REDUCTION OF PERCHLORATE AND NITRATE BY ALUMINUM ACTIVATED BY PH CHANGE AND ELECTROCHEMICALLY INDUCED PITTING CORROSION

A Dissertation

by

ADITYA BABU RAUT DESAI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2010

Major Subject: Civil Engineering

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Approved by:

Chair of Committee,	Bill Batchelor
Committee Members,	Bryan Boulanger
	Kung-Hui Chu
	Bruce Herbert
Head of Department,	John Niedzwecki

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ABSTRACT

Reduction of Perchlorate and Nitrate by Aluminum Activated by pH Change and Electrochemically Induced Pitting Corrosion. (May 2010)

Aditya Babu Raut Desai, B.E., Goa University;
M.S., Texas A&M University
Chair of Advisory Committee: Dr. Bill Batchelor

Highly oxidized species like perchlorate and nitrate that are released into the environment by anthropogenic activities are a source of concern as they have been known to contaminate groundwater. These species are extremely soluble in water and can migrate through aquifer systems, travelling substantial distances from the original site of contamination. Due to their high solubility, these oxy-anions cannot be treated using conventional treatment processes like filtration and sedimentation. Several treatment technologies are currently available to abate the human health risk due to exposure to perchlorate and nitrate. However, most of the existing treatment processes are expensive or have limitations, like generation of brines with high concentrations of perchlorate or nitrate.

Aluminum can effectively reduce perchlorate and nitrate, if the protective oxide film that separates the thermodynamically reactive Al^0 from most environments is removed. Aluminum was activated by pH change and electrochemically induced, pitting corrosion to remove the passivating oxide layer and expose the underlying, thermodynamically reactive, zero-valent aluminum. A partially oxidized species of aluminum, like monovalent aluminum, is believed to bring about the reduction of perchlorate and nitrate. This research studied the reduction of perchlorate and nitrate by aluminum that was activated by these two mechanisms.

Results indicated that aluminum activated by pH change resulted in an instantaneous decrease in perchlorate concentration without any increase in chlorate or chloride concentrations, which suggests that the perchlorate might be adsorbed on the aluminum oxide surface. However, aluminum activated by electrochemically induced pitting corrosion can effectively reduce perchlorate to chlorate. Nitrate, on the other hand, was reduced completely to ammonia by both treatment mechanisms. The studies conducted in this dissertation suggest that aluminum can be effectively used as a reducing agent to develop a treatment process to reduce perchlorate and nitrate.

DEDICATION

To my mom, dad, brother, and sister-in-law.

In memory of Dr. Tim Kramer.

ACKNOWLEDGEMENTS

I would like to start by thanking my committee chair, Dr. Bill Batchelor, for his guidance, support, and patience throughout the course of this research; and my committee members: Dr. Bryan Boulanger, Dr. Kung-Hui Chu, and Dr. Bruce Herbert, for their suggestions, availability, and commitment.

I offer my thanks and appreciation to The Texas Transportation Institute, The Space Engineering Institute and the Department of Civil Engineering for their financial support.

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Last but not the least; I would not have been able to finish my doctorate without the unconditional love and support of my family (my mother, father, brother and sister-in-law).

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CHAPTER I

INTRODUCTION

Water is a scarce and vital commodity for the survival of human beings on Earth. Groundwater accounts for more than half the drinking water supplies in United States (USGS 1996). Due to industrial activity a wide variety of pollutants are released into the environment that contaminate groundwater. Environmental pollution by highly oxidized species like perchlorate and nitrate is one of the sources of concern.

Perchlorate has emerged as a chemical of concern in the United States over the last decade. The harmful effect of perchlorate impurities in Chilean fertilizers on plant growth has been reported as early as 1896 (Sjollema 1896). Perchlorate exposure at sufficiently high levels causes a decrease in iodide uptake by the thyroid gland, which can cause problems like mental retardation, delayed development and possibly thyroid tumors in infants and children (Hershman 2005).

The Department of Defense (DoD), the National Aeronautics and Space Administration (NASA), and associated industries have been using perchlorate in the manufacturing, testing, and firing of missiles and rockets. Perchlorate was first discovered at superfund sites in the United States in 1985 and was recognized as a nationwide problem in 1997 (National Research Council 2005). The problem of perchlorate contamination was further complicated due to the unavailability of

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This dissertation follows the style of *Journal of Environmental Engineering*.

technology to measure perchlorate at low concentrations. The ion chromatography (IC) method (CDHS 1997) for perchlorate analysis was developed in 1997 and made it possible to measure concentrations as low as 4 μg/L. This analytical method made it apparent that perchlorate contamination was widespread and raised the concern in drinking water supply dramatically. Perchlorate was first added into the Federal Contaminant Candidate (CCL) list under the Safe Drinking Water Act (SDWA) in 1998. Since then the perchlorate contamination problem has been comprehensively studied. In 2005, the U.S. Environmental Agency (USEPA) established an official reference dose (RfD) of 0.0007 mg/kg/day of perchlorate, which translates to a Drinking Water Equivalent Level (DWEL) of 24.5 μg/L. Although the U.S. EPA decided not to regulate perchlorate in drinking water at a national level (U.S. EPA 2009), several state agencies have already proposed drinking water standards for perchlorate (Sellers 2007). However, U.S. EPA has set an interim health advisory of 15 ppb for perchlorate that is to be used for establishing cleanup levels at Superfund sites (U.S. EPA 2009).

Drinking sources contaminated with perchlorate have been known to also have a high nitrate concentration (Kimbrough and Parekh 2007). Increasing nitrate concentrations in rivers, lakes, and groundwater is a significant environmental problem. People who drink water from public and private water systems that are located in areas considered more vulnerable to nitrate contamination are occasionally at risk of exposure to biologically relevant doses of nitrate in their drinking water (U.S. EPA 1990 and U.S. EPA 2002). The health implications of exposure to nitrate in drinking water were first reported in the scientific literature by Comly in 1945. Nitrates, while relatively non-toxic to adults, can be fatal to infants, because they cause methemoglobinemia (also known as “blue baby syndrome”) by interfering with the oxygen-carrying capacity of blood. Anthropogenic activities, such as land disposal of sewage and other waste materials as well as leaching of fertilizers, significantly contribute to the nitrate contamination problem. The maximum contaminant level (MCL) for nitrate in drinking water was set at 10 mg/L nitrate-nitrogen (NO_3-N) or 45 mg/L nitrate (NO_3^-), on the basis of 214 methemoglobinemia cases reported to the American Public Health Association for which nitrate concentration data were available (Walton 1951).

