaction effects, in order to determine the main reduction factors (see Figures 3.8 through 3.13). Table 4.9 shows the main and interaction effects calculated from the batch perchlorate reduction experiments using Equation 4.1.

TABLE	4.9	Main	and	interaction	effects	calculated	from	the	batch	perchlorate
reductio	n ex	perime	ents.							

EFFECT	ESTIMATE	
Average	$0.8\% \pm 0.4\%$	
Main Effects		
Water Conductivity (σ)	-1.5%	
Water Electrode Gap (d)	-1.2%	
Cumulative Input Energy (E)	0.3%	
Radical Scavenger (C)	0.6%	
Two-Factor Interactions		
$\sigma \times C$	-1.2%	
E imes d	0.1%	
E imes C	-0.1%	
d imes C	-1.1%	
Three-Factor Interaction		
$E \times d \times C$	-0.1%	

The highlighted parameters, σ , $\sigma \times C$, $d \times C$, and d, have the highest impacts on perchlorate reduction. Water conductivity contributed the largest impact on the reduction

process. However, since the estimate shows water conductivity interacts with radical scavenger concentration ($\sigma \times C = -1.2\%$), no conclusive statement can be drawn for the water conductivity effect. In addition, water electrode gap has an impact on the reduction process (d = -1.2%), and there is an interaction effect between water electrode gap and radical scavenger concentration ($d \times C = -1.1\%$). The following conclusions can be drawn from the factorial analysis of the batch experiments:

- 1. Water conductivity (σ) has the highest effect on perchlorate reduction, and has an interaction with radical scavenger concentration. The interaction effect arises from the opposite trends at different levels. In PBS solution, the radical scavenger effect is -0.6%, but in tap water, the effect changed to 1.9%.
- 2. The interaction effect between the water electrode gap (d) and radical scavenger (C) is further examined in Figure 4.7. Similar to the $\sigma \times C$ interaction, the effect arises from the difference in response to radical scavenger variation for two water electrode gap distances. With the water electrode gap at the plus level, the scavenger effect is -0.4%, but with water electrode gap at the negative level, the effect changed to 1.7%. The opposite trends resulted in an apparent interaction effect.
- 3. The main effects of the cumulative input energy (E), and radical scavenger concentration (C), and the interaction effects of $E \times d$, $E \times C$ and $E \times d \times C$ are limited. They do not contribute significantly to the perchlorate reduction process, as these effects are within the confidence interval of the average effect.

These observations led to further investigation of the water conductivity's influence on the perchlorate reduction process. The interaction between the water electrode gap and the radical scavenger concentration showed that a combination of low d – high C and high d – low C result in increased perchlorate reduction.



FIGURE 4.7 Schematic diagram of the factorial model for the $d \times C$ interaction effect of the batch perchlorate experiment.

A graphical representation of the experimental data can provide further insight towards the reduction process. Therefore, graphs of perchlorate concentration versus cumulative input energy for the batch experiments are shown in Figures 4.8 (PBS), 4.9 (tap water, d = 1 mm) and 4.10 (tap water, d = 1.5 mm). Figures 4.8 through 4.10 show that all of the perchlorate concentration reduction observed in these experiments occurred between the start of the experiment and the first sampling event. No significant reduction occurred throughout the remainder of the experiments.



FIGURE 4.8 Perchlorate concentration versus cumulative input energy for batch tests in PBS and a water electrode gap (d) of 1 mm.



FIGURE 4.9 Perchlorate concentration versus cumulative input energy for batch tests conducted with tap water and a water electrode gap (d) of 1 mm.



FIGURE 4.10 Perchlorate concentration versus cumulative input energy for batch tests conducted with tap water and a water electrode gap (d) of 1.5 mm.

4.4 FLOW-THROUGH REACTOR PERCHLORATE

EXPERIMENTS

In the batch perchlorate experiments, the factorial model determined that the water conductivity is the dominant factor during the treatment process. However, further analyses suggested that, in fact, it is possible that no reduction occurred in the batch system. In order to further investigate: a) the effect of water conductivity on perchlorate reduction; and b) the "no reduction" phenomenon, experiments were performed employing the reactor in flow-through mode. The experimental conditions for the flow-through experiments are listed in Table 4.10.

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experiments.	
Reactor Volume	3 L
Water Matrix	PBS
Initial Temperature	24 °C
Pulse Rate	0.33 pulse/s
Flow Rate	50 mL/min, 100 mL/min, 600 mL/min
Total Input Energy	1440 kJ
Radical Scavenger	NaHCO ₃

TABLE 4.10 Experimental conditions for flow-through perchlorate reduction experiments

The factorial experimental design together with the results are listed in Table 4.11. A total of 18 tests were conducted. All experimental data are summarized in Appendix 2.3. Final removals are calculated from the concentration difference between the initial and final test samples.

