

University of Cincinnati

Date: 12/12/2010

I, Qiuming Zhao, hereby submit this original work as part of the requirements for the degree of Master of Science in Environmental Engineering.

It is entitled:

Reduction of Perchlorate from Contaminated Waters Using Zero Valent Iron and Palladium under UV Light

Student's name: **Qiuming Zhao**

This work and its defense approved by:

Committee chair: George Sorial, PhD

Committee member: E Sahle-Demissie, PHD

Committee member: Mingming Lu, PhD



1319

**Reduction of Perchlorate from Contaminated Waters
Using Zero Valent Iron and Palladium under UV Light**

A thesis submitted to the
Division of Research and Advanced Studies
Of the University of Cincinnati

In partial fulfillment of the
Requirements for the degree of

MASTER OF SCIENCE

In the Department of Civil and Environmental Engineering
of the College of Engineering

2010

By

Qiuming Zhao

Bachelor of Science, Chemistry, East Central University, Ada, Oklahoma, 1997

Thesis Advisor and Committee Chair: Professor George Sorial

Abstract

With the advance of the sensitive modern analytical techniques such as ion chromatography(IC), perchlorate (ClO_4^-) contamination in drinking water systems has been revealed as a widespread problem in United States, typical water contaminations are at 0.005-0.020 $\mu\text{g/L}$ (5-20 ppb) levels. Man-made perchlorate is a major contribution to contamination in the environment due to the exceptional oxidation properties of perchlorate. Although various perchlorate treatment technologies have been shown to be effective, chemical destruction may be the optimal way to remove perchlorate from water systems. In this study, perchlorate reduction by zero valent iron filings enhanced by UV light and palladium was conducted. Up to 52% perchlorate reduction from the original 1 mg/L (1ppm) was achieved using iron filings alone in a batch study. However, using UV light (0.24mW/cm², 12KW) with zero valent iron perchlorate reduction was enhanced to 83%. Palladium salt increased reduction very slightly, while UV light with palladium reduced perchlorate by 88%. Adsorption of perchlorate to the catalyst surface took place during the first 6 hours of the batch experiment under conditions of UV light and Palladium salt. In order to evaluate the effect of iron dosage, four different iron dosages, 0.25g/ml, 0.50g/ml, 0.75g/ml and 1.0g/ml, were used in the batch study. Among these, 1.0 g/ml of iron dosage showed the greatest capacity for perchlorate reduction. A mathematical correlation was established to explain the batch study reduction kinetics of perchlorate. A column flow experiment was conducted to evaluate the prediction of kinetic rate from the batch study. The reduction rate was correlated reasonably well by pseudo first order reaction kinetics under UV light.

Key Words: endocrine disruptor; ground water remediation; ion chromatography; oxidizer; perchlorate; reduction; UV light; zero valent iron

Acknowledgement

I would like to thank Dr. George A. Sorial and Dr. E. Sahle-Demessie for their earnest advice and guidance during the research. I would also like to thank Dr. Mingming Lu for her service in graduate committee. This study was supported by Sustainable Technology Division (STD), Clean Process Branch (CPB) at Environmental Protection Agency (EPA) in Cincinnati. I would like to extend my thanks to support and encouragement from the branch chief, Dr. Douglas Young and STD QA management, Mr. Daniel Young.

Table of Contents

<i>Abstract</i>	<i>III</i>
<i>Acknowledgement</i>	<i>V</i>
<i>Table of Contents</i>	<i>1</i>
<i>List of Figures and Tables</i>	<i>3</i>
List of Figures:.....	3
List of Tables:	4
1. Introduction	5
1.1 Occurrence of Perchlorate	5
1.2 Contamination	7
1.3 Toxicity of Perchlorate	9
1.4 Treatment Technology	11
1.5 Objectives.....	17
Reference	17
2. Batch Studies	22
2.1 Introduction	22
2.2 Chemicals and Materials	22
2.3 Experimental Procedure	23
2.4 Calibration	25
2.5 Ion Chromatograph.....	26
2.6 Experimental Results and Discussions.....	27
Reference	32
3. Recycle Column Study	41
3.1 Introduction	41

3.2 Experimental Procedure	42
3.3 Experimental Results.....	43
3.4 Possible Reduction Mechanism: Discussion.....	44
3.5 Conclusion.....	46
Reference	47
4. Recommendation for future work.....	54
<i>Appendix</i>	<i>55</i>
Appendix I: Raw Data.....	55
Appendix II: QAPP, SOP and Safety Plan.....	59

List of Figures and Tables

List of Figures:

Figure 1.1 Perchlorate anion (ClO_4^-) molecule structure

Figure 1.2 Kinetic Limitation (Huang and Sorial, 2006)

Figure 2.1 HF washed iron filing drying set up.

Figure 2.2 Image of iron filings before and after HF washing.

Figure 2.3 Experimental set up for perchlorate reduction using zero valent iron with UV light.

Figure 2.4 Experimental set up for perchlorate reduction using zero valent iron without UV light.

Figure 2.5 Calibration curve for perchlorate reduction in the batch study.

Figure 2.6 Reduction of perchlorate under different conditions.

Figure 2.7 Pseudo first order kinetics for perchlorate under different conditions.

Figure 2.8 Reduction of perchlorate in the presence of palladium and UV light under different iron dosages.

Figure 2.9 Pseudo first order kinetics for perchlorate under different iron dosages.

Figure 2.10 Correlation of first order reaction rate constant against iron dosage.

Figure 3.1 Experimental setup for packed column study.

Figure 3.2 Schematic diagram of the experimental setup for packed column study.

Figure 3.3 Calibration curve for the column study.

Figure 3.4 Reduction of perchlorate under 0.4 g/mL iron dosage in the presence of palladium & UV light in the column study.

Figure 3.5 Average reduction of perchlorate and pseudo first order kinetics under 0.4 g/mL iron dosage in presence of palladium & UV light in the column study.

Figure 3.6 Concept models from reduction reaction on the oxide-water interface (Scherer et al., 1988).

Figure 3.7 Possible electron and oxygen transfer process in the perchlorate reduction reaction (Huang, 2005).

List of Tables:

Table 2.1 Batch study sampling schedule.

Table 2.2 Calibration data for perchlorate for the batch study.

Table 2.3 Batch study data: percent of initial perchlorate remaining.

Table 2.4 Iron dosage study data: percent of initial perchlorate remaining.

Table 2.5 Kinetic reaction rate constant (K) for perchlorate reduction by Fe⁰ in the presence of Pd & UV light.

Table 3.1 Calibration data for perchlorate for the column study.

Table 3.2 Normalized perchlorate concentration with time for the column study.

1 Introduction

1.1 Occurrence of Perchlorate

Perchlorate (ClO_4^-) is an inorganic salt derived from perchloric acid (HClO_4). The most common perchlorate salts are ammonium perchlorate (NH_4ClO_4), potassium perchlorate (KClO_4), and sodium perchlorate (NaClO_4). Most perchlorate salts are extremely soluble in water (Urbansky, 1998). The solubility of potassium perchlorate, for example, is 15mg in 1 ml of water at room temperature. Perchlorate salts are also good oxidizers which decompose exothermically to give oxygen.

Perchlorate compounds in the environment come from both natural and man-made sources. Many studies on natural perchlorate occurrence have been done. Research has shown that natural perchlorate exists in extremely arid or semiarid climate locations. It is believed that natural occurring perchlorate in the environment starts from natural atmospheric processes. The actual mechanism of atmospheric perchlorate formation is not clear. It is hypothesized that chloride compounds are blown into the atmosphere and react with ozone to create perchlorate salt through photochemical reactions. This is similar to nitrate formation in the atmosphere (Eaton et al., 1995). Lightning also could be a major contributing factor in atmospherically produced nitrates and perchlorate (Dasgupta et al., 2005). Perchlorate from the atmosphere then deposits to the earth's surface by precipitation and accumulates because the rate of deposition in arid environments exceeds the rate of dissolution (Orris, 2004). Kang et al. (2008) investigated perchlorate formation by ozone oxidation of chloride in a lab scale. The authors concluded that perchlorate could be also produced naturally by ozone oxidation process (Kang et al., 2008). Up to now, Atacama Desert in

Chile is the only major location where a relative high concentration of natural occurring perchlorate has been found (Trumpolt et al., 2005). This location is also rich with natural born sodium nitrate (Urbansky et al., 2001). The deposit of perchlorate in mineralogical locations in Chile is believed to be associated with past local volcanic activity (Trumpolt et al., 2005). Some low concentrations of natural existed perchlorate have also been found in Peru and Bolivia (Eaton et al., 1995). Perchlorate was originally introduced into United States by importing Chilean nitrate for the fertilizer industry. Jackson et al. (2005) found that existing perchlorate in some parts of Texas was not man-made. A study by Kang et al. (2008) demonstrated in a lab scale shows that perchlorate can be produced by ozone oxidation of chloride, which provides a significant evidence of supporting the hypothesis that perchlorate is formed naturally through atmospheric process.

Man-made perchlorate compound is introduced in the environment by the dissolution of the ammonium, potassium, magnesium, as well as sodium perchlorate salts. Manufacture of ammonium perchlorate is the major source of the man-made perchlorate (Urbansky and Schock, 1999; USEPA, 2007). Perchlorate is produced through a series of processes. For example, sodium perchlorate is manufactured using sodium chlorate as feedstock. Potassium and ammonium perchlorate are produced by reacting sodium chlorate in a water solution with other chemicals to create concentrated solutions of either potassium perchlorate or ammonium perchlorate, depending on the added chemical (Eaton et al., 1995; Srinivasan and Sorial, 2009). Perchlorate crystals are then precipitated from the solution and are dried to produce a homogeneous dry granular product. These crystal perchlorate products then are shipped and sold to manufacturers to make various perchlorate-containing end products. Perchlorate has exceptional oxidizing properties. Therefore, it is widely used as an oxidizer component; a primary ingredient and energy booster in solid

propellants for rockets, missiles and explosives; in airbags and fireworks; and on spacecraft, submarines and in other esoteric situations where reliable backup or supplementary oxygen supply is needed. This is why most of the perchlorate contaminated sites found in United States are around NASA or military facilities where wastewater containing perchlorate was discharged to the ground without proper treatment. Manufacturing of rubber, aluminum refining, paints and enamels, as well as chemical fertilizers have also contributed as perchlorate contamination sources. By March of 2005, more than 150 locations in 25 different states with known perchlorate soil and groundwater contamination have been listed by the United States Environmental Protection Agency (USEPA) (Motzer, 2001; USEPA, 2005). In general, the man-made perchlorate sources are at higher concentrations, in the thousands of parts per billion (ppb, 1 ppb=1 µg/L) or more, compared to most natural sources (Greer et al., 2002). Perchlorate in a number of wells in San Gabriel Valley California, near Los Angeles, had been found by the USEPA in 1985 at concentrations ranging from 110-26,000 ppb (Kim and Logan, 2001). Since then, perchlorate in drinking water has been considered a major concern.

1.2 Contamination

Perchlorate was detectable up to 100 ppb before 1997 (Sorial, 2004). In 1997, the California Department of Health Services developed an Ion Chromatography (IC) analytical method which could detect perchlorate in water at the ppb level (Sorial, 2004). Since application of the sensitive new detection method, perchlorate contamination of groundwater has been found to be widespread in United States especially in the southwestern states of California, Nevada, and Arizona, as well as in Texas, Utah, Iowa and West Virginia (Srinivasan and Sorial, 2009). Perchlorates have also been found in surface water, such as the Colorado River. The concentration of perchlorate at these sites

are typically at the 5-20 $\mu\text{g/L}$ level (Moore et al., 2003). Perchlorate concentrations have been detected in California public water supplies in the range of 18 to 280 $\mu\text{g/L}$ (Motzer, 2001).

The high mobility of perchlorate ion makes it rapidly absorbed by agricultural plants. Therefore, perchlorate contamination is not only limited to drinking water. Livestock could be exposed to it as well. Significant levels of perchlorate have been detected in vegetables and dairy products as well as in breast milk (Kirk et al., 2003; Kirk et al., 2005; Seyfferth and Parker, 2006; Sanchez et al., 2008; Charnley, 2008; Srinivasan and Sorial, 2009). Sanchez et al. (2008) studied perchlorate exposure and the extent of perchlorate contamination in the dairy industry in the southwestern United States. The concentrations of perchlorate in the milk produced in this area are 43 to 2196 $\mu\text{g/L}$ (Kirk et al., 2003; Srinivasan and Sorial, 2009). The concentrations of perchlorate in the same area are between 2 and 5 $\mu\text{g/L}$ (Srinivasan and Sorial, 2009). The authors found that the perchlorate concentration in milk was directly related to the perchlorate contained in the food. Seven top brands of milk produced in Texas have been analyzed for perchlorate content by Kirk et al. (2003) resulting in an average of 6 $\mu\text{g/L}$. Kirk et al. (2005) also investigated the correlation between perchlorate and iodine concentration in breast milk by collecting samples from 18 states. The authors found perchlorate concentrations in breast milk to be five times higher on average than in dairy milk. Because the perchlorate concentration was inversely related to the iodine concentration (Srinivasan and Sorial, 2009), the authors concluded that perchlorate resulted in lower iodine concentration, a serious concern.

Since the People's Republic of China produces the largest amount of fireworks in the world, perchlorate contamination in the environment in China is potentially high. Extensive investigation

on perchlorate contamination in China has been done by Shi et al. (2007) who were the first to conduct this type of research in the environment in China. The authors collected and analyzed samples from sewage, rice, bottled water and milk as well, and indicated that perchlorate concentration was widespread in China. Concentrations ranged from 22 µg/kg to 380 µg/kg. Shi et al. (2007) also found perchlorate in rice samples at concentrations below 5 µg/kg, and in both dairy milk and breast milk samples at concentrations between 11 and 92 µg/L, respectively.

In conclusion, perchlorate contamination is a worldwide problem due to its high mobility property. The problem can be found in drinking water and in the food chain. Policy decisions regarding the regulation and treatment of perchlorate must be concerned with these problems.

1.3 Toxicity of Perchlorate

Perchlorate contamination in the drinking water system is potentially toxic to humans. The primary concern on human health with perchlorate is a decrease of thyroid hormone. The thyroid gland takes up iodine ion from the bloodstream and converts it to organic iodine which serves as a regulator on metabolic hormone function. However, perchlorate is a competitive inhibitor of normal iodide uptake by the thyroid gland and also can stimulate release of iodine stored in the thyroid gland. The mechanism of this process is: $I^- = SCN^- < ClO_4^-, TcO_4^-$ (Greer et al., 2002). From this mechanism, a large amount of perchlorate ion presented in the thyroid gland could reduce hormone production. Thyroid hormones are required for normal development of the brain. Thyroid is also essential for fetal development of the central nervous system (Greer et al., 2002). Lack of these hormones can cause decreased protein synthesis, decreased myelin formation, and retarded axonal generation (Eaton et al., 1995).

Perchlorate effects on human health have been studied extensively through animal toxicity tests. Clinical study on adult rats shows that exposure to perchlorate can reduce the iodide uptake by the thyroid gland and alters the functioning of the thyroid itself (Fisher and McLanahan, 2008). Liu et al. (2008) studied exposure to perchlorate and found in addition to influence on thyroid function increased arsenate toxicity which resulted in significantly increased retardation in zebra fish. Studies have shown that exposure to perchlorate in pregnant women can result in serious effects on the fetus (Srinivasan and Sorial, 2009). These developmental processes, unlike general body growth, are irreversible, lead to mental deficiency, and can lead to abnormal growth, development, reproduction, behavior, and metabolism (Greer et al., 2002). In the medical field, perchlorate is used to treat hypothyroidism which causes dry itchy skin, muscle and joint pain, headache, brittle hair, and sluggishness. Paulus et al. (2007) studied the impacts on inhibition of iodide uptake in rats exposed to perchlorate. Both normal and iodide deficient rats were used in this study. The authors found a significant impact on iodide uptake by perchlorate in the normal rats but not the iodide deficient rats except with high concentration of perchlorate. In accordance with these results, the authors assume that iodide deficient individuals may have higher resistance to perchlorate, although perchlorate effects on human health cannot be directly tested. Low levels of perchlorate may not pose a threat to human health (Gurol and Kim, 2000). Studies have shown that the most common route of exposure to perchlorate is through ingestion of water or food contaminated with perchlorate (Mattie et al., 2006). Adults exposed to a drinking water supply with perchlorate at concentrations of approximately 180 and 200 ppb at 0.5 mg/kg-day dose showed a slight downward trend in thyropropin levels in morning blood draws during perchlorate exposure (Eaton et al., 1995).

Perchlorate was listed in the drinking water Contaminants Candidates List (CCL) by the USEPA in 1998 (Gu et al., 2003). A reference dose (RfD) of 0.0007mg/Kg/day for perchlorate was established by the USEPA in 2005 (Greer et al., 2002). A study of the effect of perchlorate on thyroid function in ammonium perchlorate production workers was done by Braverman (2007). The author studied workers who had been exposed to perchlorate contaminated drinking water for short and long periods of time. The results of this study show perchlorate to be found in all workers, although the alteration of thyroid function was not measured. In October 2008, the USEPA concluded that perchlorate levels found in over 99% of drinking water systems are not of any concern to public health and recommended that perchlorate in drinking water not be regulated at a national level (Greer et al., 2002). The Safe Drinking Water Act (SDWA) required the USEPA to conduct further research on perchlorate occurrence and the associated health effects before establishing a Maximum Contaminant Level (MCL). No federal national primary drinking water regulation has been set at this point, but several states have established their own advisory level and are trying to establish a state MCL (Srinivasan and Sorial, 2009; Gurol and Kim, 2000).

1.4 Treatment Technology

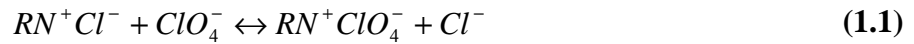
The molecular structure of perchlorate ion is shown in Figure 1.1. The chlorine atom is in a tetrahedron structure, which is surrounded by four oxygen atoms. The symmetrically arranged oxygen atoms perfectly block the chlorine from direct attack by electrons, and therefore prevent the perchlorate ion from undergoing reductive reaction, even though chlorine in the perchlorate is in its highest oxidation state. In order to make the reduction to occur, the chlorine atom requires activation energy to be excited in the amount of 120 kJ mol^{-1} (Huang and Sorial, 2006), as shown in Figure 1.2. The standard redox potential of perchlorate is +1.38 V (Huang and Sorial, 2006). The

extremely water soluble perchlorate ions are persistent in groundwater under typical environmental conditions and cannot be reduced with common reducing agents nor precipitated using commonly available cations, the treatment reagents, because of this high initial activation energy.

Since perchlorate is a chemical of health concern, its removal from drinking water sources is very desirable. The treatment of perchlorate contamination in water becomes a challenge because of its tetrahedron molecule structure. Currently, there are two major categories of available perchlorate treatment technologies for contaminated ground water: nondestructive removal technology and destructive technology. The nondestructive removal processes mainly utilize physical processes. These physical removal technologies mainly include activated carbon adsorption, ion exchange resins, and membrane technology. Granular Activated Carbon (GAC) adsorption is widely used in the drinking water treatment industry. The biggest advantages with GAC adsorption is that it is easy to target perchlorate in the water and the regeneration of the spent carbon makes this technology economically feasible. However, it is not very effective for perchlorate adsorption because it requires tailoring of GAC (Srinivasan and Sorial, 2009). The disadvantage of activated carbon adsorption is the additional requirement of the disposal of the perchlorate-laden spent carbon or regenerative brine.

Ion-exchange is the other main non-destructive removal technology. It is the most effective and commonly used technology for perchlorate removal from drinking water. Ion-exchange is a physical/chemical process, exchanging an anion (typically Cl^-) with the perchlorate ion in the water (Equation (1.1)). Up to now, a wide variety of strong basic anion-exchange (SBA) resins have been developed that have very high selectivity for perchlorate. The ion-exchange resins used to target

perchlorate are typically polymers with a strong positively charged functional group, a quaternary amine (R_4N^+) (Srinivasan and Sorial, 2009).



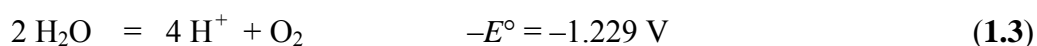
A major concern with the use of ion-exchange is the resultant brine wastewater that is high in both perchlorate and total dissolved solids (TDS) which must be disposed of or treated.

Membrane technology works by applying a semi-permeable membrane that prevents the passage of certain ions to remove the perchlorate from water. It is a pressure-driven filtration and this makes application of this technology in large scale systems complicated. Also, fouling issues result in the generation of large volumes of reject streams that would require further treatment or disposal (Srinivasan and Sorial, 2009).

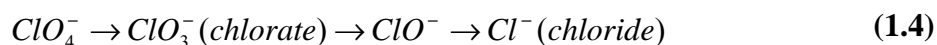
Electrodialysis is another non-destructive perchlorate removal technology. It has been found to be more effective than conventional membrane filtration for perchlorate. However, exorbitant operating costs make this technology less favorable. Technologies such as ultrafiltration(UF), nano-filtration (NF) and reverse osmosis (RO) are also a few other non-destructive perchlorate removal methods. All nondestructive removal processes are mainly concentrated on ion exchange resins and require additional steps to treat or dispose of the high concentrated perchlorate residual waste-stream that is generated.

Although the physical removal technologies are able to remove perchlorate from water, they are not preferred methods. Physical perchlorate treatments only transfer the perchlorate from one stream to another, necessitating further treatment and disposal. In contrast, destruction technology can completely reduce perchlorate in water to harmless chloride and is the optimal treatment.

According to the following standard reduction potentials (Emsley, 1989) for the half-reactions (1.2a, 1.2b), it is thermodynamically feasible to reduce perchlorate to chlorate and chloride. Perchlorate acid can oxidize water to oxygen because the water-oxygen couple has an oxidation potential of -1.229 V (Emsley, 1998), see 1.3.



However, in reality, perchlorate acid is not reactive towards most of reducing agents under cold and dilute condition because of the kinetic barrier to its reduction reaction. Equation 1.4, below, shows the pathway of perchlorate reduction. In this pathway of the reduction process, perchlorate loses an oxygen atom to form chlorate (ClO_3^-) at the first step of reaction. This step is the limiting step in the perchlorate reduction reaction. After the first step, the chlorine atom is surrounded by three oxygen atoms instead of four oxygen atoms. Thus, further reduction kinetics for the chloride ion (Cl^-) occur very quickly because of the easy access of the chlorine atom to the electrons.