Developing novel technology as well as studying existing technologies is urgent and critical to safeguarding the surface and groundwater for potable uses. Conventional treatments like coagulation, flocculation, sedimentation, and filtration are unable to remove perchlorate and nitrate from water. Advanced treatment techniques, such as reverse osmosis, ion exchange, membrane filtration, and electrodialysis, are effective for removing both anions (Sellers 2007 and Kapoor and Viraraghavan 1997). However, these treatment processes produce waste concentrated wastes or brines containing high levels of perchlorate and nitrate (Motzer 2001 and Kapoor and Viraraghavan 1997). Biological degradation has also been demonstrated to successfully remove perchlorate and nitrate from water. Biological degradation is sensitive to several factors and the reaction rates are slower than those for chemical degradation. Application of biological degradation for drinking water has a public perception problem due to fear of release of bacteria (Sellers 2007 and Kapoor and Viraraghavan 1997). High costs have been associated with several of the treatment technologies listed above, making them uneconomical for full-scale implementation (Sellers 2007 and Kapoor and Viraraghavan 1997).

The use of active metals could be an alternative process for reducing nitrate and perchlorate. The reduction of perchlorate and nitrate using various metals such as titanium, iron and metal alloys has been extensively studied (Theis 2002 and Fanning 2000). Although some literature is available on reduction of nitrate by aluminum (Dash and Chaudhari 2005 and Luk and Au-Yeung 2002), limited literature is available that demonstrates the ability of aluminum to reduce perchlorate. Aluminum is a thermodynamically reactive metal with a strong tendency to act as a reductant, as indicated by its standard reduction potential of 1.66 V. The effectiveness of aluminum, as a reducing agent, is hindered by the barrier oxide film that spontaneously forms on the surface of the metal in air and in aqueous solution. If this passivating oxide layer can be eliminated, then the zero-valent aluminum or univalent dissolved aluminum will be able to reduce the perchlorate and nitrate.

This study focuses on reduction of perchlorate and nitrate through redox reaction with aluminum. Two methods of removing this oxide layer have been employed in this dissertation to study the reduction of perchlorate and nitrate by aluminum. The first method is by controlling the pH of the solution and the second method is by applying a pitting potential to an aluminum electrode.

The specific research objectives to be pursued during the experimental investigation are:

1) Characterize perchlorate and nitrate reduction by aluminum activated by pH change.

   This objective will be accomplished by:

   (i) Examining the influence of pH and aluminum dosage on the reaction using a series of experiments in batch reactors.

   (ii) Determining the rate and order of the redox reactions and the influence of competing anions on the reaction kinetics.

2) Characterize perchlorate and nitrate reduction by aluminum activated by inducing pitting corrosion.

   This objective will be accomplished by:

   (i) Determining the relationship between critical pitting potential of aluminum and concentrations of perchlorate and nitrate in the solution.

   (ii) Examining the influence of pH, chloride concentration and electrode surface area of the reaction.

   (iii) Determining the rate and order of the redox reactions and the influence of competing anions on the reaction kinetics.

Chapter II provides a review of the background information related to contamination of perchlorate and nitrate including aspects such as physical and chemical properties, occurrence, sources, exposure pathways, toxicity, and treatment technologies.

Chapter III describes in detail the experimental methods employed in conducting the research. This chapter has been divided into two sub-parts to address the pH-activated and pitting corrosion experiments, and it documents the experimental procedures for each set of experiments. A detailed description of the methodology including materials, apparatus, and analytical methods is provided to ensure that the work is reproducible and that the appropriateness of the experimental methods can be assessed.

Chapter IV has also been divided into two sub-parts to present the results derived from the pH control and pitting corrosion experiments. Factors affecting the reaction in the pH controlled experiments such as pH and aluminum dosage have been studied along with the kinetic experiments for both perchlorate and nitrate. Factors affecting the reaction in the pitting corrosion experiments such as pH, electrode surface area and current have been studied along with the kinetic experiments for both perchlorate and nitrate. A kinetic model is developed at the end of the chapter and solution to the kinetic model using the data from the kinetic experiments is provided.

Chapter V provides the conclusions drawn from the experimental results and provides recommendations for further study on this subject.

CHAPTER II

BACKGROUND

The background information related to perchlorate and nitrate contamination needs to be reviewed before evaluating a mitigation process. This chapter first discusses the environmental chemistry followed by an investigation of occurrence, source, toxicity mechanism, and treatment technologies, for both perchlorate and nitrate. The last part of this chapter examines the technical considerations related to the proposed research.

2.1 Perchlorate

2.1.1 Physical and Chemical Properties

Chlorine is the 17th element in the periodic table and can either accept one electron to form chloride or lose up to 7 electrons to form oxides. Perchlorate has the highest oxidation state of chlorine (+7) in any chlorine-containing inorganic species (Bard et al. 1985). The standard reduction potentials between these species in acidic and basic solutions are shown in Figure 2.1.

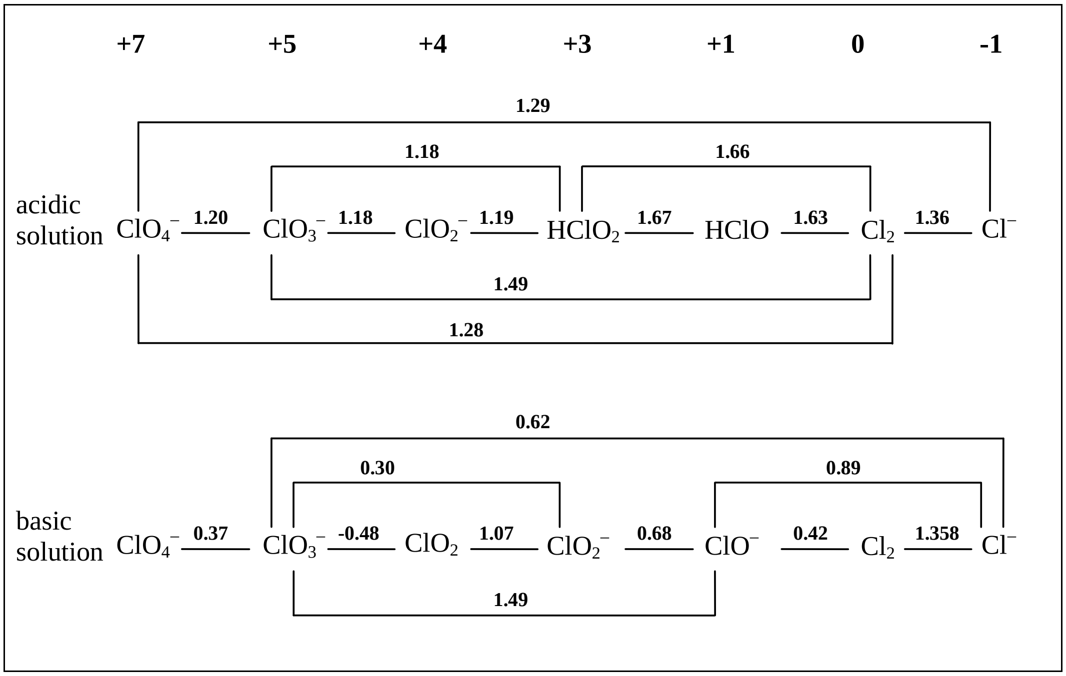

Figure 2.1 Standard reduction potentials of chlorine oxides. (Bard et al. 1985)

Perchlorate ion has a tetrahedral structure, as shown in Figure 2.2, with one chlorine atom in the center and four oxygen atom bonded to it at each corner of the tetrahedron (Urbansky and Schock 1999). The whole species has a delocalized monovalent anionic charge evenly distributed among four oxygen atoms (Gu and Coates 2006). The low charge density and large ionic size of perchlorate ion is responsible for its decreased affinity for cations, making it highly soluble in aqueous and non-aqueous media (Gu and Coates 2006, Hagstrom 1954, Urbansky 1998). Table 2.1 shows the solubility of perchlorate salts in water obtained from Sellers (2007). Inorganic perchlorate salts, with the exception of potassium perchlorate are generally extremely soluble (Urbansky 1998, Gu and Coates 2006, Sellers 2007). Perchlorate ion is the conjugate base of perchloric acid which has a pKa value of -10 (Sellers 2007).