TABLE 4.11 Factorial design and	results of the flow-through	factorial perchlorate
reduction experiments.		

		FA	CTOR		UNIT	-1	0	+1	
	1. Ret	ention T	`ime		min	5	30	60	_
	2. Cur	n. Input	Energy		kJ	720	1080	1440	
	3. Radical Scavenger (HCO ₃)				mg/L	0		8000	
Test #	1	2	3	Initial Conc.	Final Conc	•	Avg. Δ Conc.	% R	lemoval
1	-1	-1	-1		9.7			().7%
2	-1	0	-1	9.8	9.7	-	0.01 ± 0.02	().7%
3	-1	+1	-1		9.7			().7%
4	0	-1	-1		9.9			().5%
5	0	0	-1	9.9	1.0	(0.00 ± 0.04	_(0.1%
6	0	-1	-1		9.9			().1%
7	+1	-1	-1	0.9	9.8			().6%
8	+1	0	-1	9.8	9.8	,	0.00 ± 0.02	().6%

reducti	on exper	iments.						
9	+1	+1	-1	_	9.8		0.4%	
10	-1	-1	+1		9.8		0.6%	_
11	-1	0	+1	9.9	9.9	$\textbf{-0.01} \pm 0.02$	0.3%	
12	-1	+1	+1		9.8		0.8%	
13	0	-1	+1		9.8		1.6%	_
14	0	0	+1	9.9	9.8	-0.02 ± 0.04	0.8%	
15	0	+1	+1		9.8		1.5%	
16	+1	-1	+1		9.5		0.8%	_
17	+1	0	+1	9.6	9.6	0.00 ± 0.03	0.1%	
18	+1	+1	+1		9.6		0.3%	

TABLE 4.11 Factorial design and results of the flow-through factorial perchlorate reduction experiments.

The average removal for all 18 tests was 0.6%. The lowest removal observed was -0.1%, and the highest removal was 1.6%. A three-dimensional (3-D) factorial model was used to analyze the effects of each factor, and the interaction effects, in order to determine the main reduction factors (see Figures 3.14 through 3.17).

Similar to the batch experiment results, the average concentration change column does not show a clear pattern of perchlorate reduction during the treatment process. Additionally, because the 95% confidence intervals all cross zero (i.e., 0% reduction may have occurred), it can be stated that no significant reduction occurred.

Similar to the batch perchlorate reduction experiments, a 3-D factorial model was employed to analyze the main and interaction effects in the flow-through experiments. The effects were calculated using Equation 4.1.

EFFECT	ESTIMATE	
Average	$0.6\% \pm 0.2\%$	
Main Effects		
Radical Scavenger (C)	0.3%	
Cumulative Input Energy (E)	0.2%	
Retention Time (T)	0.1%	
Two-Factor Interactions		
E imes T	-0.1%	
E imes C	0.1%	
T imes C	-0.02%	
Three-Factor Interaction		
$E \times T \times C$	-0.2%	

TABLE 4.12 Calculated effects for the factorial model of the flow-through perchlorate reduction experiments.

The results of the factorial model analyses are summarized in Table 4.12. The estimated parameter effects are between -0.1% and 0.3%, with an average reduction of 0.6% from the initial 10mg/L of perchlorate, which corresponds to 0.06 mg/L of perchlorate being reduced. This concentration is below the MDL of the analytical method employed in these experiments, as noted in Table A1.6. The HPLC will not reliably quantify the concentration below the MDL. Since the reduction concentrations are below the method detection limit, it cannot be stated that reduction occurred during the treatment process.

84



FIGURE 4.11 Perchlorate concentration versus cumulative input energy for the flow-through perchlorate reduction experiments.

Figure 4.11 shows the perchlorate concentration versus the cumulative input energy for the flow-through perchlorate reduction experiments. These results confirm that no observable perchlorate reduction occurs during the PAED treatment process under these operating conditions.

85

CHAPTER 5 – CONCLUSIONS & RECOMMENDATIONS

5.1. CONCLUSIONS

The conclusions for this research are summarized according to the research objectives stated in Chapter 1.