Perchlorate reduction by biological processes under anaerobic conditions has been studied extensively and widely used in wastewater treatment industry for many years. Perchlorate-degrading microorganisms (mainly, indigenous bacteria) have been found to be widespread in the subsurface environment. In the presence of an appropriate food source (electron donor) and redox condition these bacteria have the capability to reduce perchlorate into chloride, carbon dioxide and water. Injection or placement of a food/carbon source (electron donor) into the contaminated aquifer is necessary to promote growth of the desired bacteria and effect perchlorate

degradation. It is understood that special enzymes in the microorganisms' cells act as catalysts during the degradation of perchlorate. The enzymes also effectively decrease the activation energy of perchlorate reduction. However, the use of biological treatment in the drinking water, might have a concern with regards to potential pathogenicity of the microorganisms. Therefore, chemical reduction processes for perchlorate treatment in the drinking water and ground water are favored. The challenge in the chemical reduction process of perchlorate is to find a catalyst to overcome the energy barrier (see Figure 1.2). Researchers have found that many common reducing reagents could serve this key function of overcoming the initial energy barrier. For example, Ruthenium(II) can reduce perchlorate to chlorate, where vanadium(II), vanadium(III), molybdenum(III), dimolybdenum(III), chromium(II), and titanium(III) all reduce perchlorate to chloride (Urbansky,1998). The first demonstration of perchlorate reduction by metal cation was done by Rothmund (1909). With right catalyst, many other reductants will react with perchlorate in the presence of ruthenium (III,IV) (Crowell et al., 1929), although these treatment data was insufficient. Liu et al (1984) studied treat perchlorate-contaminated water with Ti(III) chelates under anaerobic conditions. Although it produced harmless chloride and nontoxic TiO₂, the reaction occurred at pH less than 4 and the half-life for this reaction would take 50 days (Urbansky, 1998). Hurley et al developed heterogeneous catalysts for reduction of perchlorate (Hurley & Shapley, 2007) in which use Pd/Rh-C bimetallic catalyst showed perchlorate reduction in the presence of hydrogen and was able to achieve more than 99% reduction within 5 hours. The reaction occurred at pH less than 3 under pressure of 5bar, which is not feasible for conventional water treatment plan.

Moore et al. (2003, 2005) has studied extensively perchlorate reduction on zero valent iron. The mineral surfaces act as a catalyst during the reduction, which provides additional accelerated

pathways for redox processes. It is believed that the metal surface coupled with released electrons provides reduction and dehalogenation of the targeted chemicals. Although the detailed mechanism of the perchlorate reduction reaction at the aquatic mineral interface is not well understood, applications of perchlorate reduction using zero valent iron in aqueous system have been investigated in many laboratory and field studies. Laboratory studies have indicated that perchlorate can be reduced by iron under anoxic condition. However, the reaction rate is very slow (Huang and Sorial, 2006).

A study by Gurol and Kim (2000) discovered that UV light speeds up the zero valent iron reduction reaction. UV can serve as a catalyst to accelerate the reduction rate to make the reaction faster since perchlorate is known to absorb UV in the wavelength range shorter than 185 nm. UV light itself, however, is not able to make perchlorate reduction to occur. UV light is believed to promote the reaction, while metallic iron provides electrons for reduction. The addition of metallic iron combined with exposing the solutions to ultraviolet light achieved 77% reduction in perchlorate at an intensity of 0–9 W/cm (Gurol and Kim, 2000). The general perchlorate reduction reaction by zero valent iron under UV is shown below in Equation 1.5):



The most common application of perchlorate reduction by zero valent iron is the use of iron filings as a permeable reactive barrier. Iron was found to have the fastest reaction rate among other common metals. Gurol and Kim (2000) and Moore et al. (2003) discovered removal of perchlorate in water by cast iron filings. A treatment technology goal is to reduce perchlorate concentration to the 4µg/L or to lower levels in order to overcome the consequences that arise from accumulation of perchlorate in vegetables by irrigation.

1.5 Objectives

The objective of this research is to investigate perchlorate reduction by zero valent iron Fe^0 with UV light, which includes the following four tasks:

1. to conduct bench scale studies to determine the kinetics of perchlorate reduction by Fe^0 under UV light.
2. to modify the Fe^0 by adding palladium reducing metal to increase the rate of catalyst activity.
3. to develop the kinetics model from the batch study to predict the behavior of perchlorate reduction from known iron dosage.
4. to conduct column flow study to verify the kinetics from the batch study.

Reference

Braverman, L.E. (2007) Clinical Studies of Exposure to Perchlorate in the United States. *Thyroid* **17**:819-822.

Charnley, G. (2008) Perchlorate: Overview of risks and regulation. *Food and Chemical Toxicology* **46**:2307-2315.

Crowell, W.R., D.M. Yost, D.M., and Carter J.M. (1929) Catalytic Effect of Ruthenium Salts on The Reduction of Perchlorate Acid by Hydrobromic Acid. *J. Am. Chem. Soc.*, **51**:786:794.

Dasgupta, P.K., Martinelango, P.K., Jackson, W.A., Anderson, T.A., Tian, K., Tock, R.W. and Rajagopalan, S. (2005) The origin of naturally occurring perchlorate: The Role of Atmospheric Processes. *Environmental Science & Technology* **39**:1569-1575.

Eaton, A. D., Clesceri, L. S. and Greenberg, A. E. (1995) 3500-Ca Calcium *in* Standard Methods for the Examination of Water and Waste Water. American Public Health Association, American Water Works Association and Water Environment Federation, pp. 3-56.

Emsley, J.(1989) *The Elements*. Clarendon, Oxford. pp.48, 134.

Fisher, J. and McLanahan, E. (2008) Evidence for Perchlorate Altering Thyroid Function. *Toxicology Letters* **180**: S182.

Greer, M. A., Goodman, G., Pleus, R.C. and Greer, S.E. (2002) Health Effect Assessment for Environmental Perchlorate Contamination: The Dose Response for Inhibition of Thyroidal Radioiodide Uptake in Humans. *Environmental Health Perspectives* **110**: 927–937.

Gu, B., Dong, W., Brown, G. M. and Cole, D. R. (2003) Complete Degradation of Perchlorate in Ferric Chloride and Hydrochloric Acid Under Controlled Temperature and Pressure. *Environmental Science and Technology* **37**: 2291-2295.

Gurol, M. G. and Kim, K. (2000) Investigation of Perchlorate Removal in Drinking Water Sources by Chemical Methods, in: Urbansky, E. T. (ed.) *Perchlorate in the Environment*. Kluwer/Plenum Academic, New York, NY, pp. 99-107.

Huang, H. and Sorial, G.A. (2006) Perchlorate Remediation in Aquatic Systems by Zero Valent Iron. *Environmental Engineering Science* **24**: 917-926.

Hurley, K. D. and Shapley, J. R. (2007) *Environmental Science & Technology* **41**: 2044.

Jackson, A.W., Anandam, S.K., Anderson, T. Lehman, T. Rainwater, K., Rajagopalan, S., Ridley, M. and Tock, R. (2005) Perchlorate Occurrence in the Texas Southern High Plains Aquifer System. *Ground Water Monitoring & Remediation* **25(1)**:137-149.

Kim, K. and Logan, B. E. (2001) Microbial Reduction of Perchlorate in Pure and Mixed Culture Packed-bed Bioreactors. *Water Research* **35**: 3071-3076.

Kirk, A.B. Martinelango, P. K. Tian, K. Dutta, A., Smith, E. E. and Dasgupta P. K. (2003) Perchlorate in Milk. *Environmental Science & Technology* **37**: 4979-4981.

Kirk, A.B., Martinelango, P., Tian, K., Dutta, A., Smith, E. E. and Dasgupta P. K. (2005) Perchlorate and Iodide in Dairy and Breast Milk. *Environmental Science & Technology* **39**: 2011-2017.

- Kang, N., Jackson, A.W., Dasgupta, P.K. and Anderson, T.A. (2008) Perchlorate Production by Ozone Oxidation of Chloride in Aqueous and Dry Systems. *Science of the Total Environment* **405**:301-309.
- Liu, B.-Y., Wagner, P.A. and Earley, J.E. (1984) Reduction of Perchlorate Ion by (N-(hydroxyethyl)ethylene-diaminetriacetato)quotationtitanium(III). *Inorg. Chem.*, **23**:3418-3420.
- Liu, F., Gentles, A. and Theodorakis, C.W. (2008) Arsenate and Perchlorate Toxicity, Growth Effects, and Thyroid Histopathology in Hypothyroid Zebrafish *Danio rerio*. *Chemosphere* **71**:1369-1376.
- Mattie, D. R., Strawson, J. and Zhao, J. (2006) Perchlorate Toxicity and Risk Assessment, in: Gu, B. and Coates, J.D. (Eds.) *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Springer Science, New York, NY, 2006, pp. 169-196.
- Moore, A. M., De Leone, C. H. and Young, T. M. (2003) Rate and Extent of Aqueous Perchlorate Removal by Iron Surfaces. *Environmental Science and Technology* **37**: 3189-3198.
- Moore, A. M. and Young, T. M. (2005) *Journal of Environmental Engineering* **131**: 924-933.
- Motzer, W. E. (2001) Perchlorate: Problems, Detection, and Solutions. *Environmental Forensics* **2**: 301-311.
- Orris, G. J. (2004) Perchlorate in Natural Minerals and Materials. USGS Quarterly Report. (April). Available online: http://www.itrcweb.org/Documents/Perch_private/USGS_Minerals.doc (accessed on December 28, 2010).
- Paulus, B.F., Bazar, M.A., Salice, C.J., Mattie, D.R. and Major, M.A. (2007) Perchlorate Inhibition of Iodide Uptake in Normal and Iodine-deficient Rats. *Journal of Toxicology and Environmental Health, Part A*, **70**:1142-1149.
- Rothmund, V. (1909) *Z. Anorg. Chem.*, **62**: 109.
- Seyfferth, A. L. and Parker, D. R. (2006) Determination of Low Levels of Perchlorate in Lettuce and Spinach Using Ion Chromatography-Electrospray Ionization Mass Spectrometry (IC-ESI-MS). *Journal of Agricultural and Food Chemistry* **54**: 2012-2017.
- Sanchez, C. A., Blount, B. C., Valentin-Blasini, L., Lesch, S.M. and Krieger, R.I. (2008) Perchlorate in the Feed-Dairy Continuum of the Southwestern United States. *Agricultural and Food Chemistry* **56**: 5443-5450.
- Shi, Y., Zhang, P., Wang, Y., Shi, J., Cai, Y., Mou, S. and Jiang, G. (2007) Perchlorate in Sewage Sludge, Rice, Bottled Water and Milk Collected From Different Areas in China. *Environment International* **33**: 955-962.
- Sorial, G.A. (2004) The Perchlorate Dilemma in Drinking Water (editorial). *ASCE Journal of*

Environmental Engineering **130**:1-2.

Srinivasana, R. and Sorial, G.A. (2009) Treatment of Perchlorate in Drinking Water: A Critical Review. Separation and Purification Technology **69**: 7-21.

Trumpolt, C.W., Cullison, G.D.M.C., Flanagan, S.J.P., Siegel, L. and Lathrop S. (2005) Perchlorate: Sources, Uses, and Occurrences in the Environment. Remediation Journal **16**:65-89.

Urbansky, E.T. and Schock, M.R. (1999) Issues in Managing the Risks Associated with Perchlorate in Drinking Water. Journal of Environmental Management **56**: 79-95.

Urbansky, E. T., Brown, S. K., Magnuson, M. L. and Kelty, C. A. (2001) Perchlorate Levels in Samples of Sodium Nitrate Fertilizer Derived From Chilean Caliche. Environmental Pollution **112**(3): 299-302.

Urbansky, E.T. (1998) Perchlorate Chemistry: Implications for Analysis and Remediation. Bioremediation Journal **2**(2): 81-95.

USEPA (2005) Known Perchlorate Releases in the U.S. - March 25,2005 (Reuse, F.F.R.a.,ed.), Federal Facilities Restoration and Reuse Office.
Available online: http://www.epa.gov/fedfac/documents/perchlorate_releases_us_20050325.htm
(accessed on December 28, 2010).

USEPA (2007) Perchlorate. (Reuse, F. F. R. a., ed.), Federal Facilities Restoration and Reuse Office.
Available online: <http://www.epa.gov/fedfac/documents/perchlorate.htm>
(accessed on December 28, 2010).

Xiong, Z., Zhao, D. and Gang, P. (2007) Rapid and Complete Destruction of Perchlorate in Water and Ion-Exchange Brine Using Stabilized Zero-Valent Iron Nanoparticles. Water Research **41**: 3497 – 3505.

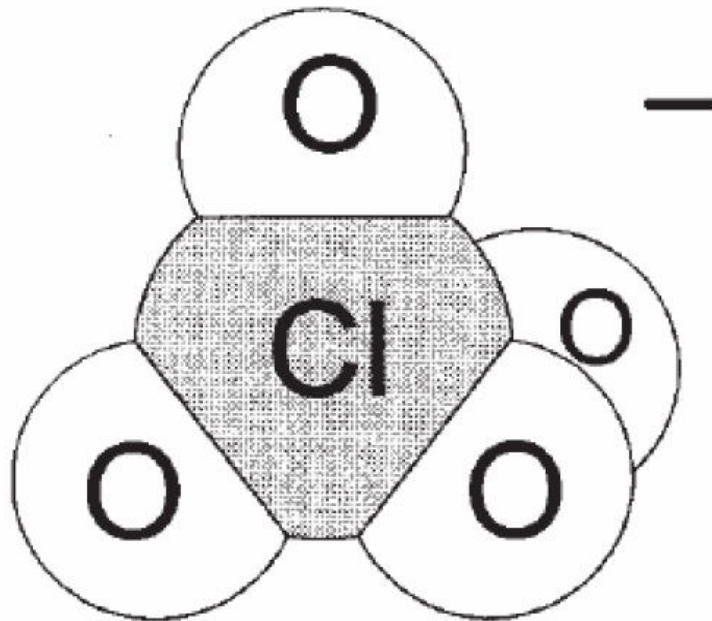


Figure 1.1 Perchlorate anion (ClO_4^-) molecule structure

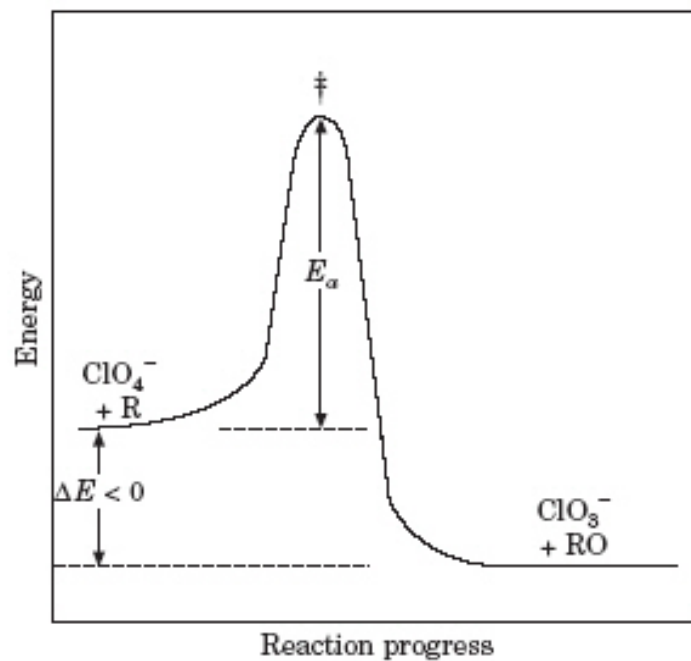


Figure 1.2 Kinetic Limitation (Huang and Sorial, 2006)

2 Batch Studies

2.1 Introduction

A batch experiment is characterized by its operation where the reactants and catalyst are introduced in the desired quantities in a closed vessel. The major advantages of batch experiments are the uniformity of temperature, efficient stirring and easy to control variables. In this perchlorate reduction study, batch experiments were designed and conducted for preliminary screening and determining the kinetics of reduction reaction. Experiments were designed to determine the effect of process variables on the reactor's performance. Four different variables are tested in the batch experiments. They were perchlorate reduction by Fe^0 in Milli-Q water in the presence and absence of UV light and with and without palladium salt. Palladium(II) nitrate catalyst was used to increase the rate of the reduction reaction. The effect of iron dosage on perchlorate reduction by Fe^0 was studied in these batch experiments. A kinetic model of the perchlorate reduction was then developed.

2.2 Chemicals and Materials

The iron filings used in this study were 50 -70 mesh particles obtained from Fisher Scientific (Hanover Park, IL, USA). A High-performance liquid chromatography (HPLC) grade sodium perchlorate monohydrate was obtained from Fisher Scientific (Hanover Park, IL, USA) to provide the target ion ClO_4^- . Perchlorate stock solution with concentration of 1 g/L ClO_4^- was prepared by dissolving 1.412g of sodium perchlorate monohydrate in 1L Mili-Q water which had a 17.5 M Ω -cm resistance obtained by a Millipore system. The main catalyst used was palladium nitrate dehydrate obtained from Across Organics. 1N Hydrofluoric (HF) acid used in acid wash of iron filling, which

was diluted using 50:50 w/w HF solution obtained from Fisher Scientific (Hanover Park, IL, USA). The UV lamp used in the experiments was 1.2KW Axial Lead obtained from ACE Glass (Vineland, NJ).

2.3 Experimental Procedure

The batch experimental work was conducted at the Containment Facility Building of the Clean Process Branch, Sustainable Technology Division, U.S. Environmental Protection Agency. The laboratories are equipped with facilities for bench scale experiments, including fume hoods, UV light cover boxes, dedicated bench space, and steam, air and cold/hot water supplies.

Iron filings purchased from Fisher Scientific were brown in color indicating the presence of ferric oxide (Fe_2O_3) and possible oily contaminants on the surface. In order to obtain iron oxide (FeO) on the surface of Fe^0 , the iron filings were washed by 1N HF acid before use. A 500 ml of 1N HF acid was used to wash about 500 g iron filings in a flask. The iron filings were constantly stirred using a glass bar until the brown color disappeared. The washed iron filings were rinsed several times by Oxygen free Milli-Q water until the rinsed water is clear and its pH is at reading of 6-7. The washed iron filings were dried under a nitrogen gas by adding a small amount of heat. The heating temperature was critical during the drying process. High temperature could turn the iron filings brown in color, which would indicate that the iron filings had been oxidized before drying. Low temperature heating could oxidize the iron filling caused by a long period of drying. The optimum temperature of the heater was between 90–100°C. Setting the mark of the heating plate at 5-6 achieved this temperature (see Figure 2.1). The color of treated iron filings was black as shown in Figure 2.2. Since HF acid expose an extreme danger potential, all apparatus used were plastic, glass

apparatus were prohibited, all acid wash iron filings process were conducted in a hood. Double glove with heavier weight (8 mil) nitrile gloves was used during entire of HF acid wash of iron filings. The flask used to wash iron filings was covered with aluminum foil to prevent over spilling of HF acid. The details on safety are included in Appendix II: QAPP, SOP and Safety Plan.

The batch experimental set up with UV light is shown in Figure 2.3 and without UV light in Figure 2.4. Perchlorate stock solution with concentration 1,000 mg/L was diluted to an initial concentration 1000 $\mu\text{g/L}$ and purged by nitrogen gas to remove any dissolved oxygen in order to reduce the interference of reduction between Fe^0 and perchlorate. For the first 1g/ml Fe^0 dosage experiments, glass sample vials 16ml in size obtained from National Scientific Company (Duluth, GA) were used in the experiments. 15g of Fe^0 was placed into the vial. The 1000 $\mu\text{g/L}$ perchlorate solution was then introduced into the glass vials and completely filled leaving no head space. The vials were then sealed by rubber septum and placed on a rotator as shown in Figure 2.3 and Figure 2.4. The rotator was kept turning during the entire experiment to ensure uniformity of mixing within the vials. The sample temperature under UV light condition was about 40°C. The pH of samples was around 4.50.

The next study included investigating the effectiveness of the Fe^0 dosage. Four Fe^0 dosages of 0.25, 0.5, 0.75, and 1.0 g/ml were used. For the palladium effectiveness study, 0.75 g palladium nitrate was added into 1.0 mg/L perchlorate solution. The perchlorate with palladium nitrate solution was mixed well and was de-oxygenized by purging with N_2 gas before use. For the UV effect study, the black metal box was closed as shown in Figure 2.3 to prevent leakage of UV light.

Samples were collected according to predetermined time intervals as indicated in Table 2.1. At each time interval, one vial was sacrificed and two samples were taken and analyzed independently. The samples were first filtered using a 0.45 μ membrane to remove any iron filling particle and then treated by an OnGuard II H cartridge (Dionex, Sunnyvale, CA) to remove any dissolved ion species which may interfere in the perchlorate analysis and might significantly reduce the sensitivity of the IC column and accumulate in the suppressor. The filtered samples were then analyzed in the ion chromatograph (IC). The method used for the perchlorate analysis is the amended EPA method 314.0 (see Appendix II: QAPP, SOP and Safety Plan).

2.4 Calibration

Quantification of perchlorate was performed by a six-point standard solutions' calibration covering a range from 62.5 to 1000 μ g/L as described in next paragraph. A linear regression model of the response against concentration with intercept was used. The calibration was performed under the 100mA SRS current. Each calibration point was performed by injecting each working standard twice. In this method of injection, the calibration event was performed in the order from the lowest concentration standard to highest concentration standard.

A standard stock perchlorate solution with concentration 1000 mg/L ClO_4^- was purchased from Spex CertiPrep, Metuchen, NJ. This stock solution was used to prepare the second stock solution of 1000 μ g/L by diluting 1000-fold. Six standard solutions of perchlorate (1000, 750, 500, 250, 100 and 62.5 μ g/L) were then prepared by diluting the second stock solution to the desired concentration in order to perform the calibration of perchlorate on the IC. All the necessary dilutions were conducted by accurately measuring the desired volume of perchlorate solution from the second

stock solution using an automatic pipette and then diluting by Milli-Q water in volumetric flasks. The prepared standards were mixed well and then transferred into a 15 ml sampling vials in preparation for injection of the IC analysis. The calibration data from IC is listed in Table 2.2.

2.5 Ion Chromatograph

Perchlorate ion detection in this study was performed using Dionex(Sunnyvale, CA, USA) IC-25 ion chromatography system with a GP-25 iso-pump, an anion self-regenerate suppressor ultra (ASRS-ultra), an ED-40 conductivity detector, an auto injection and a LC-20 chromatography enclosure. The injection volume was 1000 μ L controlled by a 1000 μ L sample loop installed in the IC system. Anion separation was obtained on a Dionex IonPac AS16 separation column (4.0 X 250 mm), with an IonPac AG16 guard column.

Helium PP gas was used to provide pressure for the eluent bottles and the auto-injector. The eluent was 50 mM NaOH and was made by adding 8g of 50%, w/w NaOH standard solution obtained from Fisher Scientific into a bottle which contains 2L of degassed Milli-Q water. The eluent bottle was capped immediately after the dilution and mixed well to ensure the eluent is homogeneous before use. The suppression current was set at 100 mA. The current was flushed through the IC system at a flow rate of 1.0 mL/min to maintain the background conductivity within 2 -5 μ S. The flow rate was controlled by the GP-25 iso-pump. At this flow rate the pressure of the IC system was around 1700 psi.

Anion separation was obtained on a Dionex IonPac AS16 separation column (4.0 X 250 mm), with an IonPac AG16 guard column to utilize the high solution of perchlorate salts and reduce the

interference with other anions. After treatment with an OnGuard Ag cartridge (Dionex, Sunnyvale, CA) followed by an OnGuard H cartridge, good recovery of perchlorate (92.6%) was achieved (Dionex Corp., 2000). The current of the suppressor (SRS) is set at 100 mA on ASRS-ultra to reduce the back ground conductivity to 1-5 μS .

The conductivity detector's signal was collected and analyzed by PeakNet 6.0 software, which provides the peak area, peak height and retention time of the target anion. Under the conditions when 100 mA suppression current and 1.0 ml/min eluent flow rate were used, the retention time of the perchlorate was about 16 minutes. The total run time of a sample was set at 25 minutes.

2.6 Experimental Results and Discussions

The calibration data are shown in Table 2.2. Each standard was analyzed twice. The coefficients of variation (CV) were calculated as the absolute percent difference of the response factor (response/concentration) at a specific dilution from the average overall response factor for all levels. These values were all within 15% (see Table 2.2).