Perchlorate exists in ionic form due to the high dissociation of perchloric acid and high solubility of its salts. Perchlorate is a poor complexing agent (Cotton et al. 1999), which combined with its extremely high solubility in water makes perchlorate a very mobile, persistent contaminant in the environment (Gu and Coates 2006).

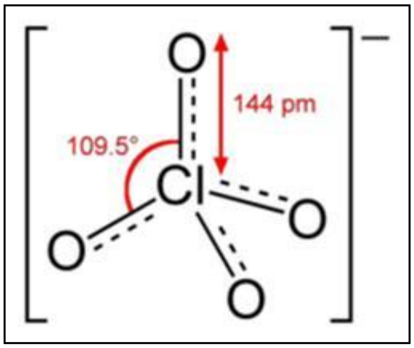

Figure 2.2 Structure and bond length of perchlorate ion.

Table 2.1 Properties of perchlorate salts and perchloric acid (Source: Sellers 2007).

	Ammonium Perchlorate	Potassium Perchlorate	Sodium Perchlorate	Perchloric Acid
Chemical Formula	NH_4ClO_4	$KClO_4$	$NaClO_4$	$HClO_4$
Molecular weight (g/mol)	117.49	138.55	122.44	100.46
Density (g/cm^3)	1.95	2.53	2.52	1.67
Solubility in water (g/L) @25 ºC	200	15	2096	Miscible

Even though perchlorate contains a highly oxidized central halogen atom, it exhibits low reactivity as an oxidant (Urbansky 1998). From a purely thermodynamic standpoint, perchlorate should oxidize water to oxygen while itself being reduced to chlorate or chloride (Gu and Coates 2006). This is evident by examining the standard potentials for the half-reactions shown in Equations 2.1, 2.2 and 2.3. Therefore, it can be concluded that the low reactivity of perchlorate is principally dictated by kinetics rather than thermodynamic stability (Urbansky 1998, Gu and Coates 2006). In fact, Gu and Coates (2006) have suggested that reduction of perchlorate does not occur spontaneously in water because the reaction requires oxygen atom transfer along with electron transfer.

$$\mathrm{ClO_4^- + 8H^+ + 8e^- \leftrightarrow Cl^- + 4H_2O} \qquad \mathrm{E^0 = \ 1.29\ V} \tag{2.1}$$

$$\mathrm{ClO_4^- + 2H^+ + 2e^- \leftrightarrow ClO_3^- + H_2O} \qquad \mathrm{E^0 = \ 1.39\ V} \tag{2.2}$$

$$\mathrm{2H_2O \leftrightarrow 4H^+ + O_2 + 4e^-} \qquad \mathrm{E^0 = -1.23\ V} \tag{2.3}$$

2.1.2 Occurrence

In the past, detection of perchlorate in drinking water was restricted by the limitation of the analytical methods. Analytical methods to detect perchlorate in drinking water have evolved significantly over the past few decades (Urbansky 2000a). A method using ion chromatography developed by the California DHS Sanitation and Radiation Laboratory (SRL) in 1997 (CDHS 1997) was later refined by the USEPA into EPA Method 314.0 (Hautman et al. 1999). With the currently available methods it is possible to detect perchlorate in concentrations of 1 ppb or less (Clewell et al. 2000 and Koester et al. 2000).

Occurrence of perchlorate in the environment is associated to the proximity of the sampling site to military installations and industrial sources that have a history of using perchlorate (Gullick et al. 2001). The relationship between perchlorate manufacture/use location and perchlorate detection in the environment is evident from Figures 2.3 and 2.4.

Several studies have examined the pervasiveness of perchlorate in drinking water sources in US. A study of groundwater and surface water sites in 17 states in US conducted by the American Water Works Service Company in 1997 and 1998 detected perchlorate concentrations equal to or above 4 ppb in groundwater in California and New Mexico (Gullick et al. 2001). An American Water Works Association (AWWA) survey monitoring for perchlorate under the Unregulated Contaminants Monitoring Rule (UCMR) found contamination of drinking water in 26 states and Puerto Rico (Brandhuber and Clark 2005). Jackson et al. (2005) studied of 254 public water supply wells and private wells in nine counties in Texas and found that about two-thirds of the wells had detectable perchlorate concentrations (>0.5 ppb) and a third of the wells had perchlorate concentrations equal to or above 4 ppb. A study conducted at Camp Edwards, Massachusetts Military Reservation identified perchlorate concentrations as high as 174 ppb in the groundwater (Clausen et al. 2004). These studies indicate that perchlorate in drinking water is a pervasive environmental problem that needs to be addressed.

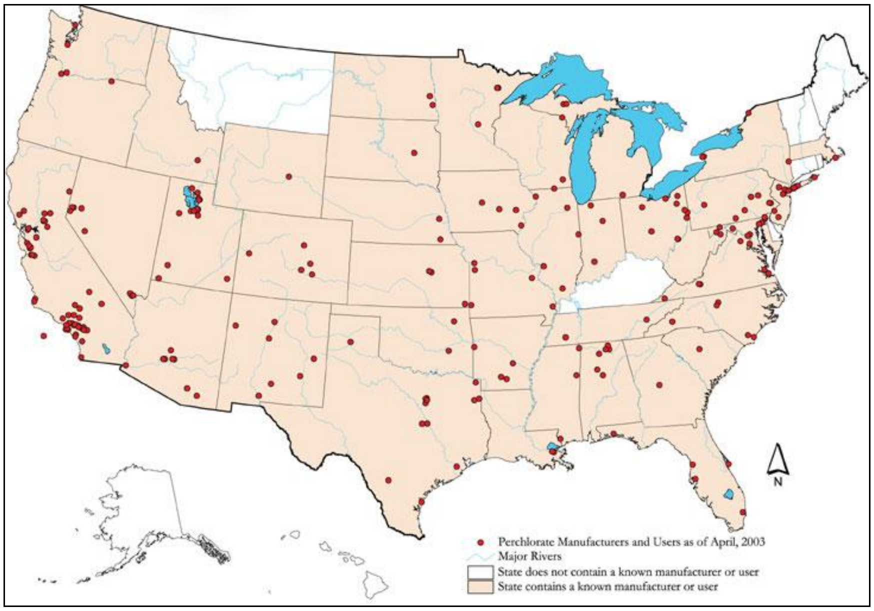

Figure 2.3 Map of perchlorate manufacturers and users in the United States. (Source: U.S. EPA 2003a)