- a) Method development for perchlorate quantification
 - Analytical methods were successfully developed to provide stable and consistent perchlorate concentration with HPLC.
 - The MDL was determined to be $0.35\mu g/L$ for perchlorate.
- b) Ozone and hydrogen peroxide generation

- The optimal system settings for ozone generation were saturated dissolved oxygen concentration, tap water matrix and water electrode gap of 1mm. These settings generated 0.1029mg/L of ozone. It should be noted here that it is unclear how reliable this maximum concentration is, due to the possible interference of oxidants present in tap water with the quantification of ozone.
- c) Perchlorate reduction experiment
 - 1.73% of nitrate was reduced to nitrite by the PAED system, indicating that the system is capable of initiating reduction reaction.
 - Neither the batch nor the flow-through experiments achieved significant reduction of perchlorate.
 - The factorial analysis showed that no individual factor provided a significant contribution to the reduction process.

5.2. **RECOMMENDATIONS**

Recommendations for future work, based on the results of these experiments are listed below:

1. A longer reaction period (i.e. increase the cumulative input energy) should be employed to obtain further ozone generation data.

- 2. A more accurate analytical technique should be implemented for H_2O_2 quantification, to see if it can be detected with a lower MDL.
- 3. More factors should be investigated for perchlorate reduction by PAED. For example, the addition of an appropriate electron donor may induce the reduction process.
- 4. The by-products generated by the PAED treatment process must be investigated.
- 5. ClO₃, ClO₂, ClO⁻, and Cl⁻ concentration in samples should be analyzed to provide more information on the reduction process.

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APPENDIX 1 – EXPERIMENTAL PROCEDURES AND STANDARD CURVES CALCULATIONS

A1.1 OPERATING PROCEDURES

A1.1.1 Ion Chromatography Equipments Operating Procedures

- 1. Turn on computer and all required IC equipments.
- 2. Check eluent and regenerant storage tank to make sure solutions are sufficient for the scheduled run period. If not, prepare and refill the tank.
- 3. Attach tubes connected to pump "C" on SDM unit into eluent bottle and close the lid with constant pressure from helium gas cylinder.
- 4. Purge eluent tubing
 - a. Open valve on SDM (black knob).
 - b. Press "C" and Run for 1 min.

- c. Press "Stop" and tighten valve.
- 5. Press "wash" button on Auto Sampler to flush the sampling loop.
- 6. During wash and purge processes, check for no air bubbles in:
 - a. Auto Sampler piston and sample loop tubing.
 - b. Eluent line tubing.
- 7. Turn on Helium gas cylinder:
 - a. Adjust the left pressure regulator to the first black line (approx. 60kPa).
 - b. Adjust and maintain a constant pressure on the gauge regulator.
 - c. Check and maintain a stable flow rate from the suppressor outlet line into the waste bottle.
- 8. Press "Serial" on Auto Sampler and start Varian workstation software.
- 9. On window 230.01, press "Pump" and wait for stability:
 - a. Stable background conductivity $(14\mu S 20\mu S)$, press offset to "0"
 - b. Pump pressure in a stable level.
- 10. Load an existing method file for sample run.
- 11. Load an existing sample list or create a new list:
 - a. New listing (Default Setting)
 - i. Input sample name
 - ii. Choose full loop option
 - iii. Select vial number
 - b. Use the "data file" option on sample list window to select directory for output files
- 12. Press "begin" on sample list
- 13. Continually Monitoring during the IC run
 - a. Pump pressure is stable
 - b. Pressure regulator to make sure flow rate from suppressor is stable
 - c. Stable background conductivity on CD25 unit
- 14. When sample analysis is completed
 - a. Press "Stop" to stop the pump on 230.01 window

- b. Press "Exit" on Auto Sampler then press "Wash" to clean the loop
- c. Shutdown software
- d. Move eluent line back to MilliQ water tank, open valve and press "C", flush for 1 min
- e. Close the gas cylinder
- f. Turn off all IC units

A1.1.2 Dissolved Oxygen (YSI MODEL 57 OPERATING PROCEDURES)

- 1. SETUP
 - a. Prepare and connect YSI 5700 Series dissolved oxygen probe.
 - b. With instrument off, adjust meter mechanical zero if necessary.
 - c. Switch to RED LINE and adjust if necessary.
 - d. Switch to ZERO and adjust to 0 on mg/L scale.
- 2. CALIBRATION (Calibration to 100% saturation)
 - a. Place probe in BOD bottle containing about "1" of water. Wait for temperature equilibration; temperature stability is essential for precise calibration.
 - b. Set SALINITY control to FRESH.
 - c. Switch to TEMP and read on °C scale.
 - d. Use probe temperature reading and true local atmospheric pressure to determine calibration values from Table A1.1 and Table A1.2.
 - e. Switch to the 0-5, 0-10, 0-20 range and adjust with CALIBRATE control to the calibration value determined
- 3. MEASUREMENT
 - a. Adjust SALINITY control to salinity of sample.
 - b. Place calibrated probe in sample.
 - c. Wait until probe equilibration by observing temperature and dissolved oxygen readings that are stable for a full minute.
 - d. Read dissolved oxygen on appropriate scale (0-5, 0-10 or 0-20 mg/L).