Homoscedasticity of the IC system is verified prior to estimation and evaluation of the calibration curve via Cochran's C test for outlying variance (Snedecor and Cochran, 1980). The test statistic is calculated as

$$C_{p,n} = \frac{SD_{\max}^2}{\sum_{i=1}^n SD_i^2} \quad (2.1)$$

where n is the number of standards used and p , the number of replicates per standard. For these data, $n=6$ and $p=2$. SD_i is the standard deviation calculated from the i^{th} standard. From the data of Table 2.2, $C_{2,6} = 1.350 \times 10^8 / 3.393 \times 10^8 = 0.398$. The Outliers package for R statistical software (Komsta, 2006) indicates that the extreme standard deviation value, SD_{max} , is not significantly different from the others ($p\text{-value}=0.227 > 0.05$). Therefore, the homoscedasticity of the system is accepted.

The calibration curve is shown in Figure 2.5. The coefficient of determination (R^2) is 0.9982 which is considered reasonable indication of linear response for the perchlorate calibration curve.

The precision of IC instrument was determined by using relative standard deviation (RSD) which is the absolute value of coefficient variation. The following is the RSD formula used to calculate the RSD for the calibration data:

$$RSD = ABS(\text{coefficient of variation}) = 100 \cdot ABS \left[\frac{ARF - ARF(\text{For all levels})}{ARF} \right] \quad (2.2)$$

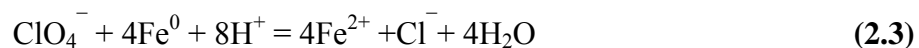
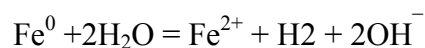
The results of perchlorate reduction from the batch study on iron filings under four different conditions are shown in Figure 2.6. The perchlorate concentration decreased over time for Fe^0 with and without UV light, Fe^0 and Pd with and without UV light, which indicates reduction of perchlorate by Fe^0 has occurred under all four reaction conditions. During the first 6-hour reaction period of the reduction reaction under the condition of Fe^0 with UV light, Fe^0 and Pd salt and without UV light, and Fe^0 and Pd salt with UV light, the perchlorate concentration decreased to 0.15 $\mu\text{g/L}$, 0.25 $\mu\text{g/L}$ and 0.53 $\mu\text{g/L}$ and went back to the initial level. Moore et al. (2003) and Huang

(2005) also noticed this behavior in their study for the initial 6-hour reaction time. Similar observation was described by Xiong et al. (2007) where they elaborated that there occurs an initial adsorption of ClO_4^- on the Fe^0 surface without any degradation. As the reaction proceeded, the surface of the Fe^0 nanoparticle was progressively oxidized to iron oxide. In the experimental pH range of 6.5–7.8, the resultant iron oxide can rapidly adsorb ClO_4^- from water, resulting in the observed rapid drop in perchlorate concentration in the solution phase (Xiong et al., 2007). However, the concurrent rapid adsorption and reduction of perchlorate rapidly depleted the perchlorate chemical potential in the solution phase such that the concentration gradient between the particle surface and the solution phase was reversed, and the adsorbed perchlorate started releasing back into the solution. This initial adsorption was observed during the initial 6 hour reduction reaction under the condition of Fe^0 with UV light, Fe^0 and Pd without UV light and Fe^0 and Pd under UV light, and was not observed from the reaction under the condition of Fe^0 with no UV light (see Figure 2.6). Following the initial 24 hours the concentration decreased at a relatively slow rate under all conditions. The perchlorate desorption was further promoted as the concentration of chloride ions resulting from the reduction of perchlorate built up (Xiong et al., 2007). The observation of desorption also can be confirmed by monitoring the change of chloride concentration on the iron surface. However, such analysis of Cl^- ion was not performed due to the presence of background chloride in the water used in batch experiments.

To determine the effect of UV light on the perchlorate degradation, the test vials were exposed to a UV light, respectively. Under the condition of UV light with Fe^0 , the concentration of perchlorate was reduced by 83% after 384 hours, compared to a 52% decrease without UV light. UV light excited the iron and, hence, enhanced the reduction reaction.

In order to study the impact of palladium catalyst on the perchlorate reduction by Fe⁰, a dosage of palladium nitrate (1.5mg/mL) was added into 1mg/L perchlorate solution. It is obvious from observation in Table 2.3 and Figure 2.6 that UV light has much greater effect than Pd salt on perchlorate reduction by Fe⁰. Also, the perchlorate degradation with Fe⁰ and Pd was much greater by using UV light than without UV light, an 88% reduction compared to 57%. Similar results are observed with Fe⁰ using UV light and without UV light, 83% reduction as compare to 52%, see Table 2.3. Adding Pd salt increased the reaction rate slightly.

Perchlorate-laden solution with zero valent iron undergoes the following competitive reactions (Gu et al., 2003):



Perchlorate ions are first adsorbed on the surface of Fe⁰ and then undergo ion transfer process facilitated by UV excitation. The UV radiation acts as a catalyst to provide photoelectron and activation energy for the reduction reaction. Iron dosage and intensity of UV light has an effect on the perchlorate reduction rate. UV light promotes the reaction while metallic iron provides electrons for reduction of perchlorate. More detailed mechanism of the reduction reaction of perchlorate on surface of Fe⁰ with aim of UV light is discussed in the next chapter.

It is seen from Figure 2.7 that the experimental data follows pseudo first order kinetics reasonably well for the reduction reactions under UV light conditions. The regression coefficient (R^2) was over 0.986 without Pd and 0.908 with Pd for the reduction reactions under UV light. The regression coefficient (R^2) was only 0.845 with no Pd salt and 0.902 with Pd salt for the reduction reactions under the conditions of no UV light. The first order reaction rate constants for the experimental runs were in the range of 0.00196 – 0.00211 for the reactions without UV light, and the 0.00454 – 0.00535 with UV light. The experimental k data is another way to show that UV light speeded up perchlorate degradation. Again, it indicates that palladium had only a very slight effect on both regression coefficient and rate constant. The experimental data and the first order regression reveal that UV light enhanced the reduction of perchlorate greatly.

In order to study the iron loading effectiveness on the perchlorate reduction and the reaction kinetics and to predict the performance of the column experiment, batch experiments with four different iron filings dosage were conducted. In order to determine the theoretical rate constant for the packed column, four levels of iron dosage, 0.25g/ml, 0.5g/ml, 0.75g/ml and 1.0g/ml, were used. The experimental procedures were the same as that of the 1.0 g/ml batch experiments. All four experimental runs were under the same condition of palladium salt and UV light. The kinetic data summary from the batch study for each dosage is shown in Table 2.4. The result of iron dosage study is shown in Figure 2.8. The highest iron dosage 1.0 g/ml used in this study with palladium nitrate under UV light achieved the highest reduction capacity (89%) after 384 h among the four iron dosages studied. This suggests that the reaction is limited by Fe^0 dosage, with higher dosages providing more surface area for the perchlorate reduction reaction.

The pseudo first order rate constants were also calculated following the same method. The regressions for the pseudo first order reactions for the different dosage considered are shown in Figure 2.9. It is seen that the data fit the pseudo first order reaction very well. The regression coefficients of determination (R^2) were 0.974, 0.998, 0.985 and 0.996 for dosages of 0.25, 0.50, 0.75 and 1.0 g/ml, respectively. The first order reaction rate constants, k , for the dosage experimental runs were 0.00238, 0.00344, 0.00387 and 0.00567 for dosages of 0.25, 0.50, 0.75 and 1.0 g/ml, shown in Figure 2.9 and Table 2.5. The relationship between the obtained pseudo first order rate constants and the iron dosages is shown in Figure 2.10,

$$\hat{K} = 0.00412 \cdot C_{iron} + 0.00127 \quad (2.4)$$

with a coefficient of determination (R^2) of 0.9403. The predicted \hat{K} is the pseudo first order rate constant (h^{-1}), while C_{iron} is the iron filings dosage (g/ml). As mentioned earlier, the dosage was based on mass of iron filling per reaction volume. As the mass of the iron filling increased, the volume of the perchlorate solution in the reactor decreased. The ratio of iron filings mass to perchlorate solution volume will increase more dramatically than the increase of dosage. In order to verify this pseudo first order reduction reaction, a flow column study was performed. The following chapter has the details about the column study.

Reference

Dionex Corp. (2000) Determination of Low Concentrations of Perchlorate in Drinking and Groundwaters Using Ion Chromatography. Dionex Corp., Application Note 134; Sunnyvale, CA.

Gu, B., Dong, W., Brown, G. M. and Cole, D. R. (2003) Complete Degradation of Perchlorate in Ferric Chloride and Hydrochloric Acid under Controlled Temperature and Pressure, *Environmental Science and Technology* **37**(10), 2291-2295.

Huang, H. and Sorial, G.A. (2006) Perchlorate Remediation in Aquatic Systems by Zero Valent Iron. *Environmental Engineering Science* **24**: 917-926.

Huang, H. (2005) Reduction Of Perchlorate By Zero Valent Iron, MS thesis, Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH.

Komsta, L. (2006) Processing data for outliers. R News, 6(2), 10-13.

Moore, A.M., De Leon, C.H. and Young, T.M. (2003) Rate and Extent of Aqueous Perchlorate Removal by Iron Surfaces. Environmental Science and Technology **37**: 3189-3198.

Snedecor, G.W. and Cochran, W.G. (1980) Statistical Methods (seventh edition). Iowa State University Press, Ames, Iowa.

Xiong, Z., Zhao, D. and Pan, G. (2007) Rapid and Complete Destruction of Perchlorate in Water and Ion-Exchange Brine Using Stabilized Zero-Valent Iron Nanoparticles. Water Research **41**:3497 – 3505.

Table 2.1 Batch study sampling schedule.

Sample Type	Sampling Time (h)
Iron Filings with No UV Light, 1.0 g/ml Iron Filling Dosage	
Iron Filings with UV Light, 1.0 g/ml Iron Filling Dosage	
Iron Filings with Pd ++ and No UV Light, (0.25, 0.50, 0.75, 1.0 g/ml)	0, 6, 24, 48, 96, 192, 384
Iron Filings with Pd with UV light,(0.25, 0.50, 0.75, 1.0 g/ml)	

Table 2.2 Calibration data for perchlorate for the batch study.

(A) Concentration (ppb)	(B) IC Area Count (μ s)	(C) Average Area Count	(B \div A) Response Factor	(C \div A) Average Response Factor	Coefficient of Variation ¹ %
62.5	98,161	96,439	0.00064	0.00065	8.9
62.5	94,716		0.00066		
100	136,596	144,813	0.00073	0.00069	16.0
100	153,029		0.00065		
250	422,878	416,108	0.00059	0.00060	0.9
250	409,337		0.00061		
500	899,452	895,441	0.00056	0.00056	6.2
500	891,429		0.00056		
750	1,359,422	1,353,673	0.00055	0.00055	6.9
750	1,347,924		0.00056		
1000	1,925,019	1,922,973	0.00052	0.00052	0.2
1000	1,920,926		0.00052		
Overall Average Response Factor =				0.00060	

¹ Absolute value of percent deviance of level average response factor from overall average

Table 2.3 Batch study data: percent of initial perchlorate remaining.

Time (h)	Treatment Combination ^{1,2}			
	Fe	Fe+UV	Fe+Pd	Fe+Pd+UV
0	Initial perchlorate concentration = 1028ppb			
6	81	85	75	47
24	75	101	100	83
49	77	72	84	77
96	77	65	83	60
192	74	46	73	45
384	48	17	43	12

¹ Fe=zero valent iron (1 mg/ml), UV=ultraviolet light,
Pd=palladium nitrate (0.75g/500ml).

² Average of 2 results.

Table 2.4 Iron dosage study data: percent of initial perchlorate remaining.

Time (h)	Iron dosage (g/ml) ¹			
	0.25	0.50	0.75	1.00
0	Initial perchlorate concentration = 941ppb			
6	98	100	96	97
24	105	95	85	89
49	91	88	76	77
96	72	69	60	58
192	69	51	45	39
384	39	27	25	11

¹ Average of 2 results.

Table 2.5 Kinetic reaction rate constant (K) for perchlorate reduction by Fe⁰ in the presence of Pd & UV light.

Fe ⁰ dosage (g/mL)	Kinetic rate constant (K)
0.25	0.00238
0.50	0.00344
0.75	0.00387
1.00	0.00567



Figure 2.1 HF washed iron filing drying set up.



Figure 2.2 Image of iron filings before and after HF washing.

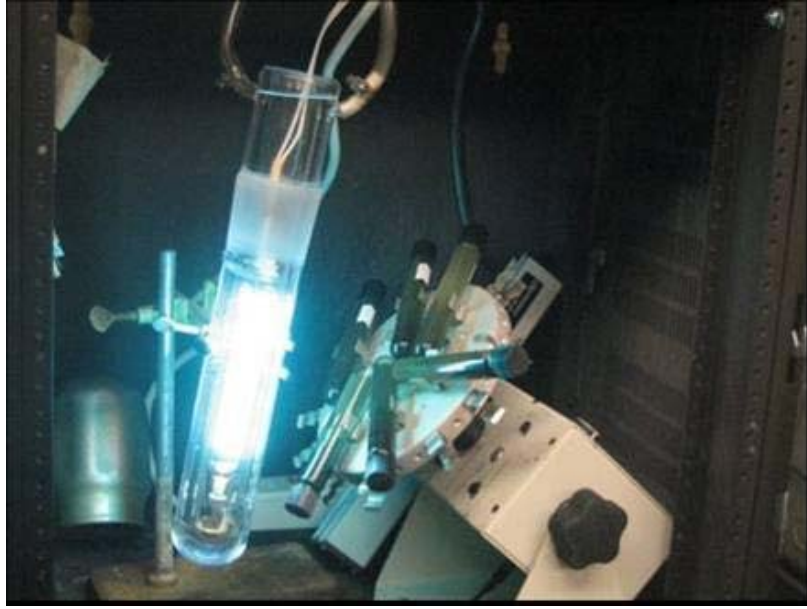


Figure 2.3 Experimental set up for perchlorate reduction using zero valent iron with UV light.



Figure 2.4 Experimental set up for perchlorate reduction using zero valent iron without UV light.

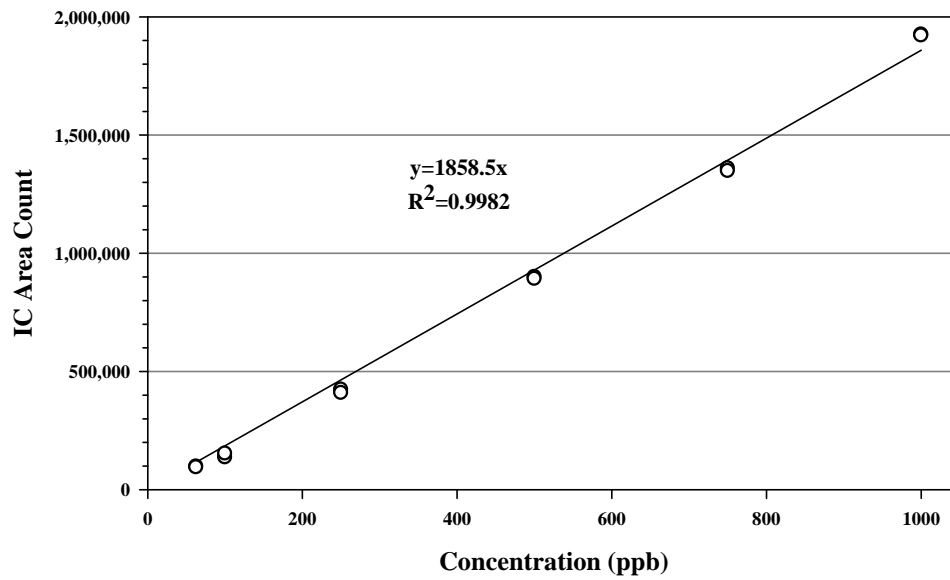


Figure 2.5 Calibration curve for perchlorate reduction in the batch study.

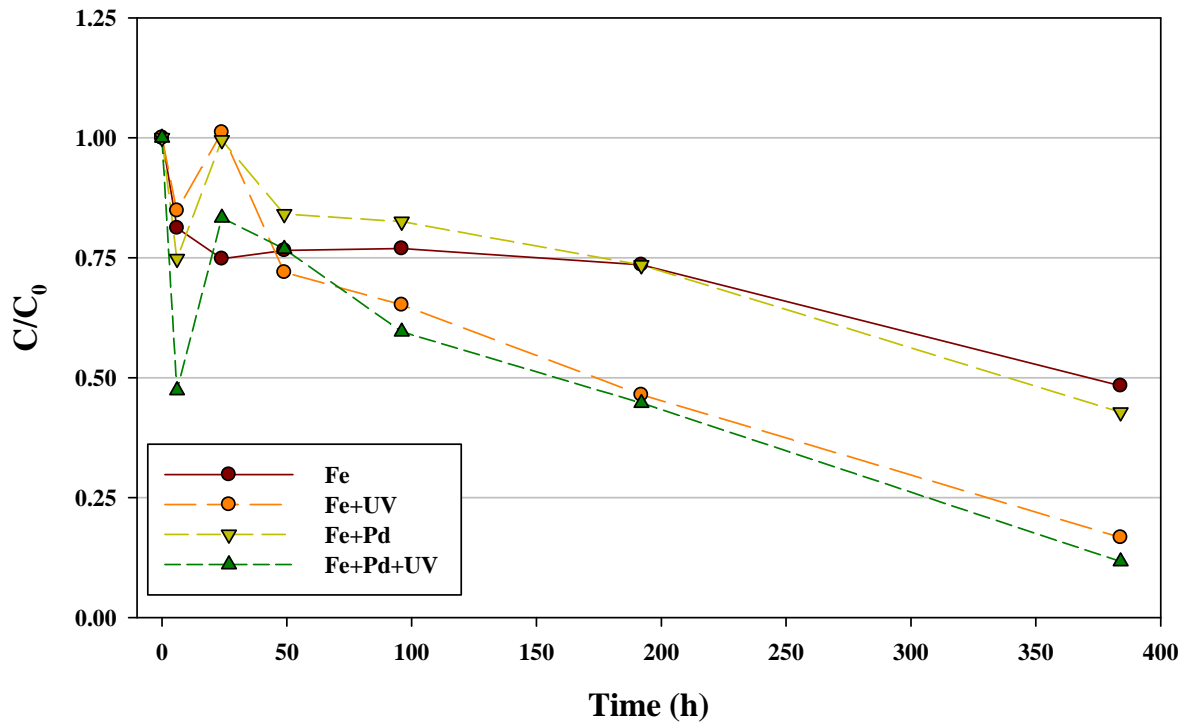


Figure 2.6 Reduction of perchlorate under different conditions.
 [C: Concentration of perchlorate at time t; C₀=initial concentration of perchlorate]

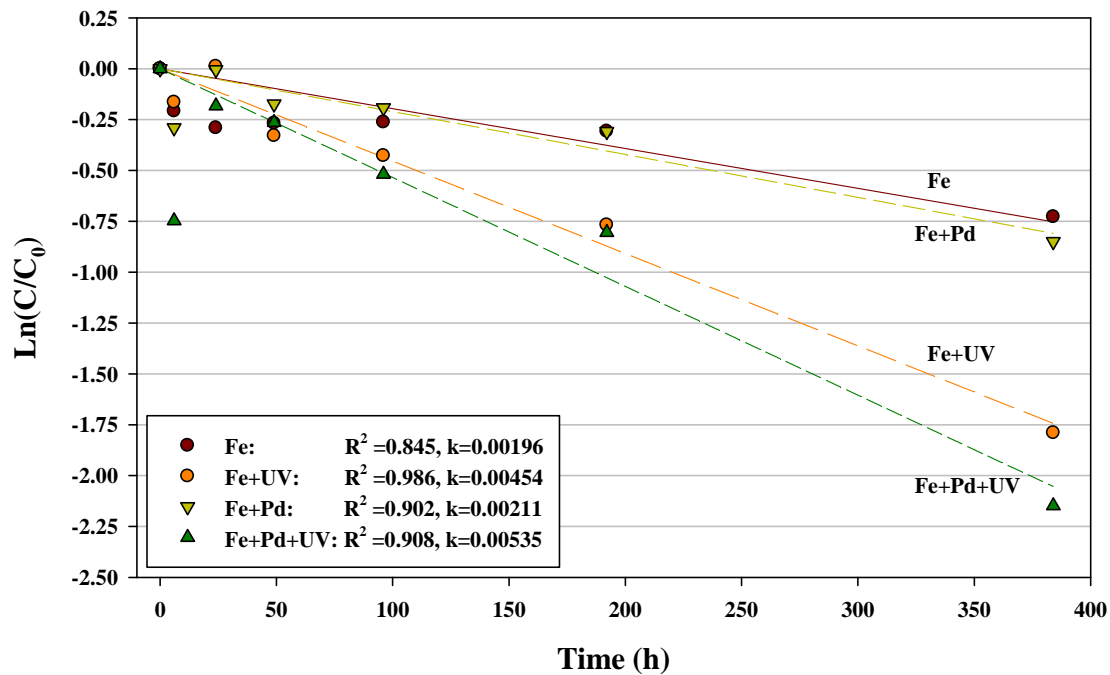


Figure 2.7 Pseudo first order kinetics for perchlorate under different conditions.

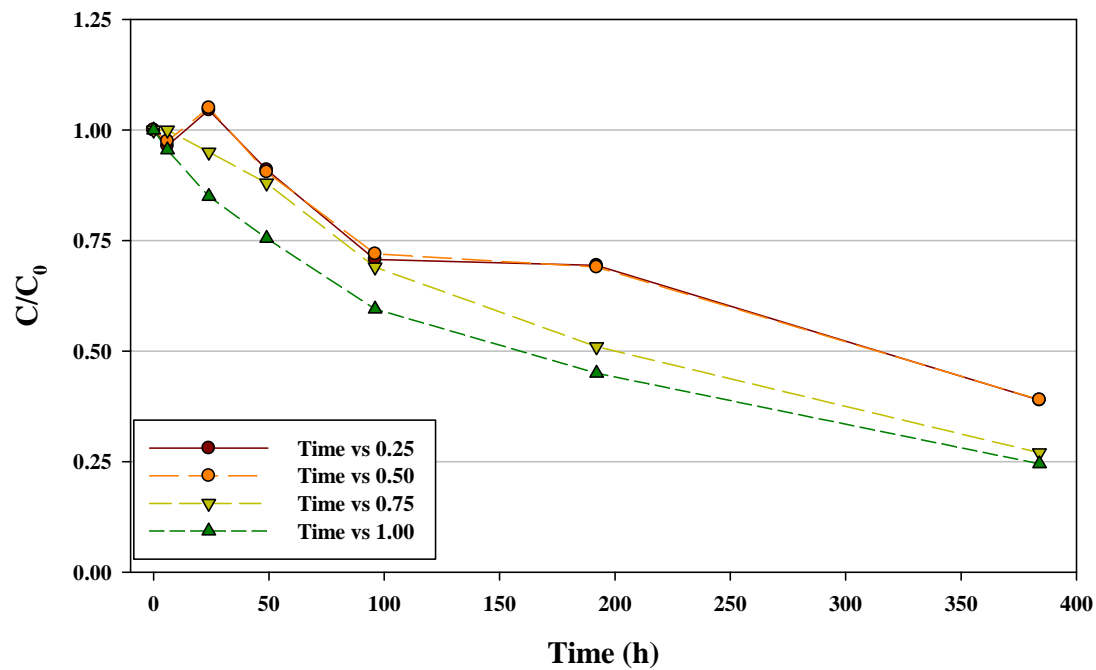


Figure 2.8 Reduction of perchlorate in the presence of palladium and UV light under different iron dosages.