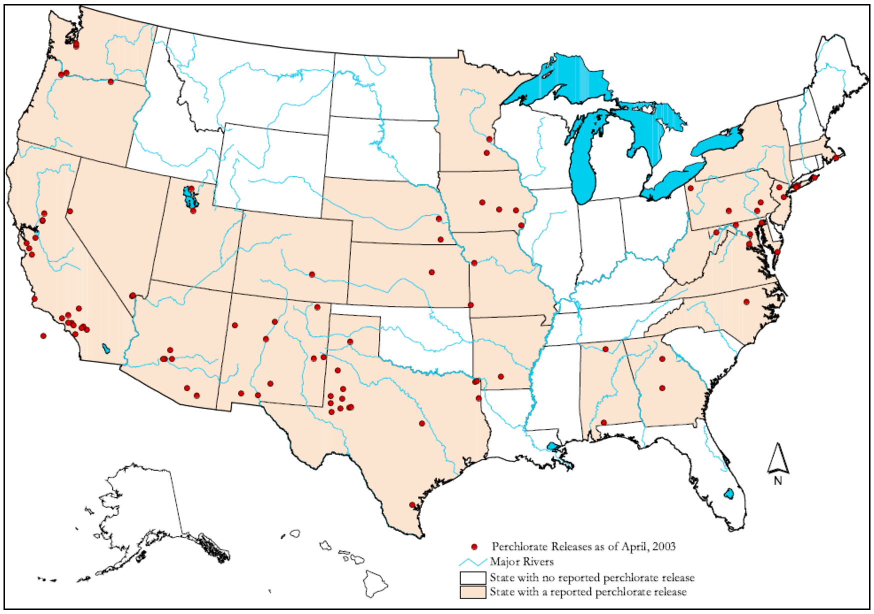

Figure 2.4 Map of perchlorate detection in the environment in the United States. (Source: U.S. EPA 2003b)

2.1.3 Sources

The presence of perchlorate ion in the environment can be attributed to either natural or anthropogenic sources. Natural sources of perchlorate include soils in arid regions derived from ancient marine seabed, and the atmosphere during lightening storms (Sellers 2007). Anthropological sources of perchlorate include the manufacture, use and disposal of perchlorate salts used as oxidants in solid propellants, fireworks, etc.

Perchlorate is one of the naturally formed impurities in sodium nitrate deposits in the Atacama Desert of Northern Chile (Ericksen 1983). Perchlorate concentrations, as high as 500 mg/kg, have been detected in the Bolivian Playa crusts in the Andean high plains (Orris et al. 2003). Perchlorate contamination in public water supply wells in West Texas (20 to 59 ppb) and New Mexico (0.5 to 4 ppb) has been attributed to naturally occurring perchlorate in the soil (Jackson et al. 2004, Jackson et al. 2005 and Sellers 2007). A study by Duncan et al. (2005) suggested that a naturally occurring source of perchlorate is associated with the Mission Valley Formation in San Diego, California. Perchlorate was detected at concentrations of about 280 mg/kg in the evaporative deposits from Searles Lake, California (Orris et al. 2003). All the locations mention above were formerly marine environments that are now located in areas with arid climate.

Recently, a mechanism using atmospheric processes has been suggested in the literature to explain the origin of naturally occurring perchlorate in the environment (Dasgupta et al. 2005, Sellers 2007 and Trumpolt et al. 2005). The mechanism proposes that chloride from the sea or land-based chloride compounds is blown into the atmosphere where it reacts photochemically with atmospheric ozone, in the presence of lightening during thunderstorm, to create perchlorate. Dasgupta et al. (2005) showed that perchlorate is readily formed from chloride aerosol by electrical discharge and by exposing aqueous chloride to high concentrations of ozone. Perchlorate creation by this mechanism is thought to be a relatively slow process. Following atmospheric creation, perchlorate is dissolved in precipitation and deposited onto the soil surface.

Anthropological sources are currently believed to be major contributors of perchlorate contamination in the environment. High concentrations of perchlorate were related to human activities like manufacturing, testing and disposal of solid rocket propellant, industrial preparation or use of perchlorate compounds (Sellers 2007). Traditionally, perchlorate salts like ammonium perchlorate and potassium perchlorate have been used as oxidants in rocket and missile propellants by the Department of Defense (DoD) and the National Aeronautics and Space Administration (NASA). Human activities contributing to perchlorate contamination include manufacture and maintenance of solid fuel for missiles and rockets; manufacture, use, demilitarization and disposal of munitions; flare disposal; use of pyrotechnics; open burning/ open detonation operations for disposal of perchlorate materials; and dye marker disposal and electroplating as an impurity.

Historically, Chilean nitrate fertilizers have been used in the U.S. and throughout the world. Commercial fertilizers produced from Chilean sodium nitrate deposit are known to contain perchlorate (Urbansky et al. 2001). Urbansky (2004) suggested that Chilean nitrate fertilizer can be neglected as a major source of perchlorate contamination, as only 0.2% of the U.S. fertilizer applications use Chilean caliches. Potash, another mineral used in producing fertilizers, is also been known to contain perchlorate (Duncan et al. 2005). Therefore, it is possible that perchlorate is present in commercially available fertilizers in the United States. However, there have been contradictory reports on fertilizers as a source of perchlorate contamination. Susarla et al. (1999) examined five mineral deposits used to manufacture fertilizers and nine commercially available fertilizers and found perchlorate in all of them. On the other hand, a study conducted by Hunter (2001) on 15 fertilizers in the U.S. found no perchlorate in any of the fertilizers investigated. Furthermore, Susarla et al. (2000) and Urbansky (2000b) concluded that the detection of perchlorate in fertilizers were isolated occurrences and were not indicative of a recurring problem.

Perchlorate has also been known to be electrochemically generated in public water supply systems. Jackson et al. (2004) reported that perchlorate contamination in public water supply system in Levelland, Texas was attributed to the cathodic protection system used in the storage tank. However, researchers also pointed out that such a phenomenon is not a common occurrence and was caused due to a malfunction in the cathodic protection system.

2.1.4 Toxicity and Exposure Pathway

Human exposure to perchlorate may come from sources beyond drinking water. Food crops irrigated with water from contaminated sources could accumulate perchlorate. Perchlorate has reportedly been found in soil, food, plants, and animal tissues. A study conducted by the Food and Drug administration (FDA) using 27 types of foods and beverages, estimated total mean population (all persons aged 2 and above) exposure to be 0.053 µg/kg/day (FDA 2007). Several other studies have reported perchlorate levels in dairy milk (Kirk et al. 2003 and Kirk et al. 2005), lettuce (Sanchez et al. 2005a, Sanchez et al. 2005b, Seyfferth and Parker 2007 and Seyfferth et al. 2008), spinach (Sanchez et al. 2005a), collards (Sanchez et al. 2005a), cucumbers (Jackson et al. 2005), tomatoes (Jackson et al. 2005), cantaloupe (Jackson et al. 2005), oranges (Sanchez et al. 2006), grapefruit (Sanchez et al. 2006), soya beans (Yu et al. 2004), and tobacco plants (Ellington et al. 2001). Although concentrations of perchlorate have been detected in the roots, stems, and leaves of several vegetation types, leaves commonly have the highest perchlorate concentrations. Xylem-supplied tissues are thought to be the final perchlorate repository rather than phloem-supplied tissues, such as fruits. This has promoted interest in and concern of perchlorate in the environment among the public and private sectors.