	mm Hg press	ure		_	
TEMP	SOLUBILITY	TEMP	SOLUBILITY	TEMP	SOLUBILITY
°C	mg/L	°C	mg/L	°C	mg/L
0	14.62	16	9.87	32	7.31
1	14.22	17	9.67	33	7.18
2	13.83	18	9.47	34	7.07
3	13.46	19	9.28	35	6.95
4	13.11	20	9.09	36	6.84
5	12.77	21	8.92	37	6.73
6	12.45	22	8.74	38	6.62
7	12.14	23	8.58	39	6.52
8	11.84	24	8.42	40	6.41
9	11.56	25	8.26	41	6.31
10	11.29	26	8.11	42	6.21
11	11.03	27	7.97	43	6.12
12	10.78	28	7.83	44	6.02
13	10.54	29	7.69	45	5.93
14	10.31	30	7.56	46	5.84
15	10.08	31	7.43	47	5.74

TABLE A1.1 Solubility of oxygen in water exposed to water saturated air at 760mm Hg pressure

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Pressure In Ha	mm Ha		Altitude Et	m	Calibration Value (%)
20.22	769	102 2			
20.23	760	102.5	-270	-04 0	100
27.72	700	101.5	0 270	0 85	100
29.01	775	00.2	2/0 550	00 170	77 00
27.33	143 727	77.5 08 2	558 841	170	70 07
29.02	720	90.3 07 2	041 1126	20	91 04
20./4	730	97.5	1120	545 421	90 05
	122 714	90.3 05 2	1413	431 510	93 04
28.11	/14	95.2	1703	519	94
27.83	/0/	94.2	1995	608	93
27.52	699	93.2	2290	698 7 00	92
27.24	692	92.2	2587	789	91
26.93	684	91.2	2887	880	90
26.61	678	90.2	3190	972	89
26.34	669	89.2	3496	1066	88
26.02	661	88.2	3804	1160	87
25.75	654	87.1	4115	1254	86
25.43	646	86.1	4430	1350	85
25.12	638	85.1	4747	1447	84
24.84	631	84.1	5067	1544	83
24.53	623	83.1	5391	1643	82
24.25	616	82.1	5717	1743	81
23.94	608	81.1	6047	1843	80
23.62	600	80	6381	1945	79
23.35	593	79	6717	2047	78
23.03	585	78	7058	2151	77
22.76	578	77	7401	2256	76
22.44	570	76	7749	2362	75
22.13	562	75	8100	2469	74
21.85	555	74	8455	2577	73
21.54	547	73	8815	2687	72
21.26	540	71.9	9178	2797	71
20.94	532	70.9	9545	2909	70
20.63	524	69.9	9917	3023	69
20.35	517	68.9	10293	3137	68
20.04	509	67.9	10673	3253	67
19.76	502	66.9	11058	3371	66

 TABLE A1.2 Calibration values for various atmospheric pressures & altitudes

A1.2 REAGENT PREPARATION

A1.2.1 Ozone Test Reagents

1. Indigo stock solution:

Add 500 mL MilliQ water and 1 mL phosphoric acid to a 1-L volumetric flask, and add 770 mg potassium indigo trisulfonate. Fill to mark with MilliQ water

2. Indigo reagent I:

Add 20 mL indigo stock solution, 10 g sodium dihydrogen phosphate and 7 mL phosphoric acid to a 1-L volumetric flask. Dilute to mark.

A1.2.2 Hydrogen Peroxide Test Reagents

1. Potassium iodide solution (1% w/v)

Dissolve 1.0 grams KI into 100 mL MilliQ water. Store capped in cool place away from light. Yellow-orange tinted KI solution indicates some air oxidation to iodine, which can be removed by adding 1-2 drops of dilute Na₂S₂O₃ solution.

2. Ammonium molybdate solution

Dissolve 9 grams ammonium molybdate in 10 mLs 6N NH₄OH. Add 24 grams NH₄NO₃ and dilute to 100 mL with MilliQ water.

3. <u>Sulfuric acid solution</u>

Carefully add one part $H_2SO_4 - 93\%$ to four parts MilliQ water.

A1.3 STANDARD CURVES

A1.3.1 Method Detection Limit (MDL)

The Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte (40 CFR part 136, Appendix B, rev. 1.11, USEPA). The MDL provides estimation of the lowest detectable solute concentration by HPLC system at specific instrument settings.