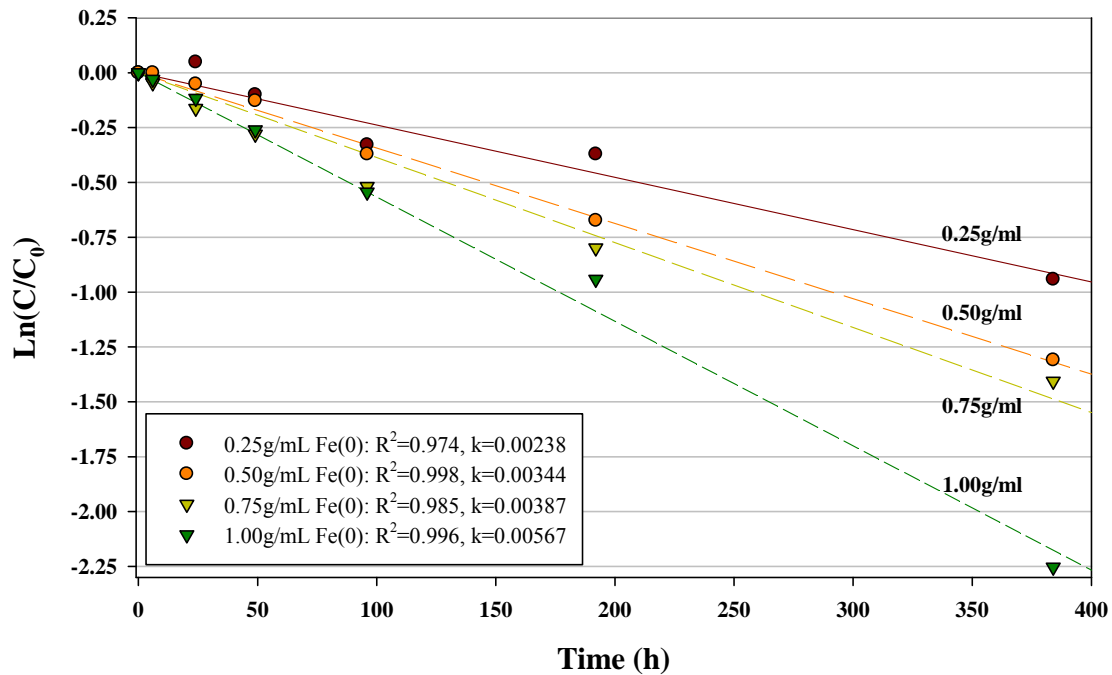


Figure 2.9 Pseudo first order kinetics for perchlorate under different iron dosages.

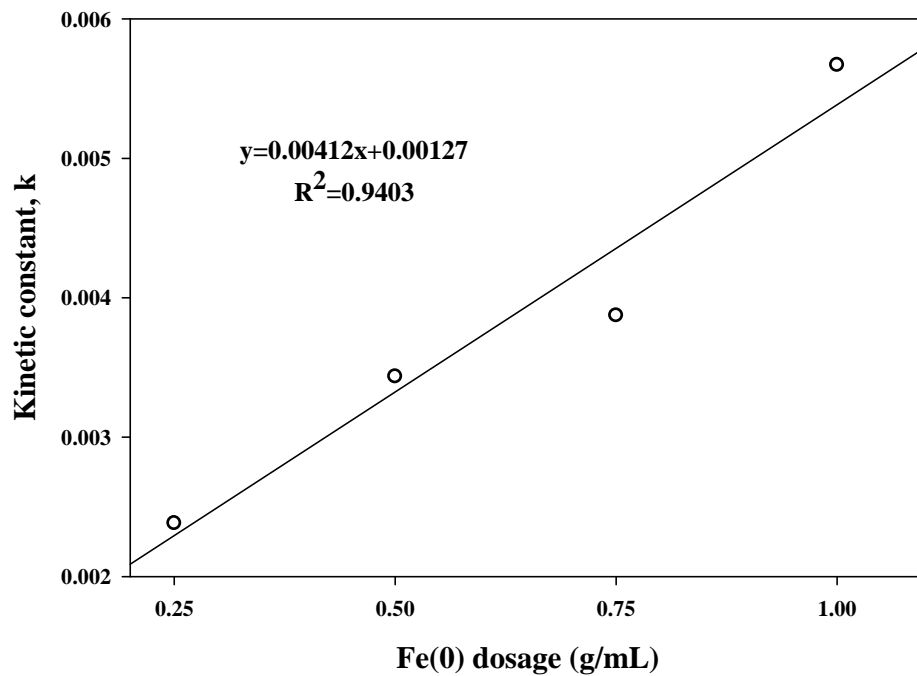


Figure 2.10 Correlation of first order reaction rate constant against iron dosage.

3 Recycle Column Study

3.1 Introduction

In the previous chapter, batch experiments were performed to determine the reaction kinetics for different iron filling dosage, which can be used in predicting the performance behavior in flow reaction from a known value of Fe^0 in the column experiment. Therefore, a column flow through experiment was conducted to verify the kinetic result of the mathematical correlation established from the batch study. Another major reason of performing the column study was to test the reproducibility of the perchlorate reduction from a small scale (batch) to a large one. The perchlorate reduction by Fe^0 in column flow was conducted under the presence of Palladium salt and UV light.

The recycle column experimental setup that was used for reduction of perchlorate ions by iron filings enhanced with UV light and palladium(II) nitrate is pictured in Figure 3.1. A schematic diagram of the setup is shown in Figure 3.2. The feed container for perchlorate was a sealed 2L glass container, which was kept under a head pressure of nitrogen gas to keep the system in an O_2 free condition. A multi-channel variable speed digital pump was used to deliver the perchlorate solution to the top of the column at a specified rate. The column was made of Plexi-Glass, was filled with the required amount of acid washed iron filings. The pump was connected to the feed tank and the column by PVC solvent resistant tubing. The UV bulb was installed inside of a glass column tube, which allows the UV bulb to be at the center of the glass tube as well as parallel to the iron

filing column. The column was connected to a cooler system as shown in Figure 3.2 in order to maintain constant temperature conditions.

3.2 Experimental Procedure

A 1000 mg/L ClO_4^- stock solution was prepared by dissolving 1.412g of sodium perchlorate monohydrate into 1L Milli-Q water. This stock solution was diluted 1000 times to achieve the 1 mg/L of perchlorate feed solution using Milli-Q water. 500 ml of this solution was placed into a 2L Plexi-Glass bottle (feed bottle). In order to completely pack the column, a 200 g of acid washed iron filings were used, which occupied the whole length of the column. The iron filings dosage was 0.4g/ml.

The feed solution was thoroughly purged with nitrogen gas to remove the oxygen in the solution before transferring it to the feed container during the experiment. The feed container for perchlorate was immediately brought under a head pressure of nitrogen to keep the system under anoxic conditions. The glass bottle has two inlet ports connected to the column. One is used for influent feed to the column and the other for receiving the effluent flow from the column. To start the flow into the column, the feed solution was pumped into the top of the column until there was a constant effluent flow. The flow rate was calibrated at 1.0 ml/minute prior to the experiment. Samples were collected using 25ml disposable plastic syringe from both inlet and outlet sample ports shown in Figure 3.2. The sampling time and sample filtration process were same as those in batch study. Samples were analyzed for the concentration of perchlorate ion by IC using the same method used previously in the batch study.

3.3 Experimental Results

A new 7-point standard solution calibration curve covering the range 25 to 1000 µg/L was established due to the change of new suppressor in IC. A linear regression model of the response against concentration with zero origin was used for quantifying the analysis. Each standard was analyzed twice. The coefficients of variation for all levels were within 15% level (see Table 3.1). The calibration curve is shown in Figure 3.3. The regression coefficient of determination (R^2) is 0.9987 which is within a reasonable linearity range.

The results of the column study using 0.4g/ml zero valent iron with palladium and UV Light are shown in Table 3.2 and Figure 3.4 Reduction of perchlorate under 0.4 g/mL iron dosage in the presence of palladium & UV light in the column study. After 170 h of reduction time, the average perchlorate reduction was 49.5%, based on samples collected from the influent and effluent in the column ports.

It is seen from Figure 3.4 that a steep decrease of perchlorate concentration occurred in the first 3 hours. This can be explained as a combination effect of both adsorption and reduction contributing to the initial decrease. A similar phenomenon occurred in the batch study during the first 6 hour under the same conditions.

The kinetic constant value, k , is calculated by using the following formula:

$$Rate = \frac{dC}{dt} = kC \quad (3.1)$$

Where k is the pseudo first order rate constant (h^{-1}), C = iron filings dosage (g/ml), t =time in hour.

The kinetic constant from the column study is calculated based on the average of the inlet and outlet port concentrations. Because these data are taken from a single recycle column, the results from one time to the next are serially correlated. This is evident in the cyclic appearance of the data points in Figure 3.4 and Figure 3.5. To correct for this, a two point linear interpolation technique has been used:

$$\ln(C_t/C^0) - \ln(C_{t-1}/C^0) = -k \cdot [t - (t-1)] \quad (3.2)$$

Additionally, the data at 3 h are not used because of the aforementioned early adsorption/reduction effect.

Based on the kinetic mathematical equation developed from batch study, the k value for the reduction reaction in column is expected to be 0.00292:

$$\hat{K} = 0.00412 \cdot C_{iron} + 0.00127 = 0.00412 \cdot 0.4 + 0.00127 = \mathbf{0.00292}$$

The k value calculated from Eq. 3.2 is 0.00318 with a range of 0.0014 to 0.0061 at the 95% confidence level, consistent with the predicted value.

3.4 Possible Reduction Mechanism: Discussion

Recent studies have shown that UV light has been used in reductive dehalogenation of chlorinated compounds such as 1,1,2-Trichlorotrifluoroethane and Trichloromethane (CFC11) (Calhoun et al., 2001; Winkelmann et al., 2006). Reduction proceeds via a radical chain mechanism on oxide surface of catalyst (Weaver and Mills, 1997). Huang (2005) has studied the perchlorate reduction by Fe⁰ and other metals and concluded that the reaction on iron surface was not a simple redox reaction. As shown in equation 5, the iron first is oxidized at the surface and forms an oxide film. This oxide film acts as an important catalyst in the reduction reaction by providing a reductive

pathway. Although the exact mechanism of the pathway is still not very clear and needs to be studied more, Scherer et al. (1998) have suggested three possible pathways, shown in Figure 3.6. The third pathway is the author's favorite pathway which suggested perchlorate reduction reactions by Fe^0 undergoes: First, the amount of Fe(II) species at the surface affects the reduction kinetics; second, the water causes iron rust in the presence of the dissolved oxygen. Fe(II) existed in absence of O_2 . A red-brown of Fe(III) in form of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ rust formed when the O_2 is sufficient, a mixture of Fe(II) and Fe(III), with a black color (Greenwood and Earnshaw, 1997), FeO and Fe_3O_4 , will be formed when O_2 is limited. In this study, the iron filling become black in color after HF acid wash and dried under the nitrogen gas. This means that FeO or Fe_3O_4 existed on the acid washed iron filings. The surface of iron filling without acid wash is having a brownish color with Fe_3O_4 only. The iron filings after acid wash showed a much faster reduction than that without acid washed which indicates the importance of the presence of Fe(II) oxide (Huang, 2005). This is the reason that HF acid washed iron filings were used in this study.

As mentioned earlier, the main barrier of the perchlorate reduction is symmetric arrangement of atoms in its ClO_4^- tetrahedral structure which block the chlorine being the attached by electron. As shown in the Figure 3.7, there is a potential association between Fe atom on the oxide film and oxygen atom because the complexes of the iron in the aquatic system can perform the electron and oxygen transfer between iron filings and perchlorate as shown in Figure 3.7. This potential association causes ClO_4^- molecule structure to be deformed which increases its oxidation ability by exposing chlorine atom to two electron donors. Also, a concentrated solution of perchloric acid exists in the water as molecular HClO_4 instead of H^+ ion and ClO_4^- ion (Huang, 2005). Therefore, the deformed and concentrated perchloric acid becomes a very strong oxidant due to a high polarity.

This hypothesis can be illustrated by Figure 3.7 (Huang, 2005). Step 2 shows the three oxygen atoms being attracted by the positive charged iron atom and stretched toward to iron atom. When the chlorine being attached by two electrons, the oxygen atom in perchlorate become totally dissociated from chlorine and associated with Fe atom in the oxide film. Further reductions occur in a similar way till finally Cl^- is released.

3.5 Conclusion

Perchlorate reduction by zero valent iron was evaluated in this study. The perchlorate reduction reaction under the different conditions with and without UV light, with and without Palladium was investigated. The UV light plays an important role on the perchlorate reduction and promotes perchlorate reduction on zero valent iron. It increases the rate of reduction reaction dramatically. The UV light was used as a catalyst since perchlorate is known to absorb UV in the wavelength range shorter than 185 nm (Gurol and Kim, 2000). The results also revealed that a slight increase of the reaction rate can be achieved by adding palladium salt. The kinetics of the reduction reactions at four different dosages were determined as well. A pseudo first order reaction correlated well the reduction kinetics for acid treated by iron filings with UV light. A linear correlation was developed based on the four different iron dosages which can be used in predicting the behavior of a reduction reaction.

A flow column experiment with zero valent iron under UV light and palladium nitrate catalyst was conducted to verify the kinetic behavior of the perchlorate reduction reaction in the flow-through column. The experiment results revealed that the performance of the column experiments was

predicted accurately by assuming a pseudo first order reaction kinetic using the equation developed from the batch studies.

Adsorption of perchlorate by iron filings were observed from both batch study and column experiments on the iron filling surface. The perchlorate reduction by zero valent iron is not a simple step of electron transfer from iron to perchlorate. It is stipulates that UV light excited the oxide film on the iron surface and provided energy to the reduction reaction. The oxide film at iron filings surface might form certain complex with perchlorate to facilitate the oxygen transfer from perchlorate ion for destructing the tetrahedron structure of perchlorate iron (Huang, 2005).

Reference

Calhoun, R. L., Winkelmann, K. and Mills, G. (2001) Chain Photoreduction of CCl_3F Induced by TiO_2 Particles. *J. Phys. Chem.* **101**: 9737-9246.

Greenwood, N.N. and Earnshaw, A. (1997) *Chemistry of the Elements*. Butterworth-Heinemann. Oxford; Boston.

Gurol, M. G. and Kim, K. (2000) Investigation of Perchlorate Removal in Drinking Water Sources by Chemical Methods, in: Urbansky, E. T. (ed.) *Perchlorate in the Environment*. Kluwer/Plenum Academic, New York, NY, pp. 99-107.

Huang, H. (2005) *Perchlorate Remediation By Zero Valent Iron*. MS Thesis, University of Cincinnati, Cincinnati, OH.

Scherer, M.M., Balko, B.A. and Tratnyek, P.G. (1998) The Role of Oxides in Reduction Reactions at the Metal-Water Interface. pp.301-322. in: Sparks, D. and Grundl, T.J. (eds.), *Kinetics and Mechanisms of Reactions at the Mineral-Water Interface*. American Chemical Society, Washington, DC

Weaver, S. and Mills, G. (1997) Photoreduction of 1,1,2-Trichlorotrifluoroethane Initiated by TiO_2 Particles. *J.Phys. Chem.* **101**: 3769-3775.

Winkelmann, K., Calhoun, R.L. and Mills, G. (2006) Chain Photoreduction of CCl_3F in TiO_2 Suspensions: Enhancement Induced by O_2 . *J. Phys. Chem.* **101**:13827-13835.

Table 3.1 Calibration data for perchlorate for the column study.

(A) Concentration (ppb)	(B) IC Area Count (μ s)	(C) Average Area Count	(B \div A) Response Factor	(C \div A) Average Response Factor	Coefficient of Variation ¹ %
10			spilled		
10			spilled		
25	43,123	44,290	0.00058	0.00056	6.6
25	45,456		0.00055		
50	100,848	100,848	0.00050	0.00050	6.4
50			spilled		
100	174,625	169,610	0.00057	0.00059	11.3
100	164,594		0.00061		
250	448,966	447,376	0.00056	0.00056	5.5
250	445,786		0.00056		
500	954,480	954,067	0.00052	0.00052	1.0
500	953,654		0.00052		
750	1,531,471	1,530,421	0.00049	0.00049	7.5
750	1,529,370		0.00049		
1000	2,068,352	2,066,015	0.00048	0.00048	8.6
1000	2,063,677		0.00048		
Overall Average Response Factor =				0.00053	

¹ Absolute value of percent deviance of level average response factor from overall average

Table 3.2 Normalized perchlorate concentration with time for the column study.

Sample Time (h)	C/C^0 at outlet	C/C^0 at inlet
0	1	N/A
3	0.84	N/A
6	0.91	0.92
20	0.91	0.93
50	0.83	0.86
75	0.80	0.82
98	0.78	0.79
122	0.68	N/A
146	0.58	0.62
170	0.46	0.55



Figure 3.1 Experimental setup for packed column study.

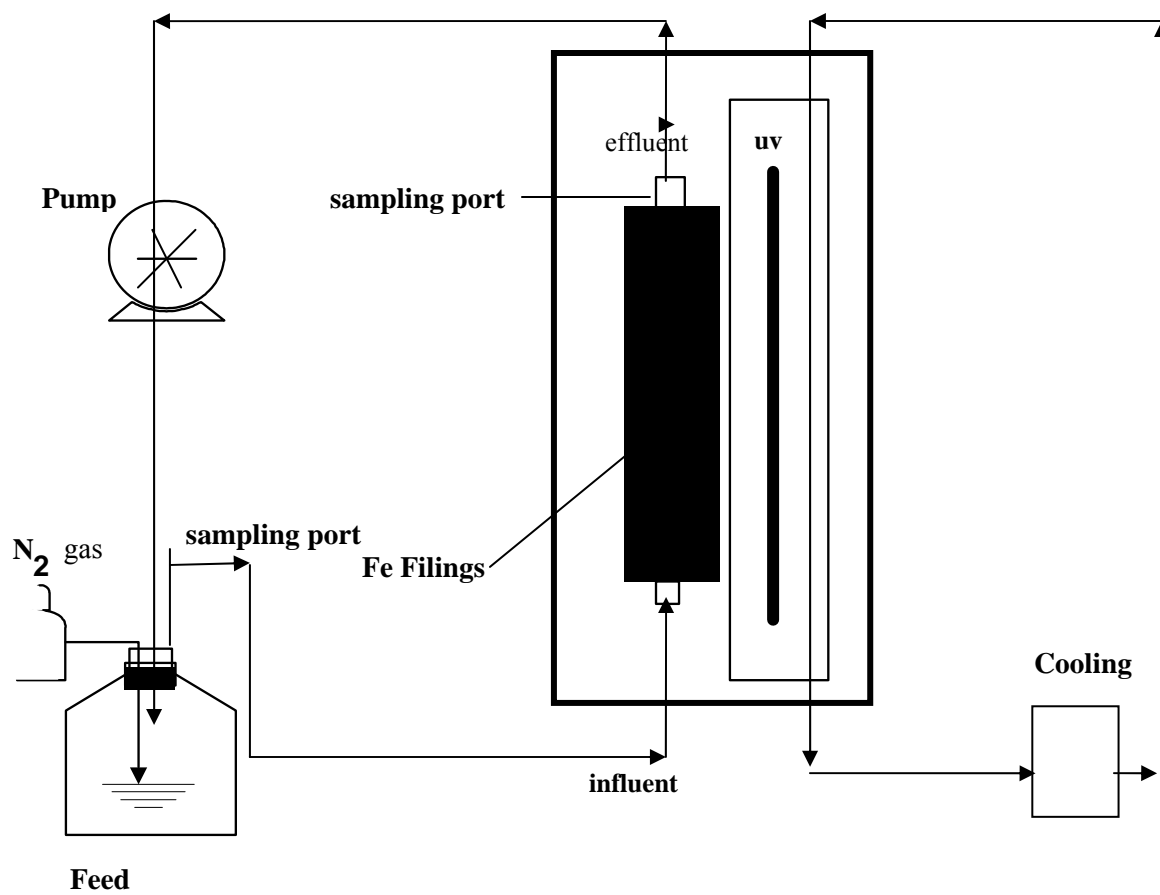


Figure 3.2 Schematic diagram of the experimental setup for packed column study.

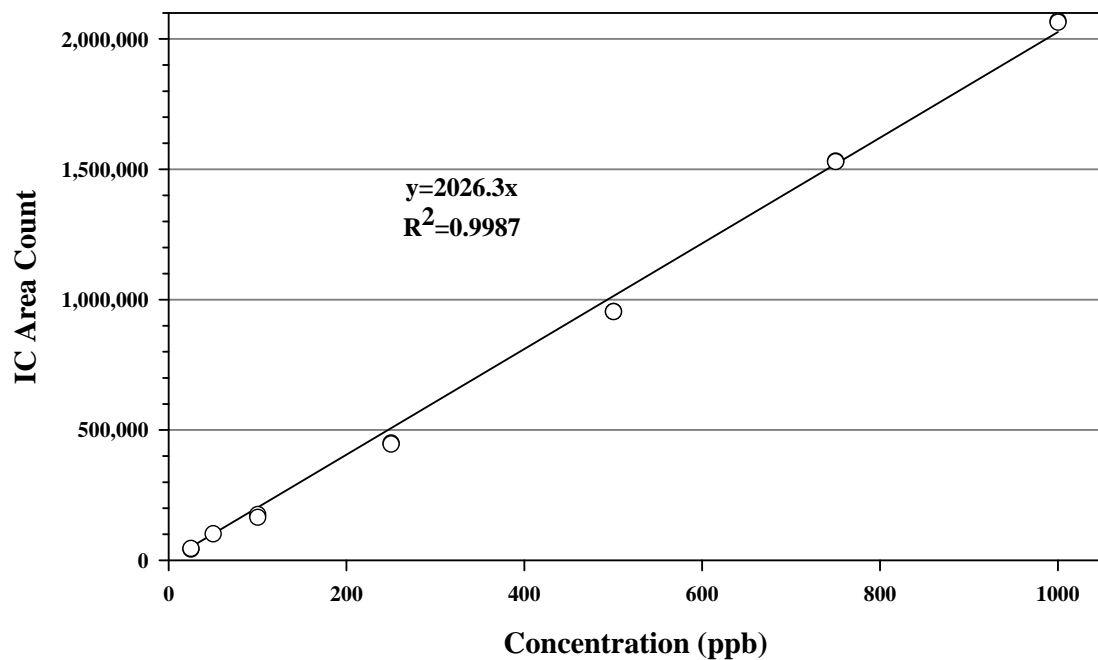


Figure 3.3 Calibration curve for the column study.