Data from animal studies indicate that perchlorate is readily absorbed from the gastrointestinal tract and distributed systemically with total body water. Results from a study by Sanchez et al. 2008, show detectable perchlorate in all feed products used by the dairy industries of the southwestern United States. These findings suggest that human exposure to perchlorate may come from sources beyond drinking water.

Perchlorate interferes with normal thyroid function by competitively inhibiting iodide uptake into the thyroid gland at the sodium iodide symporter, resulting in decreased circulating blood concentrations of triiodothyronine (T3) and thyroxine (T4) (Wolff 1998).

2.1.5 Treatment Technologies

A practical treatment technology should be cost-effective, acceptable to regulatory agencies and the public, cause no other water quality problems, and not be limited by waste disposal problems. Due to it high solubility in water, perchlorate cannot be removed by conventional filtration, sedimentation or air stripping. Several treatment technologies for removing perchlorate from drinking water have been reviewed in the literature (Urbansky 1998, Urbansky and Schock 1999, and Sellers 2007). Perchlorate remediation techniques can be classified as separation techniques and destruction techniques. Biological reduction, phytoremediation, thermal destruction, composting, chemical reduction, electrochemical reduction, UV-catalyzed reduction and organic ligand-catalyzed metal reduction are some of the techniques being studied for reducing perchlorate (Sellers 2007). Some of the techniques used for separation are ion exchange, adsorption on granular activated carbon, cationic-substance coated material, membrane filtration, capacitive deionization/carbon aerogel (Sellers 2007).

Of the above mentioned processes only ion exchange resins, granular activated carbon, biological fluidized bed reactor and thermal destruction have been implemented on a full-scale at sites (Sellers 2007). The rest of the technologies have either been evaluated on a pilot scale at sites or in laboratory studies (Sellers 2007).

2.2 Nitrate

2.2.1 Physical and Chemical Properties

Nitrogen is the 7th element in the Periodic Table and can either obtain up to three electrons to form ammonium ion or lose up to five electrons to form nitrate. The basic members of nitrogen-containing inorganic anions are nitrate, nitrite, nitrogen gas and ammonium. Nitrate has the highest oxidation state of nitrogen (+5) in the whole family. The reduction potential between these species in acidic and basic solutions is shown in Figure 2.5.

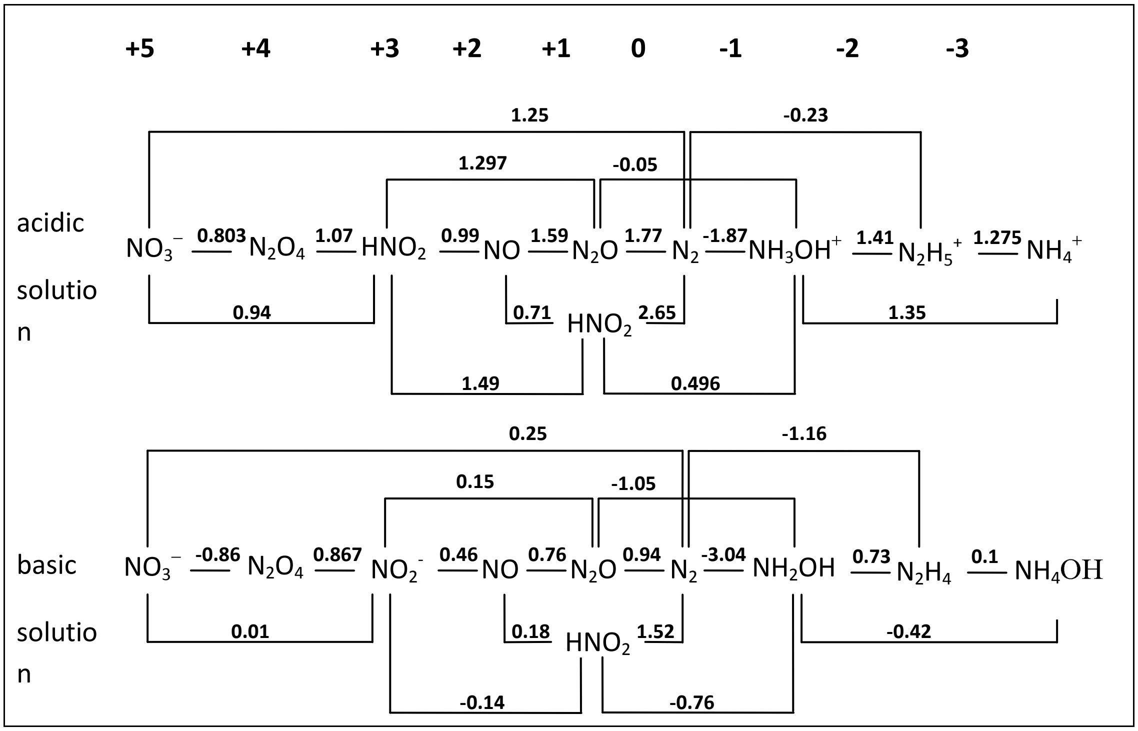

Figure 2.5 Standard reduction potentials of nitrogen oxides. Source: http://www.webelements.com/nitrogen/compounds.html

The chemical structure of nitrate ion is trigonal planar, as shown in Figure 2.6, with one nitrate atom in the center and three oxygen atom bonded to it at the corners. The nitrate ion has a single negative charge and it is distributed with each oxygen atom carrying a −2⁄3 charge and the nitrogen atom carrying a +1 charge.

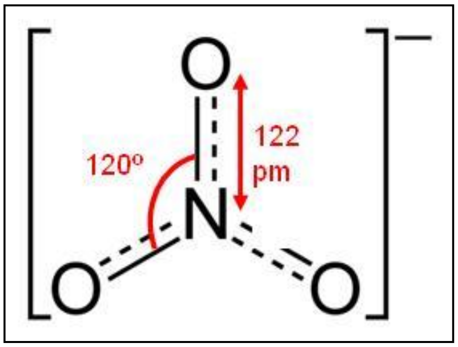

Figure 2.6 Structure and bond length of nitrate ion.

Inorganic nitrate salts are generally very soluble in water (Tables 2.2). The nitrate ion is the conjugate base of nitric acid with a pKa value of -1.3. Nitrate exists in ionic form due to the high dissociation of nitric acid and the high solubility of its salts. Even though nitrate contains a highly oxidized central nitrogen atom it is relatively stable in water with a low potential for coprecipitation or adsorption.

Table 2.2 Properties of nitrate salts (Source: Sellers 2007).