Four standard concentrations (2 μ g/L, 10 μ g/L, 20 μ g/L, 50 μ g/L, and 100 μ g/L) were used to generate calibration curve for determination of system MDL (Figure 3.6). The coefficient of determination (R²) for the curve is 0.991. Seven 2 μ g/L standard samples were primary parameters for MDL calculation. The background conductance of HPLC module was adjusted to minimum value at 2 μ S. The lowest perchlorate concentration can be accurately detected by HPLC instrument is 0.35 μ g/L. The MDL data for the perchlorate in tap water is listed in Table A1.3.

 $MDL = t^{*}(n-1, 1-\alpha = 0.99)^{*}(SD)$

Where: $t^{*}(n-1, 1-\alpha = 0.99)$ – the students' t value appropriate for a 99% confidence level and alpha standard deviation estimate with n-1 degrees of freedom. SD – Standard deviation of the replicate analyses



FIGURE A1.1 Perchlorate MDL calibration curve

Injection #	Retention Time (min)	Peak Area (mV*sec)	Calibrated Concentration (µg/L)
1	9.98	185	3.72
2	10.00	168	3.55
3	9.99	202	3.89
4	10.02	194	3.81
5	10.01	190	3.77
6	10.04	178	3.65
7	9.90	183	3.70
Average	9.99	186	3.73
SD	0.04	11.06	0.11
t _(6,0.99)			3.14
MDL*			0.35 μg/L
$\overline{\text{MDL} = \text{SD}^* t_0}$	$(6,0.99)$, Where $t_{(6,0.99)} =$	3.14 for n=7	

TABLE A1.3 Determination of MDL for perchlorate in tap water

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	Peak Area	Adj. Conc.	Average	$\overline{X}_{C=10mg/L}$	9.89 mg/L		
(mg/L)	(mV*sec)	(mg/L)	CI	1 - α	0.95		
1	558	0.88	SD _{C=10mg/L}	σ	0.0601		
1	552	0.87	Sample Size	n	3		
1	558	0.88	Upper Limit	\overline{X} + 1.96 $\frac{\sigma}{}$	9.95 mg/L		
5	3214	5.19	Lower Limit	$n = 1.50 \sqrt{n}$	9.82 mg/L		
5	3245	5.24	MDL	$SD_{C=1mg/L} \times t_{(6, 0.99)}$	0.0176 mg/L		
5	3266	5.27	CAT	Ι Π ΤΑ ΤΙ Λ ΤΙ ΤΑ Τ	ION		
10	6099	9.87	CALIBRATION EQUATION				
10	6153	9.95	$y = 615.48x + 20.421, R^2 = 0.9979$				
10	6082	9.84					

TABLE A1.4 Standard calibration model for batch perchlroate experiments (1-3)

 TABLE A1.5 Standard calibration model for batch perchlroate experiments (4 – 21)

Standard	Peak Area	Adj. Conc.	Average	$\overline{X}_{C=10mg/L}$	10.10 mg/L	
(mg/L)	(mV*sec)	(mg/L)	CI	1 - α	0.95	
- 1	1305	1.13	SD _{C=10mg/L}	σ	0.0930	
1	1307	1.14	Sample Size	n	3	
1	1333	1.16	Upper Limit	\overline{X} + 1.96 $\frac{\sigma}{}$	10.20 mg/L	
5	5977	4.78	Lower Limit	$n = 1.50 \sqrt{n}$	9.99 mg/L	
5	5946	4.75	MDL	$SD_{C=1mg/L} \times t_{(6, 0.99)}$	0.0383 mg/L	
5	5951	4.76	CALL	Ο ΓΑΤΊΩΝ ΓΩΠΑΤ	τον	
10	12667	9.99		DRAIION EQUAT	IUN	
10	12844	10.10	$y = 1280.1x + 135.56, R^2 = 0.9977$			
10	12894	10.20				

 TABLE A1.6 Standard calibration model for flow-through perchlorate experiments

TEST #	EQUATION	R ²	$\overline{X}_{C=10mg/L} \pm CI$	MDL
1-3	y = 1035x + 841.7	0.9942	9.81 ± 0.007 mg/L	0.368 mg
4 - 6	y = 1198x + 446.8	0.9995	10.01 ± 0.053 mg/L	0.320 mg
7 – 9	y = 1010x + 903.1	0.9919	9.77 ± 0.100 mg/L	0.376 mg
10 - 12	y = 1114x + 649.6	0.9984	9.92 ± 0.027 mg/L	0.343 mg
13 – 15	y = 1111x + 656.1	0.9984	9.92 ± 0.004 mg/L	0.344 mg
16 – 18	y = 945.3x + 1061	0.9837	9.64 ± 0.024 mg/L	0.398 mg