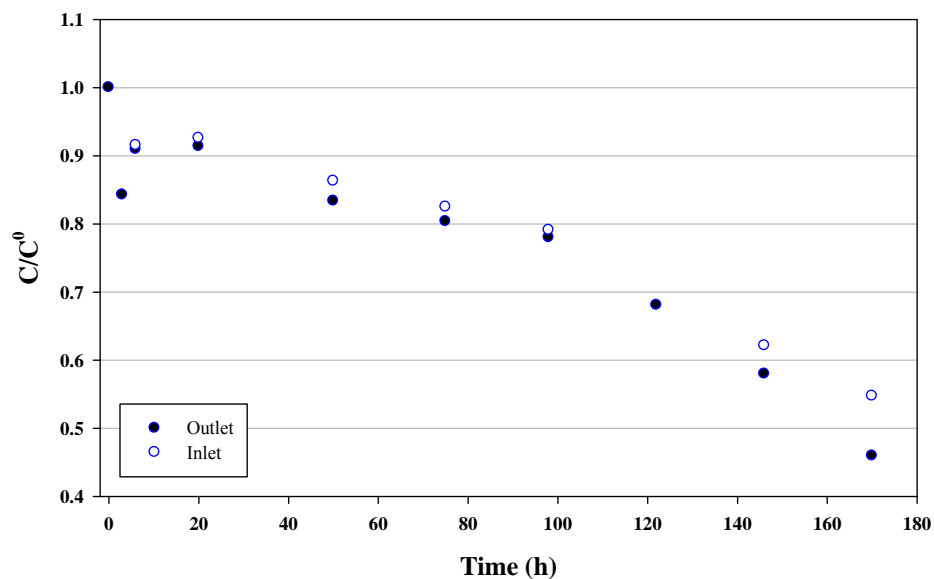


Figure 3.4 Reduction of perchlorate under 0.4 g/mL iron dosage in the presence of palladium & UV light in the column study.

[C =concentration of perchlorate at time t ; C^0 = initial concentration of perchlorate at time 0.]

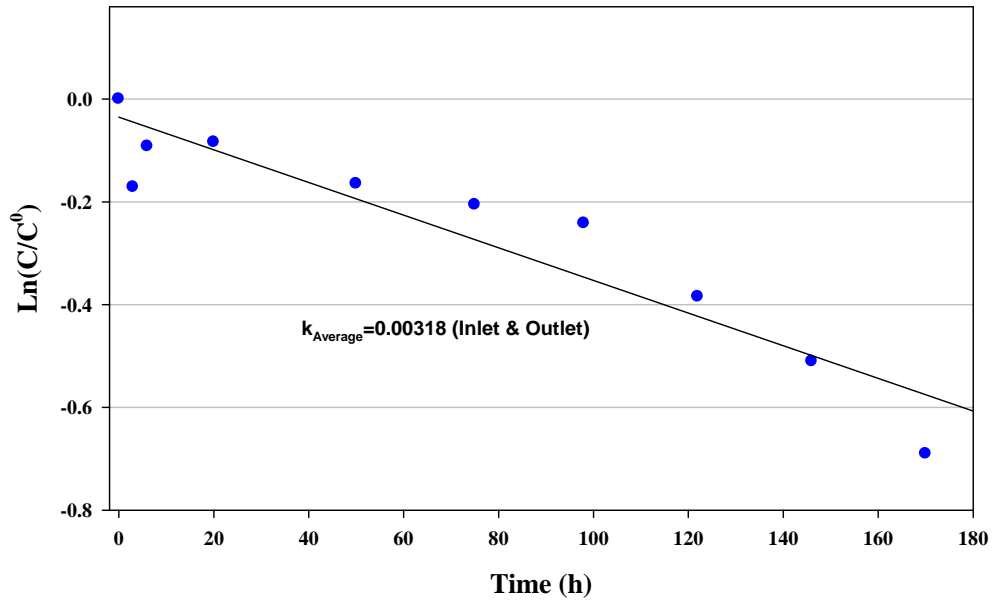


Figure 3.5 Average reduction of perchlorate and pseudo first order kinetics under 0.4 g/mL iron dosage in presence of palladium & UV light in the column study.

[C=Average concentration of perchlorate at time t; C⁰=Initial concentration of perchlorate at time 0.]

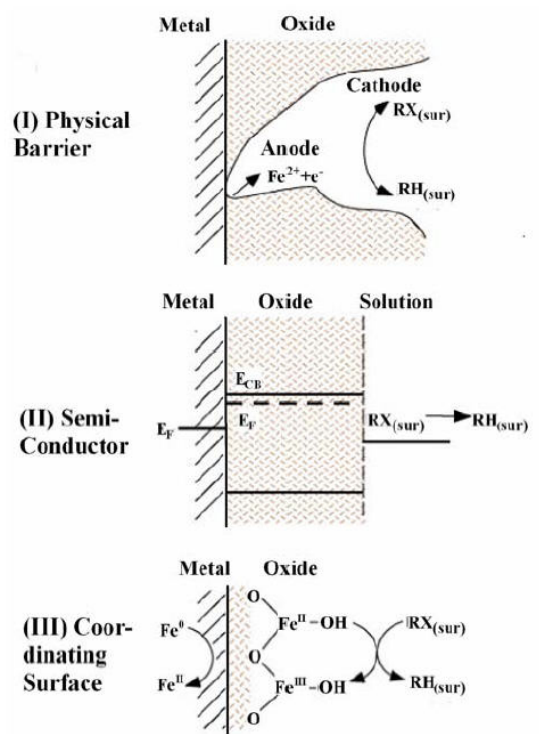


Figure 3.6 Concept models from reduction reaction on the oxide-water interface (Schere et al., 1988).

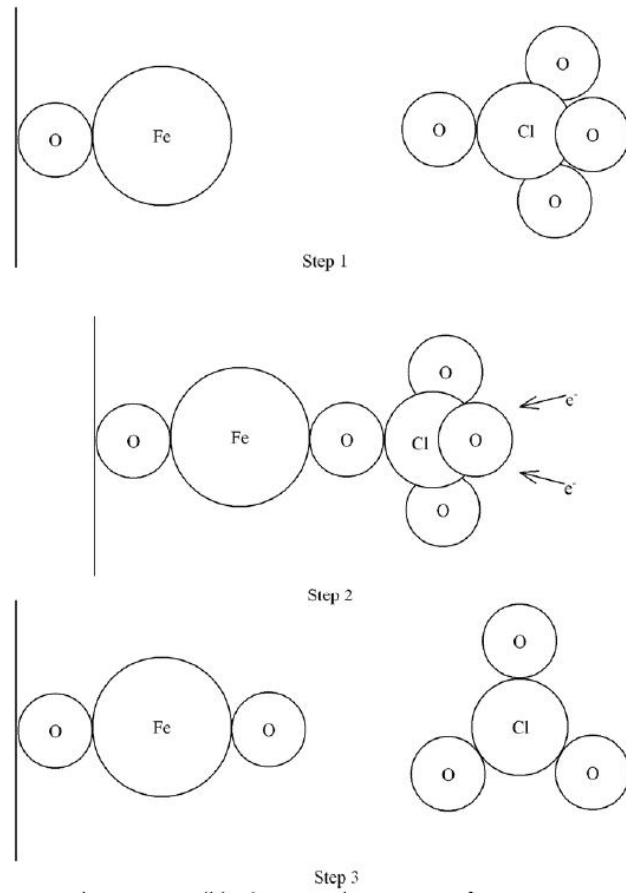


Figure 3.7 Possible electron and oxygen transfer process in the perchlorate reduction reaction (Huang, 2005).

4 Recommendation for future work

The experimental results from both the batch and column studies showed that the rate of perchlorate reduction were still slow to be used in drinking water treatment. The low reduction rate may be due to insufficient catalytic efficiency, insufficient reducing agent or/and insufficient UV light. It indicated that future research should focus on certain catalytic pathway to increase the reduction rate, such as using different intensity of UV light and/or using valent nano-iron particles to improve the catalyst's efficiency and to provide more electrons for the reduction reaction.

The highest iron dosage used in this study, 1.0 mg/L, resulted in the largest perchlorate reduction. An optimization study needs to be conducted to determine the optimum iron dosage that could result on high perchlorate removal.

The mechanism of perchlorate reduction on the iron surface and enhancement of UV light is not clearly understood. It is strongly suggested that some surface characterization studies such as transmission electronic microscopy, scan electronic microscopy and elemental analysis be conducted to investigate the difference between the treated and untreated iron as well as the enhancement by UV light.

Appendix I: Raw Data

Table A1. Raw data for Table 2.3 and Figure 2.6 and Figure 2.7

Time (h)	Experiment #1		Experiment #2	
	Area Count (μ s)	Concentration (ppb)	Area Count (μ s)	Concentration (ppb)
0	1,921,162	1,000		1,000
Fe(0), no UV, no Pd				
6	1,733,334	902	1,338,336	720
24	1,444,757	752	1,377,371	740
49	1,782,904	928	1,118,068	602
96	1,641,544	854	1,263,984	680
192	1,568,388	816	1,208,220	650
384	1,029,623	536	799,284	430
Fe(0) + UV, no Pd				
6	1,815,851	945	1,395,959	751
24	1,720,759	896	2,094,868	1127
49	1,540,793	802	1,184,056	637
96	1,395,850	727	1,072,528	577
192	995,055	518	762,108	410
384	320,992	167	sample spilled	-
Fe(0) + Pd, no UV				
6	1,601,062	833	1,230,526	662
24	2,129,358	1,108	1,639,462	882
49	1,799,884	937	1,384,806	745
96	1,766,068	919	1,358,783	731
192	1,572,798	819	1,208,220	650
384	912,771	475	706,344	380
Fe(0) + UV + Pd				
6	1,014,626	528	778,837	419
24	1,783,156	928	1,371,794	738
49	1,644,800	856	1,263,984	680
96	1,275,441	664	979,588	527
192	958,948	499	734,226	395
384	256,067	133	185,880	100

Table A2. Raw data for Table 2.4 and Figure 2.8 and Figure 2.9

Experiment #1			Experiment #2	
Time (h)	Area Count (μ s)	Concentration (ppb)	Area Count (μ s)	Concentration (ppb)
0	1,748,114	941		
0.25 g/mL Fe(0) + UV + Pd				
6	1,685,920	907	1,736,316	934
24	1,827,048	983	1,839,632	990
49	1,590,942	856	1,579,975	850
96	1,236,558	665	1,270,506	684
192	1,212,860	653	sample spilled	-
384	680,004	366	sample spilled	-
0.50 g/mL Fe(0) + UV + Pd				
6	1,736,573	934	1,771,619	953
24	<i>(Sample tubes cracked)</i>		1,667,402	897
49	1,499,410	807	1,578,340	849
96	1,248,997	672	1,173,787	632
192	894,076	481	sample spilled	-
384	344,293	185	336,056	181
0.75 g/mL Fe(0) + UV + Pd				
6	1,666,849	897	1,748,112	941
24	<i>(Sample tubes cracked)</i>		1,679,909	904
49	1,332,740	717	1,488,253	801
96	1,052,641	566	1,308,608	704
192	790,922	426	1,034,569	557
384	620,022	334	504,506	271
1.00 g/mL Fe(0) + UV + Pd				
6	1,669,114	898	1,738,452	935
24	<i>(Sample tubes cracked)</i>		1,549,857	834
49	1,353,964	729	1,349,362	726
96	1,001,018	539	1,023,702	551
192	675,305	363	675,385	363
384	355,596	191	19,892	11

Table A3. Raw data for Table 3.2 and Figure 3.4: recycle column perchlorate concentration with 0.40g/ml Fe(0) + UV + Pd

Time (h)	Area Count (μ s)		Concentration (ppb)	
	Outlet	Inlet	Outlet	Inlet
0	1,822,024	sample cracked	899	-
3	1,535,052	sample cracked	758	-
6	1,656,691	1,667,234	818	823
20	1,664,238	1,686,780	821	832
50	1,518,520	1,571,957	749	776
75	1,463,831	1,502,782	722	742
98	1,421,060	1,440,590	701	711
122	1,240,364	sample cracked	612	-
146	1,056,048	1,132,132	521	559
170	837,119	997,095	413	492

Table A4. Data for Figure 3.4: Recycle column perchlorate kinetics with 0.40g/mL Fe(0) + UV + Pd

Time (h)	C/C^0		$\ln(C/C^0)$	
	Outlet	Inlet	Outlet	Inlet
0	1	sample cracked	-	-
3	0.84	sample cracked	-0.171	-
6	0.91	0.92	-0.095	-0.089
20	0.91	0.93	-0.091	-0.077
50	0.83	0.86	-0.182	-0.148
75	0.80	0.82	-0.219	-0.193
98	0.78	0.79	-0.249	-0.235
122	0.68	sample cracked	-0.385	-
146	0.58	0.62	-0.545	-0.476
170	0.46	0.55	-0.778	-0.603

Table A5. MDL Calculation Data at 10 ppb Injections

Area Count, s	Calculated Concentration, ppb
13989	7.526
14392	7.742
14365	7.728
14418	7.757
10688	5.750
13299	7.155
12645	6.803
13858	7.455
16868	9.075
Standard Deviation	0.837
Student Value, t	2.821
MDL	2.360

QUALITY ASSURANCE PROJECT PLAN

**REMOVAL OF PERCHLORATE FROM CONTAMINATED WATERS USING UV
LIGHT AND METAL NANO-CATALYST**

U.S. EPA NRMRL, STD
26 W. Martin Luther King Drive
Cincinnati, OH 45268

In_ house Research Program

Prepared by
Q. Amy Zhao and Endalkachew Sahle-Demessie

U.S. Environmental Protection Agency
Collaboration with Dr. Sorial George
University of Cincinnati
April 14TH, 2008

Quality Assurance Project Plan Distribution List

Q. Amy Zhao, Project Leader Participant
Daniel L. Young, Quality Assurance Officer, NRML, U.S. EPA
E. Sahle-Demessie, Principal Investigator, NRML, U.S. EPA
George Sorial, Co- Principal Investigator, University of Cincinnati

Table of Contents

Section	No. of Pages	Revision No.	Date
1.0 Project Description, Objectives, and Organization	1	1	02/15/08
2.0 Experimental Approach	4	1	02/15/08
3.0 Sampling Procedures	2	1	02/15/08
4.0 Testing and Measurement Protocols	1	0	03/15/08
5.0 Quality Assurance & Quality Control Checks	4	1	03/15/08
6.0 Data Reporting, Data Reduction, and Data Validation	1	0	06/15/08
7.0 References	3	1	02/15/08

List:

EPA method 314.0 for perchlorate analysis

SOP for IC Calibration

SOP for SAMPLE ANALYSIS

Calculation procedure for experimental samples

SECTION 1.0

PROJECT DESCRIPTION, OBJECTIVES, AND ORGANIZATION

This Experiment QAPP has been prepared for in-house research at the U.S. Environmental Protection Agency (EPA), National Risk Management Research Laboratory. This section describes the purpose of the study, project site, project objectives and organization.

1.1 PURPOSE OF STUDY

Because of its low concentrations and strong resistance to most treatment technologies, perchlorate has become one of the biggest challenges currently being faced by the drinking water industry. This project researches removal of perchlorate ions in drinking water by UV light reduction with zero-valent iron and other metal oxidant. The use of zero-valent iron is expected to lessen the perchlorate ion. In this study, only spiked reagent water will be used for the test. The effectiveness of this technology will serve as a basis to further develop the proposed method to purify surface or groundwater in target zones at a larger scale.

1.2 BACKGROUND

Recognized as an endocrine disruptor chemical recently, perchlorate is a potential human health hazard in drinking water that may inhibit normal iodide uptake by thyroid glands to cause mental retardation and hearing and speech degradation (Clark 2000). Perchlorate is listed by the U.S.EPA in the drinking water contaminant candidate list (Perciasepe 1998). Therefore, the maximum contamination level and maximum contamination level goal are still not available now. Nevertheless, several states have already set up their action levels against perchlorate contamination in their drinking water supply. California lowered its action level from 18 to 4 $\mu\text{g L}^{-1}$ in 2004. Similarly, Arizona adopted an action level of 32 $\mu\text{g L}^{-1}$, while Texas adopted a level of 22 $\mu\text{g L}^{-1}$ (Motzer 2001).

A major source of perchlorate contamination is the manufacture of ammonium perchlorate used as an oxidizer and primary ingredient in solid propellant for rockets, missiles, and fireworks. Before 1997, perchlorate was carried out into sewage or natural waters without any treatment. In fact, eleven U.S. States have been reported to have such discharging sites (Urbansky & Schock 1999). Because of the mobility of perchlorate, California public water suppliers detected 33 out of the 110 examined wells had perchlorate concentration greater than 18 $\mu\text{g L}^{-1}$, with the highest concentration at 280 $\mu\text{g L}^{-1}$ (Motzer 2001).

The standard redox potential of perchlorate is +1.38 V (Espenson 2000), which makes it a strong oxidizing agent; however, because of its high activation energy of 120 kJ mol^{-1} (Gu et al. 2003) its oxidizing power is retarded. The high activation energy is mainly caused by the tetrahedron structure of perchlorate in which chlorine is surrounded by four oxygen atoms. Therefore, the attack from common reductants is blocked and this makes treating perchlorate contamination in water complicated.

Currently, perchlorate treatment technologies are classified into two categories, destruction

technologies, or removal technologies. The destructive processes can be divided further into two subcategories: biological and chemical treatments. (Urbansky & Schock 1999). The nondestructive removal or physical processes mainly focus on ion exchange resins. Physical removal processes are suitable for perchlorate removal in small-scale water treatment plants. However, such processes have some disadvantages, such as lack of selectivity and the concentrated residue that needs further treatment. As a result, destructive processes that reduce perchlorate to harmless chloride are preferable.

The pathway of perchlorate decrease has been studied by many researchers (Almeida et al. 1997; Gu et al. 2003; Lang & Horanyi 2003) and they all agree that perchlorate will lose an oxygen atom to form chlorates at the first in the reduction process; further reduction kinetics to the chloride ion is fast. Perchlorate reduction by biological processes under anaerobic conditions has been widely studied for many years (Wallace et al. 1998, Kim & Logan 2001, Gingras & Batista 2002, Okeke et al. 2002). It is postulated that special enzymes in the microorganisms' cells serve as catalysts during the degradation of perchlorate, which effectively decrease the activation energy of perchlorate decline. Because of the effectiveness of biological processes, the U.S. Army and Air Force have already installed perchlorate treatment at several military manufacturing factories (Wallace et al. 1998).

However, for drinking water treatment and groundwater remediation, biological treatment has its own limits because of the presence of unknown pathogens and requiring nutrient addition. An effective chemical reduction that is favorable for drinking water treatment and groundwater remediation is, therefore, necessary. Many common reducing reagents like a ferrous ion (Moore et al. 2003) and hydrogen gases (Lang & Horanyi 2003) have been tested without observable perchlorate reduction. The key is to find a way that can overcome the energy barrier. The answer may be found at the mineral surface. In the 1980s, experimental evidence has shown that aqueous mineral surfaces provide added accelerated pathways for redox, such as the oxygenation of metal ions and the oxidation of organic pollutants (Wehrli 1990). The reaction at the aquatic mineral boundary is a hot topic because the reaction is so complicated the mechanism is not well understood until now, although it has already been applied in the field and in the laboratory, especially with the use of zero valent iron. For example, zero valent iron has been studied for its capacity to reduce chlorohydrocarbons (Su & Puls 1999, Szecsody et al. 2004). The most common application of zero valent iron is in packing iron filings as a permeable reactive barrier. Some studies have been conducted on the removal of perchlorate on the iron surface. Lang and Horanyi reviewed converting perchlorate at different metal surfaces. Iron was found to have the fastest reaction rate (Lang & Horanyi 2003). Gurol and Kim, and Moore and coworkers discovered removal of perchlorate in water by cast iron filings, respectively (Gurol & Kim 2000, Moore et al. 2003). Moore and coworkers tried to confirm the reduction effect of iron filings by chlorine mass balance. However, the chloride impurity in cast iron made it complicated (Moore et al. 2003). In addition, one interesting point found by Moore and coworkers is that commercially available pure iron had not effect on removal perchlorate.

1.3 PROCESS, SITE, FACILITY, AND APPARATUS

The work will be conducted at the Containment Facility Building of the Clean Process Branch,

Sustainable Technology Division, US. Environmental Protection Agency. The laboratories are equipped for bench scale experiments, fume hoods, dedicated bench space, steam, air, cold and hot water supply. Further, the project team has access to the various glassware and analytical equipment that are used in the various experimental runs in this project. The various needed glassware and analytical equipment are listed below:

1.3.1 Materials

Milli-Q water: Milli-Q water produced by a Millipore system (Billerica, MA, USA) with 17.5 M Ω -cm resistance will be used for preparation of solutions.

Iron Filings: Iron filings (Fisher Scientific, Hanover PK, IL), screened to retain particles 40 mesh will be used.

Hydrofluoric acid: Hydrofluoric (HF) acid, bought from Fisher Scientific will be used for acid washing of the iron filings. The acid wash of iron filling will be done at UC laboratories.

Sodium Perchlorate: HPLC grade sodium perchlorate monohydrate (Fisher Scientific, Hanover PK, IL) will be used for preparing perchlorate stock solutions.

Palladium Nitrate: HPLC grade Palladium Chloride monohydrate (Fisher Scientific, Hanover PK, IL) will be used for preparing Palladium Nitrate stock solutions.

Syringes: 25 ml sterilized disposable plastic syringes bought from Fisher Scientific, Hanover PK, IL will be used.

Pretreatment Cartridges: 2.5 cc OnGuard II Ba/Ag/H cartridges (Dionex, Sunnyvale, CA) will be used to remove any dissolved iron species from the sample before analysis by IC.

1.3.2 Analytical Instruments

Ion Chromatograph (IC): Perchlorate concentration will be measured with an auto injection Dionex (Sunnyvale, CA, USA) ion chromatography system with an IP25 Iso-pump, an anion self-regenerate suppressor ultra (ASRS-ultra), an ED40 conductivity detector and an LC-20 chromatography enclosure.

pH: meter bought from Fisher Scientific will be used for pH .

Analytical balance: calibrated per standard laboratory procedures.