	Ammonium Nitrate	Potassium Nitrate	Sodium Nitrate
Chemical Formula	NH_4NO_3	KNO_3	$NaNO_3$
Molecular weight (g/mol)	80.04	101.10	84.99
Density (g/cm^3)	1.73	2.11	2.26
Solubility in water (g/L) @25 ºC	187	360	921

The standard potentials for the half-reactions involved in the reduction nitrate to ammonium ion are shown in Equations 2.4, 2.5 and 2.6.

$$NO_3^- + 2H^+ + 2e^- \leftrightarrow NO_2^- + H_2O \qquad E^0 = 0.84\ V \tag{2.4}$$

$$NO_2^- + 8H^+ + 6e^- \leftrightarrow NH_4^+ + 2H_2O \qquad E^0 = 0.90\ V \tag{2.5}$$

$$NO_3^- + 10H^+ + 8e^- \leftrightarrow NH_4^+ + 3H_2O \qquad E^0 = 0.88\ V \tag{2.6}$$

2.2.2 Occurrence

Nitrate is the most common chemical contaminant in the world’s groundwater (Spalding and Exner 1993). Nitrate contamination of groundwater and public water sources has been widely studied and reported in US (Kross et al. 1993, Nolan et al. 1997, Gelberg et al. 1999, Squillace et al. 2002) and in the world. Surveys have indentified nitrate concentrations in wells exceeding 10 mg/L NO_3^--N in Alabama (Liu et al. 2005), Iowa (Keeney and Deluca 1993, Kross et al. 1993), and South Dakota (Bhatt 1997). A statewide study conducted in Iowa found that 37 percent of wells had nitrate levels exceeding 3 mg/L NO_3^--N and 18 percent of wells had nitrate levels exceeding 10 mg/L NO_3^--N (Kross et al. 1993). Another study conducted on 419 drinking water wells in upstate rural New York State found detectable levels of nitrate in 95 percent of wells and nitrate levels exceeding the MCL in 16 percent of the wells (Gelberg et al. 1999). A nationwide study of 1255 domestic drinking-water wells and 242 public supply wells, found nitrate levels exceeding 3 mg/L NO_3^--N in 28 percent of the wells, with 136 domestic drinking-water wells and 5 public supply wells having nitrate concentrations exceeding 10 mg/L NO_3^--N (Squillace et al. 2002).

2.2.3 Sources

Nitrogen, an essential nutrient for plant growth, is abundant in the environment. Background nitrate concentrations of less than 5 mg/L NO_3^--N have been observed in surface waters (Fraser et al. 1980). The processes described in the nitrogen cycle maintain nitrogen-containing compounds in the environment in a state of equilibrium. Anthropological activities can disrupt the equilibrium, resulting in increased concentrations of nitrate in drinking water sources. Excessive concentrations of nitrogen-containing compounds in rivers, streams and estuaries can also cause eutrophication that can degrade the water quality and adversely affect the aquatic population. Nitrate contamination of surface and subsurface waters by anthropogenic fertilizers, animal wastes, and atmospheric deposition from nitrogen oxide emission has been well documented in the published literature. Overuse of fertilizers, due to intensive farming operations, has been identified as the major contributor to the high nitrate concentrations observed in the environment (Kladivko et al. 1991, Keeney and Deluca 1993, Spalding et al. 2001, Tomer and Burkart 2003, Elmi et al. 2004, Li et al. 2005, Song et al. 2009). The increasing contamination of municipal and private drinking water sources due to improper management practices like land application of poultry waste, anaerobic swine lagoon effluent and treated municipal wastewater has been well documented (Spalding et al. 1993, Sloan et al. 1999, Elrashidi et al. 2009, Katz et al. 2009, Reichard and Brown 2009). Livestock-feeding operations can also significantly contribute to the contamination of drinking water resources (Levison and Novakowski 2009, Vaillant et al. 2009).

2.2.4 Toxicity and Exposure Pathway

Most studies in the past have attempted to associate drinking-water nitrate levels with incidence or mortality rates in humans due to health conditions like methemoglobinemia in infants (Comly 1945, Ferrant 1946, Cornblath and Hartmann 1948, Donahoe 1949 and Walton 1951), cancers (Ward et al. 1996, Freedman et al. 2000, Weyer et al. 2001, Mueller et al. 2001, De Roos et al. 2003, Ward et al. 2003, Ward et al. 2004 and Coss et al. 2004) and adverse reproductive outcomes. These studies have exhibited diverse results, with a majority of the studies showing no association, some studies showing positive associations, and a few studies even showing inverse associations between risk and nitrate uptake.

Methemoglobinemia in infants is believed to be caused by the free-radical, nitric oxide, produced when nitrate converts hemoglobin in the blood to an abnormal oxidized form known as methemoglobin that cannot bind with oxygen properly. However, recent studies have suggested that this phenomenon may be attributed to bacterial, rather than, nitrate contamination of drinking water (Addiscott and Benjamin 2004 and Fewtrell 2004). It has also been indicated in the literature that nitrite produced from nitrate could react with a secondary amine formed in the stomach during digestion of meat or other protein to produce a carcinogenic N-nitroso compound, and thereby cause stomach cancer (Tannenbaum 1983). Studies conducted on animals have suggested that nitrate, nitrite, and N-nitroso compounds may be transported across the placenta and affect the fetus *in utero*. Epidemiological studies have been conducted to identify existence of correlation between nitrate exposure through drinking water and reproductive effects like birth defects and spontaneous abortions.

Ecological problems associated with excess nitrate in the environment include excessive growth of water plants in freshwater, algal blooms in coastal and estuarine waters and ozone destruction in the stratosphere caused by the release of nitrous oxide (Camargo and Alonso 2006).

2.2.5 Treatment Technologies

Currently, several treatment technologies are available for treating water contaminated with nitrate. Kapoor and Viraraghavan (1997) reviewed various processes used to remove nitrate from drinking water. Some of the common treatment processes they listed include ion exchange, biological denitrification (heterotrophic and autotrophic), combined ion exchange/biological denitrification, chemical denitrification, reverse osmosis, electrodialysis, and catalytic denitrification. Of the above mentioned processes, only ion exchange, biological denitrification, and reverse osmosis have been applied at full scale for nitrate removal. Even though ion exchange presents an attractive alternative for nitrate removal from water with low concentrations of total dissolved solids and organic matter, there are several problems associated this process including disposal of spent regenerant brine, fouling of resin, and corrosivity of the product water. Reverse osmosis is another process that has been shown to be effective for removing nitrate from water with low organic matter. However, reverse osmosis is an expensive process and requires disposal of water with high concentrations of total dissolved solids. Biological denitrification requires close monitoring, has extended start-up periods and requires further treatment to remove microorganisms. The other processes mentioned in literature have not been applied at full scale; however, electrodialysis has potential for full-scale application.