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Standard	Peak Area	Adj. Conc.	Average	$\overline{X}_{5mg/L}$	5.00 mg/L
(mg/L)	(mV*sec)	(mg/L)	CI	1 - α	0.95
0.5	824	0.63	SD _{C=10 mg/L}	σ	0.1156
0.5	742	0.54	Sample Size	n	3
0.5	671	0.46	Upper Limit	\overline{X} + 1.96 $\frac{\sigma}{}$	5.13 mg/L
1	1216	1.06	Lower Limit	$n = 1.90 \sqrt{n}$	4.87 mg/L
1	1044	0.88	MDL	$SD_{C=1mg/L} \times t_{(6, 0.99)}$	0.2646 mg/L
1	1085	0.92	CAL	IBRATION EQUAT	TION
5	484 1	5.05			
5	4863	5.08	y = 9	$006.8x + 252.7, R^2 = 0$).998
5	4671	4.87			

TABLE A1.7 Standard calibration model for batch nitrate experiments

TABLE 4.1 Nitrate reduction experiment result

Time	Cum. Input Energy	Peak Area	Concentration
(min)	(kJ)	(mV*sec)	(mg/L)
0	0	4703	4.90
15	90	4689	4.89
30	180	4704	4.90
45	270	4574	4.76
60	360	4645	4.84
75	450	4409	4.58
90	540	4445	4.62
105	630	4452	4.63
120	720	4626	4.82





APPENDIX 2 – EXPERIMENTAL

RESULTS

A2.1 OZONE TEST RESULTS

TABLE A2.1	O ₃ test	sample calculation

Experiment 1					
Time	30 min	Ozone Concentration			
Blank	0.1393 nm	$100 \times \Lambda A$ 100×0.0108			
Sample	0.1285 nm	=1000000000000000000000000000000000000			
ΔΑ	0.0108 nm				
	0.42				
b	1 cm	Cumulative Energy			
V	25 mL	oo . 60s 1 pulse oo kJ			
Pulse Frequency	1/3 pulse/s	$= 30 \text{ min} \times \frac{1}{10000000000000000000000000000000000$			
Power	0.3 kJ/pulse	= 270kJ			

4	Time	Pulse	Cum. Energy	Absorbance (nm)		۸ ۸	O(ma/I)
#*	(min)	Count	(kJ)	blank	sample	ΔA	O_3 (mg/L)
0	0	0	0	0.1393	0.1393	0.0000	0.0000
1	5	150	45	0.1393	0.1385	0.0008	0.0076
2	10	300	90	0.1393	0.1378	0.0015	0.0143
3	15	450	135	0.1393	0.1359	0.0034	0.0324
4	20	600	180	0.1393	0.1325	0.0068	0.0648
5	25	750	225	0.1393	0.1310	0.0083	0.0790
6	30	900	270	0.1393	0.1285	0.0108	0.1029

 TABLE A2.2 Ozone test 1

TABLE A2.3 Ozone test 2

ш	Time	Pulse	Cum. Energy	Absorba	ance (nm)	A A	\mathbf{O} (m \mathbf{a}/\mathbf{I})
#	(min)	Count	(kJ)	blank	sample	ΔA	O_3 (mg/L)
0	0	0	0	0.1393	0.1393	0.0000	0.0000
1	5	150	45	0.1393	0.1391	0.0002	0.0019
2	10	300	90	0.1393	0.1383	0.0010	0.0095
3	15	450	135	0.1393	0.1368	0.0025	0.0238
4	20	600	180	0.1393	0.1335	0.0058	0.0552
5	25	750	225	0.1393	0.1330	0.0063	0.0600
6	30	900	270	0.1393	0.1315	0.0078	0.0743

TABLE A2.4 Ozone test 3

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ц	Time	Pulse	Cum. Energy	Absorbance (nm)			$O_{ma}(ma_{ma})$	
#	(min)	Count	(kJ)	blank	sample	ΔA	O_3 (mg/L)	
0	0	0	0	0.1393	0.1393	0.0000	0.0000	
1	5	150	45	0.1393	0.1389	0.0004	0.0038	
2	10	300	90	0.1393	0.1379	0.0014	0.0133	
3	15	450	135	0.1393	0.1363	0.0030	0.0286	
4	20	600	180	0.1393	0.1327	0.0066	0.0629	
5	25	750	225	0.1393	0.1321	0.0072	0.0686	
6	30	900	270	0.1393	0.1300	0.0093	0.0886	