1.3.3 Experimental Setup

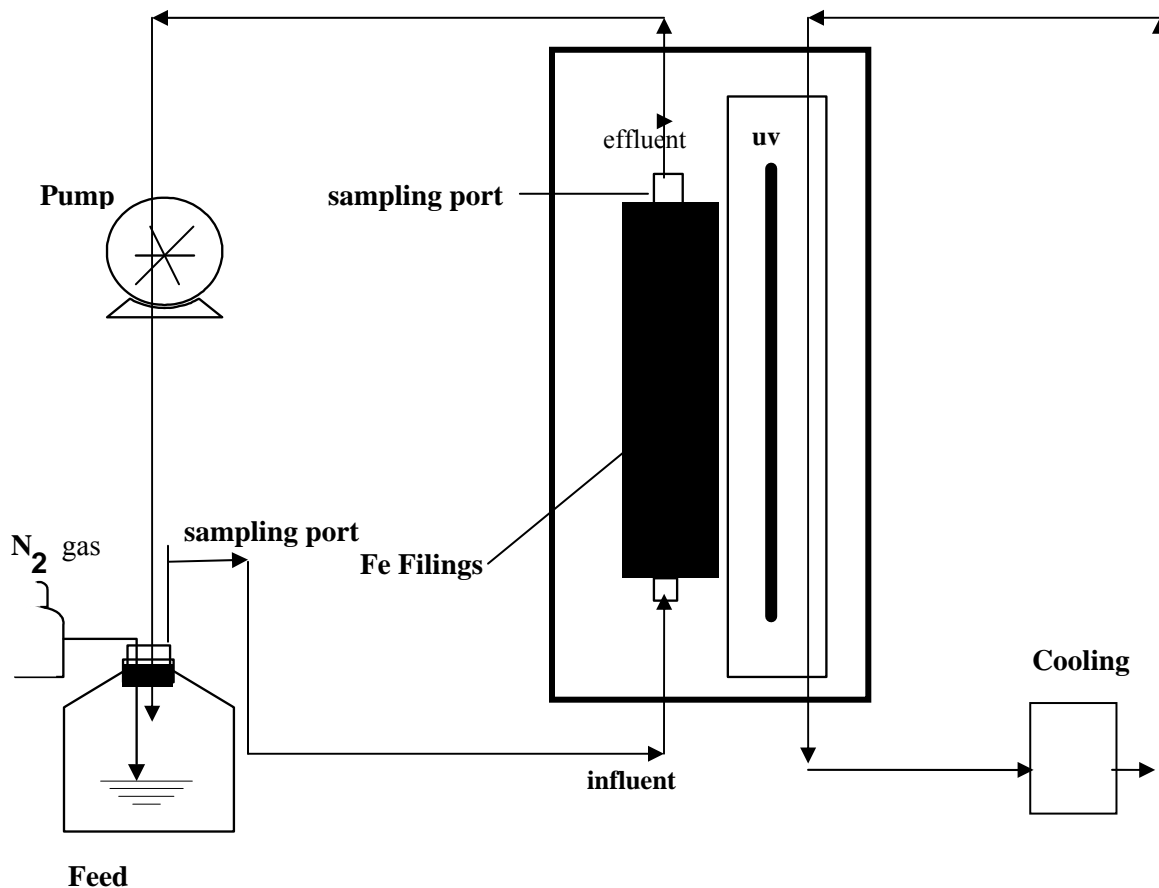


Figure 1-1. Schematic of the experimental setup

A schematic of the column experimental setup that will be used for reduction of perchlorate ions on iron filling column study is shown in Figure 1-1. The feed container for perchlorate is a sealed 2L glass container that is kept under a head pressure of nitrogen to keep the system under O₂ free condition. A multi-channel variable speed digital pump will be used to pump the perchlorate solution through the column. The column, made of Plexi-Glass that will be filled with the needed amount of iron filings that will be acid washed following a procedure discussed in the next section. The pump will be connected to the feeder and the column by PVC Solvent /Hydrocarbon resistant tubing. The UV light is installed parallel to the iron-filling column, which is connected to the cooler

1.4 STATEMENT OF PROJECT OBJECTIVES

1.4.1. Determine effectiveness of parameters.

Performing the integrated process will depend on various parameters (concentration of the iron filings and other catalyst used, such as Palladium, Cobalt, and Cupper). Statistical analysis of the results will determine factor(s) that are significant and will decide the ideal conditions for perchlorate destruction.

1.4 PROJECT ORGANIZATION AND RESPONSIBILITIES

Figure 1-2 depicts the project organizational chart for this project. Dr. E. Sahle-Demessie (EPA) and Dr. George Sorial (University of Cincinnati), are responsible as project advisors, coordinating and document review. Amy Q. Zhao is responsible for drafting Quality Assurance Project Plan (QAPP), carrying out the experimental work, project planning, sample collection and analysis and preparation of project documents. Dr. Daniel L. Young (EPA) will serve as the Quality Assurance Manager for the project.

The phone numbers for key project personnel are provided in Table 1-1.

Table 1-1. Key Project Personnel and Contact Information

NAME	TELEPHONE NUMBER
Daniel Young (EPA)	513-569-7451
E. Sahle-Demessie (EPA)	513-569-7739
Amy Q. Zhao (EPA)	513-487-2707
George Sorial (UC)	513-556-2987

SECTION 2.0

EXPERIMENTAL APPROACH

This section details the experimental design, measurements, sampling frequencies, and approach to evaluating project objectives.

2.1 *Experimental Design*

The objective of this experiment is to evaluate the effectiveness of a catalyst, palladium nitrate plus zero valent iron at different concentrations, with or without UV light for treating perchlorate-contaminated water. The data from this investigation will be evaluated by conducting a randomized design with a factorial treatment with repeated measurements, palladium + iron filling at four levels (palladium + Fe at 1.00 g/ml, palladium + Fe at 0.75 g/ml, palladium + Fe at 0.50 g/ml, palladium + Fe at 0.25 g/ml) UV light at two levels (UV light and no UV light), and sampling times at seven levels (0, 6, 24, 48, 96, 192, and 384 hours). The response variable is percent perchlorate removal where the initial concentration is 1000 ppb. The assumption is being made there is no interaction between the catalyst and the presence or absence of UV light, in other words regardless of UV light the trend in perchlorate concentration over the levels of a catalyst will be the same. The analysis of variance table for this experimental design is displayed in Table 2-1.

Table 2-1. Analysis of Variance Table for a Completely Randomized with a Factorial Treatment Structure with Repeated Measurements.

Source of Variation	Degrees of Freedom
Palladium + Iron Filling Dosage (0.25, 0.50, 0.75, 1.00 g/ml)	$4 - 1 = 3$
UV Light (no UV light, UV light)	$2 - 1 = 1$
Experimental Error	$(2 - 1)(2 - 1) = 1$
Sampling Time (0, 6, 24, 48, 96, 192, 384 hours)	$7 - 1 = 6$
Catalyst x Sampling Time	$(2 - 1)(7 - 1) = 6$
UV Light x Sampling Time	$(2 - 1)(7 - 1) = 6$
Experimental Error	6
Total	$4*2*7 - 1 = 55$

Evaluating the two catalysts by light treatment combinations will be random. Each of the two treatment combinations will be assigned a number and the numbers will be randomly selected using a computer algorithm.

2.2 ACID WASHING OF IRON FILINGS

The iron filings will be washed using 1N Hydrofluoric (HF) acid before use to remove iron oxide and other oily contaminants on the surface. The acid washed iron filings will be rinsed several times by deaerated Milli-Q water until the rinse water is free of brown color and its pH is neutral. Finally, the washed iron filings will be dried under nitrogen gas. The color of the treated iron filings should be black. This procedure will be done at UC laboratory.

2.3 INTEGRATED ZERO-VALENT IRON EXPERIMENTS

The experimental procedure for each test run listed in Section 2.1 is included in this section.

Acid washed iron filings will be added to completely pack the iron-filling column shown in Figure 1-1. A main stock solution with a concentration of $1\text{g L}^{-1}\text{ClO}_4^-$ will be prepared by adding 1.412g of sodium perchlorate monohydrate in Milli-Q water. This stock solution will be used for preparing the needed dilutions for each of the experiments discussed in section 2.1. The perchlorate feed solution will be prepared by diluting the stock solution to get a volume of 2L and an inlet concentration of 1000 ppb ClO_4^- . The feed solution will be thoroughly purged with nitrogen gas to remove the oxygen in the solution before transferring it to the feed container. The feed container for perchlorate will be immediately brought under a head pressure of nitrogen to keep the system under anoxic condition.

A two L Plexi-Glass bottle contained 1000ppb concentration Perchlorate feed solution will be used. The glass bottle has two ports- one port will be connected to the inlet of column and the other port will be connected to outlet of the column. To start the flow into the column, the feed solution

will be pumped into the system until there is a constant effluent flow. This flow rate is 1 ml/min, which is calibrated before the experiment. The acceptable range of the flow rate will be $\pm 5\%$.

Samples will be collected using 25ml disposable plastic syringe (Fisher) from the sample ports. A time zero sample will be taken when the test starts. The sample will be filtered through a 0.45 μ m membrane and then treated by an OnGuard II H cartridge (Dionex, Sunnyvale, CA) to remove any dissolved iron species, which may interfere in the perchlorate analysis and might significantly reduce the sensitivity of the IC column and gather in the suppressor. The samples will then be analyzed for perchlorate by IC using an adjusted EPA method 314.0 Attachment 1).

Table 5-1. Summary of Analytical QC Checks and Frequencies*

Parameter	QC Checks	Frequency	Acceptance Criteria	Corrective Action
rchlorate Concentrati on	Initial Demonstration of Precision	Initially	The %RSD must be $\leq 10\%$	The source of the problem must be identified and corrected
	Initial Demonstration of Accuracy	Initially	The mean recovered concentration (Cx) must be within 10% of the true value	The source of the problem must be identified and corrected
	Quality control sample (QCS) from an external & second source	Initially, on reestablishing calibration/ at least quarterly	QCS should be within 10% of the true value	The source of the problem must be identified and corrected
pH	Initial Calibration	Initially	RF for each concentration level less than 10% of the average RF	Prepare new standards and re-calibrate
	Standard calibration check	After every 10 samples (4 samples + method blank) or every 4 samples if method blank is not analyzed then	Percent recovery 90-110%	Correct problem; recheck calibration standard; re-check calibration
	Method Blank	Two replicates conducted on the first day and two replicates conducted on the last day of the test	< DL	Examine to find source; re-run blanks
	Calibration against 4, 7 & 10 pH standards	Daily	± 0.2 pH units	Recalibrate

*: DL: detectable limits

SECTION 3.0

SAMPLING PROCEDURES

3.1 SAMPLING PROCEDURES

Samples of 25 ml are withdrawn from the sample port using disposable plastic syringe. The sample is then analyzed for pH. It is either taken immediately for analysis with IC or stored at refrigerator with 4°C temperature until the time of analysis.

Table 3-1. Sampling Procedure

Parameter	Sample Type	Container	Preservation	Holding Time
Water samples withdrawn sampling port, the sampling port is flushed before each sample)	liquid	25 Plastic Syringe	None	Immediate measurement of pH,

3.2 ANALYTICAL INSTRUMENTS

The analytical instruments are listed in Table 3-2.

Table 3-2. Analytical Instruments

Analyte	Instrument
Perchlorate	Dionex DX-500 (Sunnyvale, CA, USA) ion chromatography (IC) system with a GP-50 gradient pump, an anion self-regenerate suppressor ultra (ASRS-ultra), a CD-25 conductivity detector and a LC-20 chromatography enclosure.
pH and Conductivity	Accumet AR 50 dual channel pH

SECTION 4.0

TESTING AND MEASUREMENT PROTOCOLS

4.1 PREPARATION OF STANDARDS

Perchlorate calibration standard solutions for calibrating the Ion Chromatograph (IC) are prepared

from the perchlorate stock solutions. The procedure is outlined in Appendix 2.

The IC requirement is as following: A AS16 analytical (4X250mm) anion exchange column, a guard column IonPac AG16 (4 x 50mm), and a ASRS ULTRA II (4mm) Anion Self-Regenerating Suppressor will be used. The Sample Loop will be 1000µL. Effluent is 50mM NaOH at flow Rate 1.0 mL/min. with a 100mA suppressor current. The peak of perchlorate will come out at 17min.

When there are alkaline earth and transition metals ions in the sample. The sample has to be pretreated to remove these cations before injected into IC.

Nitrogen Gas, PP will be used for IC.

4.2 CALIBRATION OF INSTRUMENTS

Prior to any analysis, the IC is turned on and allowed a 20-minute warm-up period for the detectors and lamps to become stable. The procedure for calibration of the IC is shown in Appendices 2 and 4.

pH meter: A three-point calibration using commercially prepared buffers(Fisher Scientific, Pittsburgh, PA) of pH 4, 7, and 10 will be performed on the meter. 50mL solution of each buffer is used to calibrate the pH meter with all the pH reading of the buffers being ±0.2 units of their values for analyses to proceed. A best-fit line is determined from the buffer pH and used to calibrate the pH meter internally.

4.3 EXPERIMENTAL SAMPLE ANALYSIS

The procedure for experimental sample analysis is outlined in Appendix 4.

SECTION 5.0

QA & QC CHECKS

5.1 PRECISION, ACCURACY, AND METHOD DETECTION LIMIT

5.1.1 *Precision for calibration*

The IC instrument precision objectives during calibration are determined by using the relative standard deviation (RSD) for percent dispersant effectiveness based on five calibration standards. The acceptance is based on RSD less than 10%.

$$\text{RSD} = \frac{\text{Standard Deviation of replicates}}{\text{Average Concentration}} \times 100 \quad (1)$$

If the RSD is greater than 10% due to the value of one calibration standard, this standard will be flagged and will be repeated. However, if two or more calibration standard values are different, all the standards will be rerun and the original data flagged.

Five calibration standards will be run to set up a calibration curve before a sample analysis. They are 50 ppb, 100 ppb, 250ppb, 500ppb, 750ppb, and 1000ppb. Each standard will be analyzed twice repeatedly.

5.1.2 Internal QC Checks for Calibration

Before samples are analyzed for perchlorate, the ion chromatograph is checked for meeting an instrument stability calibration. This criterion is determined with the six concentration levels for perchlorate. The response factor (RF) for each standard concentration level is then determined by using equation 1 in Appendix 2. The instrument stability for initial calibration is acceptable when the RF for each concentration level of the standard solutions is below 10% from the overall mean value for the five standard solutions. For the calibration curve to be accepted, both the precision (5.5.1) and internal QC check (5.1.2) criteria have to be satisfied.

5.1.3 Accuracy

The accuracy is determined by using a mid-point standard calibration check after every 10 experimental samples analyzed. The acceptance is based on a percent recovery of 90-110%. The percent recovery is determined by using the following equation:

$$\%R = 100\% * \left[\frac{C_m}{C_a} \right] \quad (2)$$

where:

% R = percent recovery, C_m = measured concentration of check standard,
 C_a = concentration of check standard.

5.1.4 Method Blank:

For IC, is injection, Milli-Q water is used as the method blank.

5.1.5 Method Detection Limit:

An MDL will be set up for the IC, using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit. To control MDL values, seven replicates will be processed through the entire analytical method over a three-day period. The MDL will be calculated as follows:

$$\text{MDL} = (t) \times (S_{n-1}) \quad (3)$$

where,

t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]

S_{n-1} = sample standard deviation (n-1) of the seven replicate analyses.

The reporting limits (RLs) of the IC for perchlorate will be determined. The RLs are the low end of the calibration curves for the analytes. The analysis of all the samples will be measured within the calibration concentration range. If the measured concentration of any of the samples is above the range, the sample will be diluted, and will be again analyzed to it in the calibrated concentration range. If the measured concentration of any of the samples is below the MDL, the data will be reported as below detection limits.

5.2 FREQUENCY OF QA & QC CHECKS

A summary of the QC checks necessary for this QAPP is given in Table 5-1. Data that do not meet the required QA objectives will not be used in reporting results.

SECTION 6.0

DATA REPORTING, DATA REDUCTION, AND DATA VALIDATION

6.1 DATA REPORTING

The effectiveness of perchlorate removal will be reported as percent

6.2 DATA REDUCTION

Data reduction for all the analyses will be computerized when applicable to reduce the likelihood of transcription and calculation errors. Computerized calculations will be confirmed before use. Documentation of the spreadsheet confirmation will be placed in the project central files.

6.3 DATA VERIFICATION AND VALIDATION

Calibration and QC data will be examined by the individual analyst to ensure that all instruments are functioning properly and that QA objectives for precision, accuracy, and MDL are being met.

The following principal techniques will be used to verify the integrity of data during collection and reporting:

- Confirmation that all calibration standards are within the range of acceptable values.
- Reporting of all calibration checks and method blanks.

- Maintenance of all the required documentation.

Data verification and validation for all the analyses conducted will be carried out after each stage of the analytical process by the PI as outlined in Table 6-1. The PI will initial each entry and calculation of the data.

6.4 REPORT FORMAT

Results will be reported as Excel workbook spreadsheet. A final written report that follows the format of a peer reviewed journal article will be prepared. An appendix to the report will contain tables of raw experimental data.

REFERENCES

ALMEIDA, C. M. V. B. GIANNETTI, B. F. & RABOCKAI, T. (1997). Electrochemical Study of Perchlorate Reduction at Tin Electrodes. *Journal of Electroanalytical Chemistry* **422**, 185-189.

AMERICAN PUBLIC HEALTH ASSOCIATION, AMERICAN WATER WORKS ASSOCIATION & WATER ENVIRONMENT FEDERATION. (1995). 3500-Ca Calcium. In *Standard Methods for the Examination of Water and Wastewater* (Ed Eaton, A. D. Clesceri, L. S. & Greenberg, A. E.), pp 3.56. Washington DC: American Public Health Association.

CHEN, W. CANNON, F. S. & RANGEL-MENDEZ, J. R. (2005). Ammonia-tailoring of GAC to enhance perchlorate removal. II: Perchlorate adsorption. *Carbon* **43**(3), 581-590.

CLARK, J. J. J. (2000). Toxicology of Perchlorate. In *Perchlorate in the Environment* (Ed E. T. Urbansky), pp. 15-29. New York: Kluwer Academic/Plenum.

ESPENSON, J. H. (2000). The Problem and Perversity of Perchlorate. In *Perchlorate in the Environment* (Ed E. T. Urbansky), pp. 1-7. New York: Kluwer Academic/Plenum.

GINGRAS, T. M. & BATISTA, J. R. (2002). Biological Reduction of Perchlorate in Ion Exchange Regenerant Solutions Containing High Salinity and Ammonium Levels. *J. Environ. Monit.* **4**, 96-101.

GREENWOOD, N. N. & EARNSHAW, A. (1997). *Chemistry of the Elements*. Oxford; Boston: Butterworth-Heinemann.

GU, B. DONG, W. BROWN, G. M. & COLE, D. R. (2003). Complete Degradation of Perchlorate in Ferric Chloride and Hydrochloric Acid under Controlled Temperature and Pressure. *Environmental Science and Technology* **37**(10), 2291-2295.

GUROL, M. G. & KIM, K. (2000). Investigation of Perchlorate Removal in Drinking Water Sources by Chemical methods. In *Perchlorate in the Environment* (Ed E. T. Urbansky), pp. 99-107.

New York: Kluwer Academic/Plenum.

HUANG, H. & SORIAL, G. A. (2006). Statistical Evaluation of an Analytical IC Method for the Determination of Trace Level Perchlorate. *Chemosphere* **64**(7), 1150-1156.

KIM, K. & LOGAN, B. E. (2001). Microbial Reduction of Perchlorate in Pure and Mixed Culture Packed-bed Bioreactors. *Water Research* **35**(13), 3071-3076.

LANG, G. G. & HORANYI, G. (2003). Some Interesting Aspects of the Catalytic and Electrocatalytic Reduction of Perchlorate Ions. *Journal of Electroanalytical Chemistry* **552**, 197-211.

MINITAB StatGUIDE (2003). <http://www.minitab.com/support/docs/rel14/default.aspx>

MOORE, A. M. DE LEON, C. H. & YOUNG, T. M. (2003). Rate and Extent of Aqueous Perchlorate Removal by Iron Surfaces. *Environmental Science and Technology* **37**, 3189-3198.

MONTGOMERY, D.C. (1997) Design and analysis of experiments. 4th ed. *John Wiley*, New York, NY.

MOTZER, W. E. (2001). Perchlorate: Problems, Detection, and Solutions. *Environmental Forensics* **2**, 301-311.

OKEKE, B. C. GIBLIN, T. & FRANKENBERGER, W. T. (2002). Reduction of Perchlorate and Nitrate by Salt Tolerant Bacteria. *Environmental Pollution* **118**, 357-363.

PERCIASEPE, R. (1998). Part III. Environmental Protection Agency. Announcement of the drinking water contaminant candidate list; notice". *Federal Register* **63**(40), 10273.

SCHERER, M. M. BALKO, B. A. & TRATNYEK, P. G. (1998). The Role of Oxides in Reduction Reactions at the Metal-Water Interface. In *Mineral-Water Interfacial Reactions: Kinetics and Mechanisms* Eds D. L. Sparks & T. J. Grundl, pp. 301-322. Washington DC: American Chemical Society.

SU, C. & PULS, R. W. (1999). Kinetics of Trichloroethene Reduction by Zerovalent Iron and Tin: Pretreatment Effect, Apparent Activation Energy, and Intermediate Products. *Environmental Science and Technology* **33**(1), 163-168.

SZECSODY, J. E. FRUCHTER, J. S. WILLIAMS, M. D. VERMEUL, V. R. & SKLAREW, D. (2004). In Situ Chemical Reduction of Aquifer Sediments: Enhancement of Reactive Iron Phases and TCE Dechlorination. *Environmental Science and Technology* **38**(17), 4656-4663.

URBANSKY, E. T. (1998). Perchlorate chemistry: implications for analysis and remediation. *Bioremediation Journal* **2**(2), 81-95.

URBANSKY, E. T. & SCHOCK, M. R. (1999). Issues in managing the risks associated with

perchlorate in drinking water. *Journal of Environmental Management* **56**, 79-95.

WALLACE, W. BESHEAR, S. WILLIAMS, D. HOSPADAR, S. & OWENS, M. (1998). Perchlorate Reduction by a Mixed Culture in an Up-flow Anaerobic Fixed Bed Reactor. *Journal of Industrial Microbiology & Biotechnology* **20**, 126-131.

EPA method 314.0 for perchlorate analysis (File 'EPA method-314.pdf' is attached)

METHOD 314.0

DETERMINATION OF PERCHLORATE IN DRINKING WATER USING ION CHROMATOGRAPHY

Revision 1.0
November 1999

Daniel P. Hautman and David J. Munch, US EPA, Office of Ground Water and Drinking Water
Andrew D. Eaton and Ali W. Haghani, Montgomery Watson Laboratories

**NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268**

DETERMINATION OF PERCHLORATE IN DRINKING WATER USING ION CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method covers the determination of perchlorate in reagent water and finished drinking water using ion chromatography.

1.2 The single laboratory reagent water Method Detection Limit (MDL, defined in Section 3.16) for the above analyte is listed in Table 1. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample and the specific instrumentation employed.

1.3 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.4 This method specifies an IC column and analytical conditions that were determined to be effective for perchlorate analysis.

2. SUMMARY OF METHOD

2.1 A 1.0 mL volume of sample is introduced into an ion chromatograph (IC). Perchlorate is

separated and measured, using a system comprised of an ion chromatographic pump, sample injection valve, guard column, analytical column, suppressor device, and conductivity detector.

NOTE: This large sample loop (1.0 mL) can be made using approximately 219 cm (86 inches) of 0.03 inch i.d. PEEK tubing. The exact volume is not critical since all standards and samples will use the same sample loop. However, the volume should be verified to be within 5% of this volume by weighing the sample loop empty, filling the loop with deionized water and re-weighing the loop. The volume can then be approximated by assuming the density of water is 1.0 mg/uL.

3. DEFINITIONS

3.1 ANALYSIS BATCH -- An Analysis Batch must also include all required QC samples, The required QC samples include:

- Instrument Performance Check Standard (IPC)
- Laboratory Reagent Blank (LRB)
- Initial Calibration Check Standard (ICCS)
- End Calibration Check Standard (ECCS)
- Either a Field Duplicate, a Laboratory Duplicate or a duplicate of the LFM

3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution(s) or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 INITIAL CALIBRATION STANDARDS -- A series of CAL solutions used to initially establish instrument calibration and develop calibration curves for individual target anions, which is perchlorate anion.

3.4 INITIAL CALIBRATION CHECK STANDARD (ICCS) -- A CAL solution, which is analyzed initially, prior to any sample analyses, which verifies the previously established calibration curve. The concentration for the initial calibration check standard MUST be at or below the MRL (Section 3.17) level.

3.5 CONTINUING CALIBRATION CHECK STANDARDS (CCCS) -- A CAL solution that is analyzed after every tenth sample analyses, not including QC samples that verifies the previously established calibration curve and confirms accurate analyte quantitation for the previous ten samples analyzed. The concentration for the continuing calibration check standards should be either at a middle calibration level or at the highest calibration level.