2.3 Reduction of Perchlorate and Nitrate Using Aluminum

2.3.1 Aluminum

Aluminum is the 13th element in the Periodic Table and can lose up to 3 electrons to form monovalent or trivalent aluminum ion. Equation 2.7 shows that aluminum has a standard reduction potential of –1.68 volts, indicating that it is a very good reducing agent.

$$\mathrm{Al}^{3+} + 3\mathrm{e}^- \leftrightarrow \mathrm{Al}^0 \qquad\qquad \mathrm{E}^0 = \ -1.68\ \mathrm{V} \tag{2.7}$$

Aluminum is far more active than iron, which has a standard reduction potential of –0.44 volt. However, it is a well known fact that iron is highly susceptible to corrosion, while aluminum resists corrosion in most environments. Aluminum owes its excellent corrosion resistance to the barrier oxide film that is bonded strongly to its surface, protecting it from further reaction. If the passivating oxide layer is removed, then the underlying aluminum would reduce perchlorate and nitrate in the solution.

2.3.2 Passivating Oxide Layer

2.3.2.1 Characteristics of the Oxide Layer

The passivating oxide film on aluminum surface is about 5 nm (50 Å) thick when formed in air and more than 10 nm thick when formed in water (Davis 1999, Phambu 2003, Cabrera and Mott 1949). Bayerite is the predominant form of aluminum oxide films formed at ambient conditions and is generally amorphous and deficient in aluminum (Davis 1999, Jeurgens et al. 2002, Phambu 2003). The oxide film is in a state of dynamic equilibrium between forces that tend to form the compact layer and those that tend to break it down. In the absence of a strong disruptive force, the film has a tendency to mend itself when damaged (Davis 1999). The oxide film formed on aluminum surface is composed of two layers (Davis 1999). The inner oxide layer next to the metal is a compact amorphous barrier layer, whose thickness is dependent on temperature of the environment. An outer layer of thicker, more permeable hydrated oxide covers the barrier layer. Vrublevsky et al. (2005) observed that anodically formed oxide layers tend to have more than one layer based on the dissolution rate. The innermost layer in such films tends to have the lowest dissolution rate (Vrublevsky et al. 2005, Vrublevsky et al. 2006, Vrublevsky et al. 2007). Carrier et al. (2007) observed that the anodically formed aluminum oxide film is converted to gibbsite in the acidic pH range, and bayerite in the neutral and alkaline pH range.

The Pourbaix diagram used to express the conditions for the thermodynamic stability of the oxide film, shows that aluminum is protected by its oxide film (or is passive) in the pH range of about 4 to 8.5 (Figure 2.7). However, the protective oxide film is known to be stable in aqueous solutions in the pH range of 4 to 10 (Kolics et al. 2001).

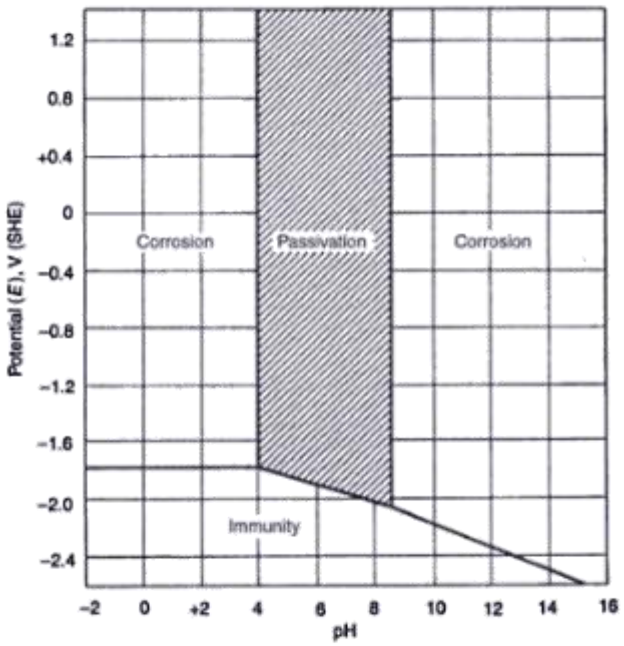

Figure 2.7 Pourbaix daigram showing the conditions of thermodynamic stability of aluminum oxide. (Davis 1999)

This thermodynamic stability of the oxide layer is dependent on temperature, characteristics of oxide film, and presence of substances that can form soluble complexes or insoluble salts with aluminum (Graedel 1989). Outside the passive range, oxides of aluminum are readily soluble in strong acids and bases (Figure 2.8). Dissolution of the aluminum oxide film yields Al^{3+} ions in acids and AlO^{2-} ions in bases (Davis 1999).

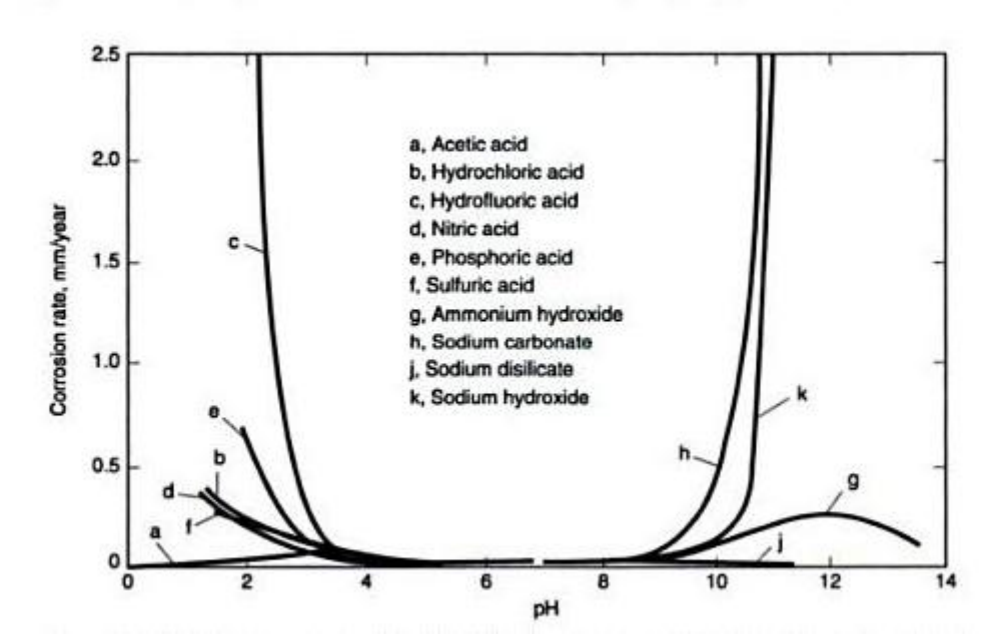

Figure 2.8 Effect of pH on corrosion of aluminum alloy (1100-H14) by various acids and bases. (Davis 1999)

Other factors that amplify the dissolution rate of the oxide layer are presence of dissolved oxygen and aggressive anions. The addition of anions like nitrate and nitrite seem to have an inhibiting effect on the corrosion of aluminum, while addition of halides result in acceleration of corrosion (Khalil et al. 2003). Sulfates had no significant effect on the corrosion behavior of aluminum (Khalil et al. 2003).