<u>и</u>	Time	Pulse	Cum. Energy	Absorbance (nm)		A A	O_2 (mg/L)	
#	(min)	Count	(kJ)	blank	sample	ΔA	03 (mg/L)	
0	0	0	0	0.1393	0.1393	0.0000	0.0000	
1	5	150	45	0.1393	0.1390	0.0003	0.0029	
2	10	300	90	0.1393	0.1383	0.0010	0.0095	
3	15	450	135	0.1393	0.1379	0.0014	0.0133	
4	20	600	180	0.1393	0.1370	0.0023	0.0219	
5	25	750	225	0.1393	0.1334	0.0059	0.0562	
6	30	900	270	0.1393	0.1302	0.0091	0.0867	

TABLE A2.5 Ozone test 4

TABLE A2.6 Ozone test 5

4	Time Pulse		Cum. Energy	Absorbance (nm)		Λ Λ	$O_{1}(ma/I)$	
#	(min)	Count	(kJ)	blank	sample	ΔA	03 (IIIg/L)	
0	0	0	0	0.1278	0.1278	0.0000	0.0000	
1	10	300	90	0.1278	0.1272	0.0006	0.0057	
2	20	600	180	0.1278	0.1258	0.0020	0.0190	
3	30	900	270	0.1278	0.1222	0.0056	0.0533	

 TABLE A2.7 Ozone test 6

4	Time Pulse		Cum. Energy	Absorbance (nm)		Λ Λ	$O_{2}(mg/I)$	
 	(min)	Count	(kJ)	blank	sample	Δ Α	03 (mg/L)	
0	0	0	0	0.1278	0.1278	0.0000	0.0000	
1	10	300	90	0.1278	0.1277	0.0001	0.0010	
2	20	600	180	0.1278	0.1262	0.0016	0.0152	
3	30	900	270	0.1278	0.1233	0.0045	0.0429	

TABLE A2.8 Ozone test 7

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<u> </u>	Time	Pulse	Cum. Energy Absorbance (nm)		^ A	$O_{\tau}(mg/I)$		
#	(min) Count		(kJ)	blank	sample	ΔA	03 (mg/L)	
0	0	0	0	0.1278	0.1278	0.0000	0.0000	
1	10	300	90	0.1278	0.1275	0.0003	0.0029	
2	20	600	180	0.1278	0.1263	0.0015	0.0143	
3	30	900	270	0.1278	0.1232	0.0046	0.0438	

TABLE	A2.9	Ozone	test 8	

#	Time	Pulse Cum. Energy Absorbance (nm)				A	O(ma/I)	
	(min)	Count	(kJ)	blank	sample	ΔA	03 (mg/L)	
0	0	0	0	0.1278	0.1278	0.0000	0.0000	
1	10	300	90	0.1278	0.1274	0.0004	0.0038	
2	20	600	180	0.1278	0.1266	0.0012	0.0114	
3	30	900	270	0.1278	0.1227	0.0051	0.0486	

TABLE A2.10 Ozone test 9

ц	Time	Pulse	Cum. Energy	Absorbance (nm)			$O_{\rm mg}$	
#	(min)	Count	(kJ)	blank	sample	ΔA	03 (mg/L)	
0	0	0	0	0.1168	0.1168	0.0000	0.0000	
1	10	300	90	0.1168	0.1162	0.0006	0.0057	
2	20	600	180	0.1168	0.1150	0.0018	0.0171	
3	30	900	270	0.1168	0.1135	0.0033	0.0314	

TABLE A2.11 Ozone test 10

4	Time	Pulse	Cum. Energy	Absorb	ance (nm)		O(ma/I)	
#	(min)	Count	(kJ)	blank	sample	ΔA	U3 (mg/L)	
0	0	0	0	0.1168	0.1168	0.0000	0.0000	
1	10	300	90	0.1168	0.1163	0.0005	0.0048	
2	20	600	180	0.1168	0.1144	0.0024	0.0229	
3	30	900	270	0.1168	0.1142	0.0026	0.0248	

TABLE A2.12 Ozone test 11

ш	Time	Pulse	Cum. Energy	n. Energy Absorbance (ni			$O(m \sigma/I)$	
<i>#</i>	(min)	Count	(kJ)	blank	sample	ΔA	O_3 (mg/L)	
0	0	0	0	0.1168	0.1168	0.0000	0.0000	
1	10	300	90	0.1168	0.1162	0.0006	0.0057	
2	20	600	180	0.1168	0.1147	0.0021	0.0200	
3	30	900	270	0.1168	0.1140	0.0028	0.0267	

TABLE A2.13 Ozone test 12

щ	Time Pulse		Cum. Energy Absorbance (nm		bsorbance (nm)		$O_{\rm mg}({\rm mg}/{\rm I})$	
#	(min)	Count	(kJ)	blank	sample	ΔA	O_3 (mg/L)	
0	0	0	0	0.1168	0.1168	0.0000	0.0000	
1	10	300	90	0.1168	0.1164	0.0004	0.0038	
2	20	600	180	0.1168	0.1145	0.0023	0.0219	
3	30	900	270	0.1168	0.1138	0.0030	0.0286	