3.6 END CALIBRATION CHECK STANDARD (ECCS) -- A CAL solution that is analyzed after the last field sample analyses which verifies the previously established calibration curve and confirms accurate analyte quantitation for all samples analyzed since the last continuing calibration check. The end calibration check standard should be either the middle or high level continuing calibration check standard.

3.7 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution containing a

specific concentration of perchlorate and other test substances (namely chloride, sulfate and carbonate) used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.8 LABORATORY DUPLICATE (LD) -- Two sample aliquots (LD1 and LD2), taken in the laboratory from a single sample, and analyzed separately with identical procedures.

3.9 LINEAR CALIBRATION RANGE (LCR) – The concentration range over which the instrument response is linear.

3.10 MATERIAL SAFETY DATA SHEET (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.11 METHOD DETECTION LIMIT (MDL) – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.12 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.13 PEAK AREA TO HEIGHT RATIO (A/H) – The ratio of the peak area divided by the peak height that is used as a tool to monitor analytical performance. This ratio is used to establish and monitor the MCT and represents an objective means of assessing analytical performance when analyzing high conductivity matrices. A gradual distortion of the baseline is typically observed in the retention time window for perchlorate as the matrix conductivity increases (consistent with elevated levels of common anions) which will more significantly influence peak height relative to the influence on peak area. As the distortion of the baseline increases, this ratio increases, and the integrity of the measured perchlorate will be compromised.

3.14 QUALITY CONTROL SAMPLE (QCS) – A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the

source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.15 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing perchlorate that is either prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4. FILTRATION OF SAMPLE

4.1 All reagent solutions (eluent, external water for ASRS suppressor, etc...) used by the instrument must be filtered through no larger than a 0.45 um nominal pore size membrane or frit to remove particulates and prevent damage to the instrument, columns and flow systems. Sample filtration must also be employed on every sample prior to analysis. This applies not only to field samples but also to the laboratory reagent blank (LRB) and laboratory fortified blank (LFB). The LRB and LFB samples function as controls and must be filtered to confirm no bias is attributable to the filtration.5 Filter the samples through a membrane or frit with no larger than a 0.45 um nominal pore size. Syringe mounted, cartridge type, filters work well. Filters specifically designed for IC applications should be used.

SAFETY Plan

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are specifically listed below in Section 5.3 for hazardous materials.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable. Additional references on laboratory safety are available.

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.4 Sodium Hydroxide (NaOH), used in the preparation of the eluent is considered caustic.

6. EQUIPMENT AND SUPPLIES

6.1 Ion chromatograph (IC) -- Analytical system complete with eluent reservoirs, an ion chromatographic pump, injection valves, both guard and analytical separator columns, suppressor, conductivity detector, and computer based data acquisition system.

6.1.1 Anion guard column -- Dionex AG16 4 mm (P/N 55377), or equivalent. This column functions as a protector of the separator column. If omitted from the system, the retention times will be shorter.

6.1.2 Anion separator column -- Dionex AS16, 4 mm (P/N 55376). The AS16, 4 mm column using the conditions outlined in

6.1.3 Anion suppressor device -- The data presented in this method were generated using a Dionex Anion Self Regenerating Suppressor (4 mm ASRS, ULTRA, P/N 53946). An equivalent suppressor device may be utilized provided comparable conductivity detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 5 nS per minute over the background conductivity. Proper suppressor performance is essential to analytical data reproducibility and sensitivity of the conductivity detector.

6.1.3.1 The ASRS was set to perform electrolytic suppression at a current setting of 100 mA using the external water mode. External water was delivered to the suppressor directly from a pressurized source at a flow rate of 5 mL/min.

6.2 Data Acquisition System -- The Dionex Peaknet Data Chromatography Software was used to generate all the data.

6.3 Analytical balance -- Used to accurately weigh target analyte salt for stock standard preparation (± 0.1 mg sensitivity).

6.4 Weigh boats -- Plastic, disposable - for weighing eluent reagents.

6.5 Micro beakers -- Plastic, disposable - used during sample preparation.

6.6 Syringes -- Plastic, disposable, 10 mL - used during sample preparation.

6.8 Bottles -- High density polyethylene (HDPE) or glass, amber or clear, 30 mL, 125 mL, 250 mL. For sampling and storage of calibration solutions.

6.9 Particulate filters -- 0.45 micron syringe filters, specifically designed for IC applications (Gelman IC Acrodisc, PN 4485, or equivalent). These cartridges are used to remove particulates from the sample matrix while loading the sample manually or if the autosampler employed does not filter the sample during loading.

7. REAGENTS AND STANDARD

7.1 Reagent water -- Distilled or deionized water 17.8 Mohm or better, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.2 Eluent solution -- 50 mM sodium hydroxide (NaOH, [CASRN 1310-73-2]), dissolve 8.0 grams of 50% (W/W) sodium hydroxide in reagent water to a final volume of 2.0 L.

NOTE: This eluent solution is specific to the columns listed in Table 1. Any alternate columns will likely have unique and specific conditions identified by the manufacturer.

7.2.1 Solutions of NaOH are very susceptible to carbonate contamination resulting from adsorption of carbon dioxide from the atmosphere. This contamination will result in poor reproducibility of perchlorate retention times, elevated instrument background conductivity, and increased baseline noise/drift. Consequently, exposure to the atmosphere should be minimized by storing these eluent solutions in sealed reservoirs under low pressure (3 to 5 psi) helium. In addition, these solutions should be regularly prepared and held for no more than 5 days. When refilling the eluent reservoir, completely replace old eluent solution by emptying the old eluent, rinsing the reservoir with reagent water, and refilling with the freshly prepared eluent solution. With this eluent, the suppressed conductivity detector background signal should be between 2 -5 uS.

7.2.2 This eluent solution must be purged for 10 minutes with helium prior to use. This effectively removes dissolved gases that may form micro bubbles in the IC, compromising system

performance and adversely effecting the integrity of the data. Alternatively, an in-line degas apparatus may be employed.

7.2.3 A system or apparatus that automatically generates the hydroxide eluent (Dionex EG40, or equivalent) is an acceptable alternative to physically preparing this hydroxide eluent.

7.3 Perchlorate stock standard solution, 1000 mg/L (1 mg/mL) – A stock standard solution may be purchased as a certified solution or prepared from ACS reagent grade, sodium salt as listed below. (NOTE: Sodium perchlorate represents a molar weight fraction of 81.2 % perchlorate anion)

7.3.1 Perchlorate (ClO₄⁻) 1000 mg/L -- Dissolve 0.1231 g sodium perchlorate (NaClO₄, CASRN [7601-89-0]) in reagent water and dilute to 100 mL in a volumetric flask.

NOTE: Stability of standards -- Perchlorate stock standards, stored at room temperature, appears to be very stable and may be stable for an extended period. However, specified expiration dates should be marked on each prepared stock standard as part of any laboratory's quality control program. In this regard, it is recommended that stock standards for perchlorate be held for no more than 12 months and an expiration date should be clearly specified on the label.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples may be collected in plastic syringes. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis and laboratory fortified matrix analysis, if required, and minimize waste disposal.

8.2 Sample preservation and holding times for Perchlorate anion is 28 days.

NOTE: Perchlorate has been shown to be stable for more than 28 days⁶ but extended holding time studies (beyond 35 days) were not conducted by EPA. Typically, when analytes are believed to be stable, a 28 day holding time is established as a sufficient time to permit a laboratory to conduct the analysis.

9. QUALITY CONTROL

9.1 Initial Demonstration of Accuracy (IDA) -- Prepare and analyze 7 replicate LFBs fortified at 25.0 ug/L. Calculate the mean measured concentration (C₀) of the replicate values as follows.

$$(C_1 + C_2 + C_3 + \dots C_n)$$

$$C_0 = \frac{\quad}{n} \quad \text{where,}$$

C₀ = Mean recovered concentration of the replicate analysis.

C₁, C₂, ...C_n = Recovered concentrations of the replicate 1,2...n.

$$n = 7$$

To pass the IDA, the value derived for C₀ must be within ± 10% of the true value or between 22.5 ug/L and 27.5 ug/L.

9.2, calculate the percent relative standard deviation (%RSD) of the replicate analysis, as indicated below. To pass the IDP, the %RSD must be less than 10%.

$(S_{n-1}) \%RSD = \text{-----} \times 100(C_0)$ where,
S_{n-1} = sample standard deviation (n-1) of the replicate analyses.
C₀ = mean recovered concentration of the replicate analysis.

9.2.1 Quality Control Sample (QCS) – After calibration curves have initially been established or have been re-established, or as required to meet data quality needs, verify both the calibration and acceptable instrument performance with the preparation and analyses of an external/second source QCS.

9.2.2 Method Detection Limit (MDL) – An MDL must be established using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit.^{7, 8} To

be very stable and may be stable for an extended period. However, specified expiration dates should determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method over a three day period. These seven MDL replicate analyses may be performed gradually over three days or may represent data that has been collected, at a consistent MDL estimated concentration, over a series of more than three days. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$MDL = (t) \times (S_{n-1})$ where,

t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]
S_{n-1} = sample standard deviation (n-1) of the seven replicate analyses.

9.2.3 MDLs should be periodically verified, but **MUST** be initially determined when a new operator begins work or whenever there is a significant change in the background, or instrument response.

NOTE: Do not subtract blank values when performing MDL calculations.

9.3 Minimum Reporting Level (MRL) – The MRL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The MRL should be established at an analyte concentration either greater than three times the MDL or at a concentration which would yield a response greater than a signal to noise ratio of five. Setting the MRL too low may cause repeated QC failure upon analysis of the ICCS. **Although the lowest calibration standard may be below the MRL, the MRL must never be established at a concentration lower than the lowest calibration standard.**

9.4 Laboratory Reagent Blank (LRB) – An LRB must be prepared and treated exactly as a typical

field sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with field samples.

9.5 Calculate the relative percent difference (RPD) of the initial quantitated concentration (IC) and

duplicate quantitated concentration (Dc) using the following formula.

$$*(IC - Dc)*RPD = \text{-----} \times 100 \text{ } ([IC + Dc]/2)$$

9.6 Duplicate analysis may exhibit a matrix dependence. If the RPD for the duplicate measurements of perchlorate falls outside $\pm 15\%$ and if all other QC performance criteria are met, laboratory precision is out of control for the sample and perhaps the analytical batch.

10. AUTOMATED ANALYSIS WITH METHOD 314.0

11.1 Laboratories conducting analyses on large numbers of samples often prepare large analysis batches that are run in an automated manner. When conducting automated analyses, careful attention must be paid to ensure sufficient volume of eluent in the reservoir is available to sustain extended operation. In order to ensure their data are of acceptable quality, laboratories must ensure that all QC performance criteria are met throughout the analysis batch through subsequent careful inspection of the data.

11.2 Analysis sequences must be carefully constructed to meet required QC specifications. This schedule is included only as an example of a hypothetical analysis batch that contains normal sample matrices as well as samples that have failed the MCT. Within this analysis batch, references to exact concentrations for the ICCS, CCCS and ECCS are for illustrative purposes only.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify perchlorate in the sample chromatogram by comparing the retention time of a suspect peak within the retention time window to the actual retention time of a known analyte peak in a calibration standard. If the perchlorate retention time has slightly shifted (generally towards shorter times) since the initial calibration, but is still within acceptance criteria and are reproducible during the analysis batch, the analyst should use the retention time in the daily calibration check standards to confirm the presence or absence of perchlorate anion.

12.2 Report ONLY those values that fall between the MRL and the highest calibration standards. Samples with a perchlorate response that exceeds the highest calibration standard concentration must be diluted and reanalyzed. When this is not possible the alternate calibration procedures described in Section 11.2.5 must be followed. Samples

with perchlorate identified but quantitated below the concentration established by the lowest calibration standard, may be reported as “trace present” above the MDL but below the minimum reporting limit (MRL) and therefore not reported as a quantitated concentration.

12.3 Report results in µg/L.

13. WASTE MANAGEMENT

13.1 The Environmental Protection Agency requires that laboratory waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16. REFERENCES

1. "Determination of Perchlorate by Ion Chromatography." State of California, Department of Health Services, Sanitation and Radiation Laboratories Branch, Rev. No. 0 (June 3, 1997).
2. "Analysis of Low Concentrations of Perchlorate in Drinking Water and Ground Water by Ion Chromatography." Application Note 121, Dionex Corporation, Sunnyvale, CA (1998).
3. "Perchlorate by Ion Chromatography, Modified EPA 300.0 Using IonPac AS11." Standard Operating Procedure, Montgomery Watson Laboratories (March 17, 1998).
4. Jackson, P.E.; Laikhtman, M.; and Rohrer, J.S. "Determination of Trace Level Perchlorate in Drinking Water and Ground Water by Ion Chromatography," *Journal of Chromatography A*, 850 (1999), 131-135.
5. Okamoto, H.S.; Rishi, D.K.; Steeber, W.R.; Baumann, F.J.; and Perera, S.K. "Using Ion Chromatography to Detect Perchlorate," *Journal AWWA*, Vol. 91 (October 1999), 73-84.
6. Inter-Agency Perchlorate Steering Committee, Analytical Subcommittee Report (1998). Report on the interlaboratory validation of IC methods for perchlorate.
7. Glaser, J.A.; Foerst, D.L.; McKee, G.D.; Quave, S.A. and Budde, W.L. "Trace Analyses for Wastewater," *Environmental Science and Technology*, Vol. 15, Number 12, page 1426, December, 1981.
8. Code of Federal Regulations 40, Pt. 136, Appendix B (July 1, 1998).
9. "OSHA Safety and Health Standards, General Industry," (29CFR1910). Occupational Safety and health Administration, OSHA 2206, (Revised, Jan. 1976).
10. ASTM Annual Book of Standards, Part II, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, 1986.
11. "Carcinogens-Working with Carcinogens," Publication No. 77-206, Department of Health,

Education, and Welfare, Public Health Service, Center for Disease control, National Institute of Occupational Safety and health, Atlanta, Georgia, August 1977.

12. "Safety In Academic Chemistry laboratories," 3rd Edition, American Chemical Society Publication, Committee on Chemical Safety, Washington, D.C., 1979.

13. U.S. EPA Method 300.1. EPA Document number: EPA/600/R-98/118. NTIS number PB98-169196 INZ.

14. "Anion Self-Regenerating Suppressor (ASRS) Quickstart Procedure", Document Number 031368-01, Dionex Corporation, Sunnyvale, CA, March,1988.

15. "Installation Instructions and Troubleshooting Guide for the Anion Self-Regenerating Suppressor-Ultra", Document Number 031367, Rev. 03, Section 5.1, Dionex Corporation, Sunnyvale, CA, December, 1988.

16. CRC Handbook of Chemistry and Physics. Standard Solutions for Calibrating Conductivity Cells, p. D-166, 70th Ed., 1989-1990, CRC Press, Boca Raton, Florida.

17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR PERCHLORATE.

Standard Conditions and Equipment(a):

Ion Chromatograph: Dionex DX500

Sample Loop: 1000 μ L

Eluent: 50 mM NaOH

Eluent Flow: 1.5 mL/min

Columns : Dionex AG16, 4 mm / AS16, 4 mm

Typical System Backpressure: 2600 psi

Suppressor: ASRS ULTRA (P/N 53946), external water mode, 300 mA current

Detectors: Suppressed Conductivity Detector, Dionex CD20

Background Conductivity: 2 - 3 μ S

Determined MCT(b): 6100 uS/cm

Recommended method total analysis time: 15 minutes (may be shortened to 12 minutes)

SOP for IC Calibration

- a. EPA standard method 314.0 shown in Appendix 1 will be used for ClO_4^- analysis using the IC.
- b. Prepare a 1g/L perchlorate stock solution by adding 1.412g of sodium perchlorate monohydrate to 1L of Milli-Q water. Note that the water of hydration is taken into consideration in determining the perchlorate concentration.

- c. Dilute the 1g/L stock solution to get 1mg/L perchlorate solution. Prepare six calibrations standards, namely 50, 100, 250, 500, and 750 $\mu\text{g/L}$ from the 1 mg/L perchlorate solution prepared above by diluting accordingly.
- d. Inject a solvent blank (Milli-Q water) into the IC.
- e. Inject 2.5 mL of the standards in the order of increasing concentrations. Determine the area under the peak for perchlorate from the conductivity vs. time plot generated by the instrument.
- f. Before samples can be analyzed for perchlorate concentration, the IC must meet an instrument-stability criterion. This criterion is determined with the six calibration standards analyzed in step c and involves determination of response factors (RFs) at each concentration level. The response factor at each concentration level is determined by using the following equation:

$$RF = \frac{\textit{Theoretical Concentration}}{\textit{Area}} \quad (1)$$

where: theoretical concentration = perchlorate concentration in $\mu\text{g/L}$ in standard solution; Area = the area under the conductivity vs. time curve.

- g. Instrument stability for the initial calibration is acceptable when the RFs of the six standard extracts are <10% different from the overall mean value for the six standards.

$$\% \textit{ difference} = \frac{|RF - \textit{Av. RF}|}{\textit{Av. RF}} \times 100 \quad (2)$$

- h. If one or more of the standards does not meet this linear-stability criterion, then the “offending” standard(s) must be prepared a second time. If replacement of the re-analyzed standard solution(s) in the standard curve meets linear stability (i.e., no $RF > 10\%$ different from the overall mean), then the analysis of the samples can begin.
- i. If the initial-stability criterion is still not satisfied, analysis of the samples cannot begin, and the source problem (e.g., preparation protocol for the calibration standards, instrument stability, etc.) must be determined and corrected.
- j. Determine the slope of the calibration points by using linear regression with zero intercept.

$$y = mx \quad (3)$$

where: y = area under conductivity curve; x = perchlorate concentration, µg/L; m = slope

- k. The initial six-point calibration of the IC is required at least once per day.

SOP for SAMPLE ANALYSIS

The SOP for sample analyses is shown below and is the same for all three instruments- IC,

- a. Once a successful initial calibration curve has been established and verified, introduce the experimental method blank sample (Milli-Q water), followed by 3mL of the experimental samples. Analyze the samples and record the values.
- b. If any sample result exceeds the highest calibration standard the sample needs to be diluted and re-analyzed to fall within the calibration range of the instrument. If any sample result is less than the lowest calibration standard, report the result with a footnote indicating that the concentration value was lower than the lowest calibration standard.
- c. Introduce a source check directly after running the calibration standards and a mid-point standard every 10 samples and at the end of the batch. All valid samples will be bracketed by a set of valid check standards.
- d. Review QC results as early as possible to determine if acceptable criteria (see Section 5.0) are met. Rerun the sample if any QC check falls outside of acceptance limit.

Calculation Procedure for Experimental Samples

- a. The calculation procedure for determining the calibration curve for the different instruments is presented under Appendix 1 through 3.
- b. Determine the system performance (i.e., perchlorate percent removed) :

$$Eff \% = \frac{C_0 - C_e}{C_0} * 100 \quad (11)$$

where:

C₀ = Inlet perchlorate concentration, µg/L

C_e = Effluent perchlorate concentration, µg/L

- c. Report all the calculations in the form of a spread sheet.

- d. Report number of times test acceptance criteria (when the replicates for the experimental samples are conducted) were violated and how the problem was rectified.
- l. EPA standard method 314.0 shown in Appendix 11 will be used for ClO_4^- analysis using the IC.
- m. Prepare a 1g/L perchlorate stock solution by adding 1.412g of sodium perchlorate monohydrate to 1L of Milli-Q water.
- n. Dilute the 1g/L stock solution to get 1mg/L perchlorate solution. Prepare six calibrations standards, namely 10, 25, 50, 75, 100, 250, 500, 750 $\mu\text{g/L}$ from the 1 mg/L perchlorate solution prepared above by diluting accordingly.
- o. Inject a solvent blank (Milli-Q water) into the IC.
- p. Inject 2.5 mL of the standards in the order of increasing concentrations. Determine the area under the peak for perchlorate from the conductivity vs. time plot generated by the instrument.
- q. Instrument stability for the initial calibration is acceptable when the RFs of the six standard extracts are <10% different from the overall mean value for the six standards.

$$\% \text{ difference} = \frac{|RF - \text{Av. RF}|}{\text{Av. RF}} \times 100 \quad (2)$$

- r. If one or more of the standards does not meet this linear-stability criterion, then the “offending” standard(s) must be prepared a second time. If replacement of the re-analyzed standard solution(s) in the standard curve meets linear stability (i.e., no $\text{RF} > 10\%$ different from the overall mean), then the analysis of the samples can begin.
- s. If the initial-stability criterion is still not satisfied, analysis of the samples cannot begin, and the source problem (e.g., preparation protocol for the calibration standards, instrument stability, etc.) must be determined and corrected.
- t. Determine the slope of the calibration points by using linear regression with zero intercept.

$$y = mx \quad (3)$$

where: y = area under conductivity curve; x = perchlorate concentration, $\mu\text{g/L}$; m = slope

The SOP for sample analyses is shown below and is the same for all three instruments- IC,

- e. Once a successful initial calibration curve has been established and verified, introduce the experimental method blank sample (Milli-Q water), followed by 3mL of the experimental samples. Analyze the samples and record the values.
- f. If any sample result exceeds the highest calibration standard the sample needs to be diluted and re-analyzed to fall within the calibration range of the instrument. If any sample result is less than the lowest calibration standard, report the result with a footnote indicating that the concentration value was lower than the lowest calibration standard.
- g. Introduce a source check directly after running the calibration standards and a mid-point standard every 10 samples and at the end of the batch. All valid samples will be bracketed by a set of valid check standards.
- h. Review QC results as early as possible to determine if acceptable criteria (see Section 5.0) are met. Rerun the sample if any QC check falls outside of acceptance limit.

QA/QC Checks

PRECISION, ACCURACY, AND METHOD DETECTION LIMIT

Precision for calibration: The IC, AAS and UV-Vis instrument precision objectives during calibration are determined by using the relative standard deviation (RSD) for percent dispersant effectiveness based on five calibration standards. The acceptance criterion is based upon RSD less than 10%.

(1)

If the RSD is greater than 10% due to the value of one calibration standard, this standard will be flagged and will be repeated. However, if two or more calibration standard values are different, all the standards will be rerun and the original data flagged.

Internal QC Checks for Calibration: Before samples are analyzed for perchlorate, the ion chromatograph is checked for meeting an instrument stability calibration criterion. This criterion is determined with the six concentration levels for perchlorate. The response factor

(RF) for each standard concentration level is then determined by using equation 7 in Appendix 4. The instrument stability for initial calibration is acceptable when the RF for each concentration level of the standard solutions is below 10% from the overall mean value for the five standard solutions. For the calibration curve to be accepted, both the precision (5.5.1) and internal QC check (5.1.2) criteria have to be satisfied.

Accuracy: The accuracy is determined by using a mid-point standard calibration check after every 5 experimental samples analyzed (4 experimental samples or 4 replicates + method blank) or 4 experimental samples if a method blank is not analyzed. The acceptance criterion is based on a percent recovery of 90-110%. The percent recovery is determined by using the following equation:

$$\%R = 100\% * \left[\frac{C_m}{C_a} \right] \quad (2)$$

where:

% R = percent recovery, C_m = measured concentration of check standard,
 C_a = actual concentration of check standard.

Method Blank: For IC, is injection, Milli-Q water is used as the method blank.

Method Detection Limit: An MDL will be established for the IC, using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit. To determine MDL values, seven replicates will be processed through the entire analytical method over a three day period. The MDL will be calculated as follows:

$$MDL = (t) \times (S_{n-1}) \quad (3)$$

where, t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates] S_{n-1} = sample standard deviation (n-1) of the seven replicate analyses.