A2.2 BATCH PERCHLORATE TEST RESULTS

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Time	Cum. Input	TEST	1	TEST	2	TEST	3		
1 me	Energy	Peak Area	Conc.	Peak Area	Conc.	Peak Area	Conc.		
(min)	(kJ)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)		
0	0	5422	8.77	5865	9.49	5389	8.72		
5	30	5264	8.51	5845	9.45	5390	8.72		
10	60	5421	8.77	5835	9.44	5373	8.69		
15	90	5398	8.73	5840	9.45	5376	8.69		
20	120	5393	8.72	5838	9.44	5438	8.79		
25	150	5393	8.72	5840	9.45	5425	8.77		
30	180	5425	8.77	5828	9.43	5415	8.76		
40	240	5416	8.76	5834	9.44	5430	8.78		
50	300	5420	8.77	5834	9.44	5416	8.76		
60	360	5419	<u>8.76</u>	5835	9.44	5417	8.76		

TABLE A2.14 Batch perchlorate experiment 1-3

 TABLE A2.15 Batch perchlorate experiment 4 – 12

Time	Cum. Input	TEST 4 – 6		TEST 7 – 9		TEST 10 – 12	
	Energy	Peak Area	Conc.	Peak Area	Conc.	Peak Area	Conc.
(min)	(kJ)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)
0	0	12264	9.68	12612	9.95	12794	10.09
30	180	12153	9.59	12598	9.94	12631	9.96
60	360	12185	9.62	12435	9.81	12469	9.84
90	540	12124	9.57	12605	9.94	12550	9.90
120	720	12190	9.62	12381	9.77	12566	9.91
150	900	12197	9.62	12450	9.82	12359	9.75
180	1080	12228	9.65	12298	9.70	12505	9.86

TABLE A2.16 Batch perchlorate experiment 13 – 21

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Time	Cum. Input	TEST 13 – 15		TEST 16 – 18		TEST 19 – 21	
	Energy	Peak Area	Conc.	Peak Area	Conc.	Peak Area	Conc.
(min)	(kJ)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)
0	0	12690	10.01	12360	9.75	12163	9.60
30	180	12685	10.00	12354	9.75	12150	9.59
60	360	12665	9.99	12338	9.73	12123	9.57
90	540	12589	9.93	12298	9.70	12112	9.56
120	720	12595	9.93	12328	9.73	12220	9.64
150	900	12602	9.94	12254	9.67	12105	9.55
180	1080	12556	9.90	12357	9.75	12065	9.52

A2.3 FLOW-THROUGH PERCHLORATE TEST RESULTS

Time	Cum. Input	TEST 1 – 3		TEST 4 – 6		TEST 7 – 9	
	Energy	Peak Area	Conc.	Peak Area	Conc.	Peak Area	Conc.
(min)	<u>(</u> kJ)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)
0	0	11021	9.81	12378	9.96	10865	9.83
30	180	11031	9.82	12334	9.92	10877	9.84
60	360	11023	9.81	12344	9.93	10886	9.85
90	540	11024	9.81	12356	9.94	10837	9.80
120	720	10948	9.74	12322	9.91	10812	9.77
150	900	10953	9.74	12228	9.83	10826	9.79
180	1080	10945	9.73	12396	9.97	10805	9.77
210	1260	10949	9.74	12346	9.93	10818	9.78
240	1440	10970	9.76	12373	9.95	10830	9.79

TABLE A2.17 Flow-through perchlorate experiment 1 – 9

 TABLE A2.18 Flow-through perchlorate experiment 10 – 18

Time	Cum. Input	TEST 10 – 12		TEST 13 – 15		TEST 16 - 18	
	Energy	Peak Area	Conc.	Peak Area	Conc.	Peak Area	Conc.
(min)	(kJ)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)	(mV*sec)	(mg/L)
0	0	11686	9.90	11685	9.91	10217	9.62
30	180	11688	9.90	11682	9.91	10185	9.58
60	360	11653	9.87	11684	9.91	10178	9.58
90	540	11620	9.84	11656	9.89	10165	9.56
120	720	11618	9.84	11509	9.75	10149	9.54
150	900	11600	9.82	11590	9.83	10119	9.51
180	1080	11652	9.87	11594	9.83	10208	9.61
210	1260	11649	9.86	11506	9.75	10186	9.58
240	1440	11601	9.82	11515	9.76	10195	9.59