The reporting limits (RLs) of the IC for perchlorate will be determined. The RLs are the low end of the calibration curves for the analytes. The analysis of all the samples will be measured within the calibration concentration range. If the measured concentration of any of the samples is above the range, the sample will be diluted, and will be again analyzed to it in the calibrated concentration range. If the measured concentration of any of the samples is below the MDL, the data will be reported as below detection.

HASP #: 2009-002	Approval Date:
Expiration Date:	Next Review Date:

(This section completed by the Safety Health and Environmental Management (SHEM) Office)

Health and Safety Plan

Title:	New Technologies for the Destruction of Perchlorate in Water
Principal Investigator(s):	E. Sahle-Demessie
Branch ID:	CPB
Laboratory/Division:	NRMRL / STD
Project Location:	Full Containment Facility , #11 0
Start Date:	
Estimated Research Completion Date:	

Approvals

<u>Name</u>	<u>Phone</u>	<u>Signature</u>	<u>Date</u>
Amy Zhao PREPARER			
E. Sahle-Demessie PRINCIPAL INVESTIGATOR			
Douglas Young BRANCH CHIEF			
Steve Musson CHEMICAL HYGIENE OFFICER			
(Additional Approvals: such as CO-PI or Contractor Manager)			

(Additional Approvals: such as CO-PI or Contractor Manager)

Project Description

Objective

This safety plan covers all NRMRL/STD research activities on research work related to the use of reduction technology for the removal of Perchlorate from water.

Perchlorate has been found to be a major inorganic contaminant in drinking water and has been detected in a number of public drinking water systems. Adsorption processes are not very effective and biological removal of perchlorate has its own limitations in drinking and ground water remediation. Hence, an effective chemical reduction process is necessary. Chemical reduction of perchlorate is retarded by its high activation energy. Studies have found that

iron, when used as a reducing agent, provides the necessary catalytic effect to overcome the energy barrier. This study will evaluate the removal of perchlorate by zero valent iron filings in the presence and absence of catalyst enhanced by UV light. The reduction reaction rate kinetic will be studied. The effectiveness of iron dosage will be also investigated.

Experimental Procedure

Batch experiments will be conducted in 16mL sample vials to evaluate the effectiveness of iron dosage on perchlorate reduction rate, to evaluate the perchlorate degradation by zero valent iron and other metal oxidants enhancement of UV light and determine the kinetics of the reduction reaction. Experiment system is always kept closed during run.

1. A 1000ppm stock solution of perchlorate in M.Q. water will be prepared. The stock solution will be diluted into several other standard solutions.
2. 500ml of 1ppm solution will be deoxygenated using nitrogen gas. (A 0.75mg/L of Palladium Nitrate will be added into 1ppm Perchlorate solution for catalyst study) This step will eliminate the oxygen gas excising in M.Q. water and reduce the interference of reduction between Fe and perchlorate.
3. Iron Filings obtained from Fisher Scientific (Pittsburgh, PA)(Mesh 40) will be acid washed using 1M Hydro Floric Acid to remove rust and oily contaminants at the surface and will be treated under protection of nitrogen gas.
4. Iron Dosage will be 0.25, 0.5, 0.75 and 1g/ml.
5. For catalyst study Palladium Nitrite from Fisher Scientific will be used.
6. Tests were conducted in the absence and presence of UV light
7. The perchlorate solution will be introduced into the vials and complet filled leaving no head space. The vials will be then sealed by caps with Teflon lining.
8. The tube will be placed into rotator either shaker in or outside of UV box .
9. UV light will be off during sampling time.
10. Sample will be filtered with 0.45 μ syringe filter to remove any particle and OnGuard II H Cartridges to remove alkaline earth and transition metals before analyzed by IC.
- 11.. Samples will be analyzed using EPA Method 314.0 with a IP-25,ED-40,IonPac AS16 Column, Ion Chromatograph system (Dionex).

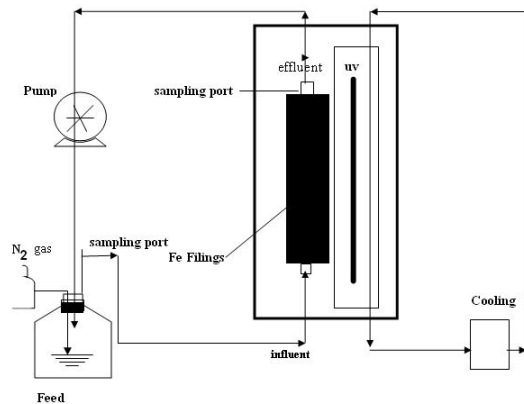


Figure 1. column experiment set up

oded Auto Analysis Tubing obtained from Cole Palmer. A 0.25 mm inner diameter pump tubing will be used which can provide a flow rate of 1.0 mL min^{-1} . The pump, the perchlorate feed solution container and the column will be connected by PVC Solvent/Hydrocarbon resistant extension tubing with an I.D. of 1.42 mm. The glass columns were obtained from Ace Glass (Vineland, NJ). Two different inner-diameters were used. One had a 15 mm I.D. and the other had 25 mm I.D. The length of both columns was 450 mm. The length of the reactive zones was sandwiched between two short layers of pre-packed Ottawa sand. The Iron filings were acid washed as described previously before being packed into the column. Flow through column experiment will be conducted to verify a mathematical correlation for different iron dosages. The experimental setup is shown in Figure 1. A 2 liter glass container will be used as a feed container for perchlorate. The container was sealed by a stopper to prevent atmospheric oxygen from entering the solution. The stopper had two openings. One opening will be used for passing the pump tubing through a stainless steel tube. The other opening had through which a stainless steel tube will be connected to a nitrogen gas cylinder for providing a An Ismatec Compact Multichannel variable-speed digital pump, obtained from Cole Palmer (Vernon Hills, IL), will be used to pump the perchlorate solution (feed) through the column. The pump tubing used was Pharmed Three-Stop Color-C

Responsibilities

E. Sahle-Demessie (US E.P.A.) is the principal investigator for this project and he is also responsible for overseeing the project progress and manuscript preparation.

Amy Zhao is responsible for conducting of experiments and analysis, responsible for QA/QC goals

George A. Sorial" (UC professor, Civil Engineering Department) as an advisor to the project and a co-PI.

Tom Deinlien (SEEP) provides technical and engineering assistance.

Other E.P.A support scientists conduct SEM and TEM imaging and x-ray diffraction of catalysts.

Process, Site, Facility and Apparatus

This work will be conducted at the US EPA, Andrew W. Breidenbach Environmental Research Center, NRMRL (Containment Facility), Cincinnati. The laboratories are equipped with facilities for bench-scale experiments including shaker, oven, UV reactor, Ionic Chromatograph (IC).

General Safety Considerations

Exposure to hazardous chemicals used in this project are minimal. Hazardous chemicals would include sodium perchloride, sodium hydroxide, Palladium Nitrite, nitrogen gas, Hydro floric Acid. . Gloves and eyeglass are always worn when preparing or using chemicals. UV protection will be worn when UV light is on during an experiment. Chemical solution will be prepared in a fume hood.

Other safety practices include:

- All researchers in the laboratory, should wear protective equipment, including personal protective equipment for eyes, face, head, and extremities, protective clothing, and protective shields and barriers, shall be provided, used, and maintained in a sanitary and reliable condition wherever it is necessary by reason of hazards of processes or environment, chemical hazards, or mechanical irritants encountered in a manner capable of causing injury or impairment in the function of any part of the body through absorption, inhalation or physical contact.
- Access to the laboratory is limited or restricted when experiments are in progress.
- All eye and skin contact of any of these chemicals is prohibitions as specified by any OSHA health standard shall be observed
- Lab personnel wash their hands after handling chemicals, after removing gloves, and when they leave the laboratory.
- All sample standards will be prepared in fume hoods.
- The PI, post docs and other researches shall determine that compressed gas cylinders under his/her control are in a safe condition to the extent that this can be determined by visual inspection. Visual and other inspections shall be conducted as prescribed in the Hazardous Materials Regulations of the Department of Transportation (49 CFR parts 171-179 and 14 CFR part 103).

- Eating, drinking smoking, handling contact lenses, and applying cosmetics are not permitted in the laboratory. Food is stored outside the work area.
- All operators of the reactor should wear chemical splash goggles whenever experiments are running or there is a danger of chemicals coming in contact with the eye.
- Mouth pipetting is prohibited. Mechanical pipetting devices are used.
- All procedures are performed carefully to minimize the creation of aerosols.

All project personnel are required to take the mandatory 24 hours safety training before initiating laboratory work. All project personnel will also take the annual refresher safety training required by NERL. SEE and ORISE personnel assigned to this project also take the refresher safety training.

Engineering controls, personal protective equipment, hygiene practices, and administrative controls each play a role in a comprehensive laboratory safety program. Implementation of specific measures must be carried out on a case-by-case basis, using the following criteria for guidance in making decisions.

Engineering controls

a) Fume Hoods

The laboratory fume hood is the major protective device available to laboratory workers. It is designed to capture chemicals that escape from their containers or apparatus and to remove them from the laboratory environment before they can be inhaled. Characteristics to be considered in requiring fume hood use are physical state, volatility, toxicity, flammability, eye and skin irritation, odor, and the potential for producing aerosols. A fume hood should be used if a proposed chemical procedure exhibits any one of these characteristics to a degree that (1) airborne concentrations might approach the action level (or permissible exposure limit), (2) flammable vapors might approach one tenth of the lower explosion limit, (3) materials of unknown toxicity are used or generated, or (4) the odor produced is annoying to laboratory occupants or adjacent units.

Procedures that can generally be carried out safely outside the fume hood include those involving (1) water-based solutions of salts, dilute acids, bases, or other reagents, (2) very low volatility liquids or solids, (3) closed systems that do not allow significant escape to the laboratory environment, and (4) extremely small quantities of otherwise problematic chemicals. The procedure itself must be evaluated for its potential to increase volatility or produce aerosols.

In specialized cases, fume hoods will contain exhaust treatment devices, such as water wash-down for perchloric acid use, or charcoal or HEPA filters for removal of particularly toxic materials.

b) Safety Shields

Safety shields, such as the sliding sash of a fume hood, are appropriate when working with highly concentrated acids, bases, oxidizers or reducing agents, all of which have the potential for causing sudden spattering or even explosive release of material. Reactions carried out at non-ambient

pressures (vacuum or high pressure) also require safety shields, as do reactions that are carried out for the first time or are significantly scaled up from normal operating conditions.

c) Other Containment Devices

Other containment devices, such as glove boxes or vented gas cabinets, may be required when it is necessary to provide an inert atmosphere for the chemical procedure taking place, when capture of any chemical emission is desirable, or when the standard laboratory fume hood does not provide adequate assurance that overexposure to a hazardous chemical will not occur. The presence of biological or radioactive materials may also mandate certain special containment devices. High strength barriers coupled with remote handling devices may be necessary for safe use of extremely shock sensitive or reactive chemicals.

Highly localized exhaust ventilation, such as is usually installed over atomic absorption units, may be required for instrumentation that exhausts toxic or irritating materials to the laboratory environment. Ventilated chemical storage cabinets or rooms should be used when the chemicals in storage may generate toxic, flammable or irritating levels of airborne contamination.

Chemical Spills

All chemical spills shall be reported in writing to the EPA Safety Office, regardless of size. The report shall include the date, time, location, chemical(s) and their volume, and names of all persons involved, including any visitors who were exposed and personnel involved in the clean up and the reason for the spill. A copy of this report shall also be kept by the Branch and PI office

- a. Confine or contain the spill to a small area. Do not let it spread.
- b. For small quantities of inorganic acids or bases, use a neutralizing agent or an absorbent mixture (e.g., soda ash or diatomaceous earth). For small quantities of other materials, absorb the spill with a non-reactive material (such as vermiculite, clay, dry sand, or towels).
- c. For larger amounts of inorganic acids and bases, flush with large amounts of water (providing the water will not cause additional damage). Flooding is not recommended in storerooms where violent spattering may cause additional hazards or in areas where water-reactive chemicals may be present.
- d. Mop up the spill, wringing out the mop in a sink or a pail equipped with rollers.
- e. Carefully pick up and clean any cartons or bottles that have been splashed or immersed.
- f. If needed, vacuum the area with a HEPA filtered vacuum cleaner approved and designed for the material involved.
- g. If the spilled material is extremely volatile, let it evaporate and be exhausted by the laboratory hood (provided that the hood is authorized for use with the spilled chemical).

Laboratory Activities:

Physical Hazards Summary

Physical Hazards	Yes	No	Physical Hazards	Yes	No
Electrical Hazards	X		Noise		X
Radioactive Materials		X	Temperature	X	
Non-Ionizing Radiation		X	Illumination		X
Ionizing Radiation		X	Compressed Gas	X	
Heavy Lifting		X	Sharp Objects / Tools		X
Vibration		X	Slips, Trips, Falls	X	
Will this research require protection from radionuclides?					X
Will this research require protection from toxic chemicals?					X
Will the products being used require protection from contamination by the researchers?					X

PPE Summary

PPE Level Required	D		C	B	A
Level D the PPE Level Required					
See PPE Hazard Assessment Table					
Face / Eye Protection	Yes	No	Yes	No	
Safety Glasses w/ Side Shields	X		Face Shield – potential for use with corrosive materials	X	
Chemical Splash Goggles	X		safety glass		
Ear Protection					
Ear Plugs (Foam Inserts)		No	Ear Muffs		
Both Ear Plugs and Ear Muffs		No			
Hand Protection					
Chemical - Nitrile	X		Chemical - Silver Shield ®		
Chemical – BPalladium Nitrite	X				
Latex	X		Cut Resistant (Kevlar ®)		
Cotton			Other (specify)		
Protective Clothing					
Lab Coat (Tyvek ®, Cotton)	X		Jumpsuit		
Lab Apron			Other (specify)		
Respiratory Protection*					
Air Purifying Full Face Respirator			Air Purifying Half Face Respirator		
N-95 Particulate Respirator			P-100 Particulate Respirator		
Nuisance Dusk Mask			Other (specify)		

**Note: Employees Wearing Respiratory Protection must be enrolled in the Respiratory Protection Program, must be medically cleared to wear a respirator and have current, annual training. Please see SHEM Staff for additional requirements*

Respiratory Protection	Yes	No
Is respiratory protection required?		X
If respiratory protection is required, are all authorized personnel medically cleared to wear respirators?		X
If respiratory protection is required, are all authorized personnel current with respiratory protection training?		X

Equipment Requirements (Check all that apply)

4' Chemical Fume Hood	X	Clear Air Bench (laminar flow hood)	
5' Chemical Fume Hood	X	Local Exhaust Ventilation	
6' Chemical Fume Hood	X	Spot Ventilation Unit (Snorkel)	
Specialty Fume Hood		Canopy Hood	
Walk-in / Bulking Hood		Liquid Scintillation Counter	
Radiological Fume Hood		Refrigerator / Freezer	
Biological Safety Cabinet		Deep Freezer	
Other (specify)		Other (specify) shaker, oven, UV reactor, Ionic Chromatograph (IC)	X

Chemicals to be Used

(Federal law under SARA, Title III, (also known as the Emergency Planning and Community Right to Know Act) requires that Material Safety Data Sheet (MSDS) be readily available for every chemical in the facility. EPA utilizes an online service to assist in meeting this requirement: <http://epa.chemwatch.us> User Name: **epauser**; Password: **12021970**. If the MSDS is not available through Chemwatch, a hardcopy of the manufacturer supplied MSDS must accompany the HASP. The NFPA hazard rating table is supplied below)

Item #	Chemical Name	CAS#	NFPA Hazard Rating	Max Qty stored	Disposal Method for Excess Chemicals			MSDS: C:Chemwatch H:Hardcopy
					Sink	Contract*	Trash	
1	Perchlorates (Sodium perchloride)	7601-89-0	202	250g		X		
2	Iron Filling	7439-89-6	000	1,000g		X		
3	Palladium Nitrite	13463-67-7	000	10g		X		
4	Nitrogen Gas	7727037-9	300					
5	Hydro Floric Acid	64-18-67	320	100ml		X		
7	Sodium Hydroxide	1310-73-2	301	8g		X		
8	Water	7732-18-5	000		X			
10	UV Light	PC122121						

* Indicates that material will be sent for proper waste management by the SHEM office

Biological Research

Does the project in any way involve manipulation of recombinant DNA?	No
If yes, are all proposed activities specifically exempted from the NIH Guidelines for Research Involving Recombinant DNA Molecules?	No
Does the project in any way involve human subjects or biological materials obtained from human subjects?	No
If yes, is the project exempt from the Health and Human Services Policy for Protection of Human Subjects?	No
Does the project involve animals requiring Institutional Animal Care & Use Committee (IACUC) approval? (includes vertebrate & invertebrates animals)	No

Waste Management

All sample waste will be sent to CHEMICAL HYGIENE OFFICER for proper disposal. Sodium Hydroxide elluent from IC will be nutrolized by 1M HCl solution till pH reads 7 before discharged to sink.

Sample Management

No specific sample management procedures for this study. However, if the sample spilled or sample vials break, the spill response procedure will be followed.

Will Hazardous Waste Be Generated?

Yes

Will the Treatability Exemption be Utilized?

No

Spill Response

Gloves will be used for handling cleaning of the spill. Paper towel will be used to absorb the water solution.

The procedures listed below are intended as a resource for your department in preparing for emergencies before they happen. If you are currently experiencing an emergency such as a chemical or blood spill, please contact the Department of Environmental Health and Safety at (513) 569-7969, (513) 569-7268.

Complete spill response procedures are described in the Hazardous Chemical Waste Management guidebook (<http://www.dehs.umn.edu/guidebook/guidebook3.html>). However, the quick reference guide is included for convenience in this Laboratory Safety Plan.

UV light will be used in a black metal box. The box will be wrapped with aluminum foil and no light will be leaked outside of the box. A UV protected glass will be required during experiment.

Authorized Personnel

Training and medical monitoring requirements will vary depending on the complexity and materials used in the process. Therefore, only personnel appropriately trained and monitored will be permitted to work under this plan. To be “authorized”, employees must have completed the training as outlined below.

40 - hour Hazwoper		Hearing Protection	
Current 8 - hour Hazwoper refresher		First Aid / CPR / AED	
Respiratory Protection		SPCC	
24 - hour Laboratory Safety	X	Personal Protective Equipment	X
Current Laboratory Safety Refresher	X	DOT	
Biosafety / Bloodborne Pathogens		RCRA	X
Radiation Safety		Other (specify) – applicable HASPs, SOPs, and JHAs	X

References:

Greer, M.A., Goodman, G., Pleuss, R.C., Greer, S.E. 2002. Health effect assessment for environmental perchlorate contamination: The dose response for inhibition of thyroidal radioiodide uptake in humans. Environ. Health Perspect. 110:927-937.
Lawrence, J.E., Lamm, S.H., Pino, S., Richman, K., Braverman, L.E. 2000. The effect of short-term low-dose perchlorate on various aspects of thyroid function. Thyroid 10(8):659-663

Laboratory Staff Concurrence

I have read, understood and will comply with all the requirements of the attached Health and Safety Plan, MSDS's, and the rules contained in the U. S. EPA-Cincinnati Facilities Chemical Hygiene Plan. I have also had the opportunity to ask any questions, and had my questions satisfactorily answered prior to my beginning work under this plan.

Safety, Health and Environmental Management

Personal Protective Equipment, PPE Hazard Assessment Table

Hazard Source	Operation	Room / Area	Hazard - Assessment of Hazards	Risk	PPE	PPE Criteria
water samples – the dilute dosing solutions	Taking samples and performing various analytical techniques	FCF 110 / 104	Chemical exposure. –due to splash with dosing solutions - Cuts.	Potential skin irritation	Gloves, eye protection, lab coats.	Safety Glasses shall meet ANSI Z87 specifications – standard PPE as listed in Plan
Chemical solutions	Preparation of reagent solutions / samples	FCF 110 / 104	Chemical exposure.	Potential skin irritation or “caustic” burns with NaOH	Gloves, eye protection, lab coats.	Safety Glasses shall meet ANSI Z87 specifications – standard PPE as listed in Plan
Thermal hazards – furnace / oven	Glassware cleaning	FCF 110 / 104	Thermal burns from handling glassware associated with the muffle furnace / oven	Thermal burns to hands / face	Gloves, eye protection, lab coats with the addition of thermal protective gloves	Safety Glasses shall meet ANSI Z87 specifications – standard PPE as listed in Plan

PPE Checklist

	Yes	No
1. Has the workplace been assessed to determine if hazards that require the use of head, eye, face, hand, or foot protection are present or likely to be present?	X	<input type="checkbox"/>
(a) Did the assessment include an identification and evaluation of equipment and process?	X	<input type="checkbox"/>
(b) Were accident records reviewed?	<input type="checkbox"/>	X
(c) Were the sources of hazards identified?	X	<input type="checkbox"/>
(d) Is the selected PPE adequate for the task?	X	<input type="checkbox"/>
2. Have all affected employees been trained on the proper use of PPE?	X	<input type="checkbox"/>
3. Can employees demonstrate an understanding of the training?	X	<input type="checkbox"/>
4. Has training been documented through a written certification?	X	<input type="checkbox"/>
5. Have any of the following situations occurred that require a re-evaluation of the workplace?	<input type="checkbox"/>	X
(a) The purchase of any new types of PPE?	<input type="checkbox"/>	<input type="checkbox"/>
(b) The procurement of new equipment or facilities?	<input type="checkbox"/>	<input type="checkbox"/>
(c) The introduction of new operations or procedures?	<input type="checkbox"/>	<input type="checkbox"/>
6. If you answered yes to any of the questions in question 5, was the workplace re-evaluated using questions 1-4?	<input type="checkbox"/>	<input type="checkbox"/>

Job Hazard Analysis

Sequence of Basic Job Steps	Potential Hazards	Recommended Action or Procedure
Chemical Handling	Skin contact / inhalation - during chemical transfers and decontamination of the work area (EtOH, bleach, salts, NaOH, buffers) - Minimal hazard due to established controls NaOH is a corrosive material; the methanol is flammable - sodium perchlorate is a strong oxidizing material	Proper PPE as listed above – chemical transfers should be conducted in a chemical fume hood where possible; the need for a face shield should be evaluated for corrosive materials and based on volume, concentration, and established controls; ensure no ignition sources in the vicinity when decontaminating work area with methanol; use good chemical hygiene practices in accordance with the Chemical Hygiene Plan
<p>Assembly of the falling film reactor set up</p> <p>UV Light is 30-40mW/cm² which is a small amount</p>	<ul style="list-style-type: none"> - Use if ring clamp assembly and peristaltic pump; potential pinch points – injurious contact - Heavy lifting with pump – potential for shoulder / back injury if not lifted properly - 100 L water = approximately 220 lbs. - potential back / shoulder / wrist injury while manipulating the water sample <p>UV Light is hazardous for eye.</p>	<p>Utilize proper lifting procedure when handling heavy equipment; keeping load close to body, minimize bending/twisting, etc. - ensure proper PPE is worn (lab coat, nitrile or equivalent gloves, safety glasses with side shields) - check the integrity of the system by periodically conducting a visual inspection of clamps, hose rings, tubing, etc. ensure pump is maintained according to manufacturer's recommendations - identify pinch points; ensure appropriate hand clearance</p> <p>UV protective eyeglass will be worn and the experiment system will be always enclosed closed during run.</p>