2.3.2.2 Oxide Layer Removal by pH Activation

As discussed in the previous section of this chapter, the dissolution of the barrier layer on the aluminum surface is dependent on the pH of the solution. The oxide layer formed on the aluminum surface can be removed by a localized corrosion process that involves three distinct processes. The reactive anions in the bulk solution are adsorbed on the oxide film, where they react with the aluminum ion in the aluminum oxide lattice to form a soluble oxide layer that is removed by dissolution (Foley 1986). Several anions including chloride, sulfate, perchlorate and nitrate have been reported to be absorbed into the oxide layer (Augustynski 1978, Horanyi and Joo 2000, Kolics et al. 1998). Hydroxide ions and chloride ions are also known to form strong complexes with aluminum ions and will react with the oxide layer. Therefore, aluminum will dissolve in concentrated solution of hydrochloric acid and sodium hydroxide. Immersion of aluminum in sodium chloride solution will result in the dissolution of the surface oxide layer due to formation of a soluble chloride-complex (Cheng et al. 2003). The aluminum oxide film dissolution is pH-dependent and increases with a decrease in pH below 4 or with an increase in pH above 10 (Kolics et al. 2001).

Another important consideration is the anomalous behavior of aluminum during dissolution resulting in formation of monovalent aluminum as an intermediate (Drazic 2005). Monovalent aluminum could react with oxyanions and bring about their reduction (Raijola and Davidson 1956). Perchlorate and nitrate reduction by aluminum has been reported in literature to form chloride and ammonia, respectively (Epelboin et al. 1958, Lang and Horanyi 2003, Murphy 1991, Gu and Coates 2006, Polatides and Kyriacou 2005). Chemical reduction of nitrate using zero-valent aluminum has been observed to occur in high-pH environments (Murphy 1991, Luk and Au-Yeung 2002). Electrochemical reduction of nitrate has also been reported in literature (Dash and Chaudhari 2005). Painot and Augustynski (1975) reported the ability of zero-valent aluminum to reduce perchlorate to chloride.

2.3.2.3 Oxide Layer Removal by Electrochemically Induced Pitting Corrosion

Pitting corrosion is a two-stage process that involves initiation of pit formation in the oxide layer and subsequent growth of the pits (Szklarska-Smialowska 1986). Pit formation is started by the formation of metastable pits that are very small in size and grow and repassivate in less than a few seconds. Pit formation on the surface oxide film is dependent on the presence of aggressive anions, such as, chloride (McCafferty 2003, Pyun and Lee 2001, Van Gheem et al. 2002, Drazic et al. 1983, Tomcsanyi et al. 1989). The action of these aggressive anions can be described by either intrusion into the oxide film to form soluble complexes; adsorption onto the oxide layer resulting in thinning of the film; or hindering of the oxide film recovery process (Frankel 1998). Pit growth will be observed when the pH and aggressive anion content in the pits is sufficiently high. The pits grow in the downward direction in the presence of nitrate and in the lateral direction in the presence of sulfate (Pyun et al. 2001). Pit initiation and growth is also affected by potential, temperature, metal composition and presence of other anions (Szklarska-Smialowska 1986, Bohni and Uhlig 1969). The applied potential at which stable pits are formed on the aluminum surface is called its pitting potential and is dependent on the concentration of anions in the bulk solution. The relationship between pitting potential of aluminum and solute concentrations of perchlorate, nitrate and chloride has been extensively studied (McCafferty 2003, Breslin et al. 1994, Amin et al. 2006, Burstein and Organ 2005). Once stable pits are formed, perchlorate and nitrate can react with the zero-valent or monovalent aluminum to form chloride and ammonia, respectively. Reduction of perchlorate and nitrate using electrochemical processes has been reported by several researchers (references in Szklarska-Smialowska 1986, Li et al. 2004, Polatides and Kyriacou 2005).

CHAPTER III

MATERIALS AND METHODS

This chapter is devised to help the reader understand the experimental details of the research. A detailed description of the methodology is provided to ensure that the work is reproducible and the appropriateness of the research can be assessed. The description includes information on chemicals and apparatus used, as well as, the experimental and analytical methods employed.

3.1 Chemicals

Deionized water (>18 MΩ-cm) was used in this study during all experimental procedures and was obtained using a water purification system (Water Pro Plus, LABCONCO). Sodium perchlorate (98+%, Sigma-Aldrich) and sodium nitrate (99%, Sigma-Aldrich) were used in this research as the source of the target contaminants. Aluminum granules (99+%, -10+60 mesh, Aldrich) used in the chemical reduction experiment were obtained from Aldrich. Aluminum sheets (ESPI) were used as the working electrodes for the electrochemical reduction experiments. Hydrochloric acid, nitric acid, sulfuric acid and hydrofluoric acid were used in the procedure for synthesizing four types of acid washed aluminum granules. Hydrochloric acid (36.5-38%, ACS, EM Science) and sodium hydroxide (10N, Aldrich) used for pH adjustment were trace metal grade.

Chlorite, chloride, chlorate and perchlorate concentrations were measured using the DX-500 ion chromatography system for which the two eluents were prepared using sodium hydroxide (10 N, Aldrich). Standards for chlorite, chloride, chlorate and perchlorate used to calibrate this system were obtained from ULTRA Scientific, RI.

Chloride, nitrite and nitrate concentrations were measured using the DX-80 ion chromatography system. The eluent was prepared with AS14A eluent concentrate (Dionex) and the regenerant was prepared from concentrated sulfuric acid (95-98%, ACS, EM Science). The seven anion standard II combined standard (Dionex) was used for the calibration.

Ammonia was formed as the final product of nitrate reduction and its concentrations were measured by the phenate method (APHA et al. 1995) using the following chemicals: phenol (liquefied, min. 88%, EMD), ethanol (99.5%, Sigma Aldrich), sodium nitroferricyanide (III) (dihydrate, 99%, Sigma), sodium citrate (dihydrate, 99.9%, ACS, EMD), and sodium hypochlorite (5% w/w, certified traceable to NIST, VWR). Ammonia standards for the phenate method were prepared using ammonium chloride (99.8%, ACS, EM).

3.2 Experimental Reactor Systems

3.2.1 pH-Activated Experiments

Three types of completely mixed batch reactor systems were used for experiments that investigated chemically induced removal of the oxide layer on aluminum. One set of experiments evaluated optimum conditions and the other measured reaction kinetics.

3.2.1.1 Optimum Conditions Experiments

The experiments to determine the optimum pH and aluminum dosage used two types of completely mixed batch reactor systems. A 25-mL polypropylene bottle having an effective solution volume of 20 mL (Figure 3.1 (a)) was used as a reactor in the first three repetitions of experiments. The reactor was placed in an orbital shaker (Lab-Line Orbit Environ-Shaker, Model # 3948, Lab-Line Instruments Inc., Melrose Park, IL) that maintained the temperature of the solution in the reactor at 25 °C and kept the aluminum granules suspended by operating at 300 rpm.. The fourth repetition of the experiments was carried out in a 25-mL glass bottle with a septum cap having an effective solution volume of 20 mL (Figure 3.1 (b)). During the reaction, the suspension of acid-washed aluminum granules was continuously mixed using a magnetic stirrer (15 mm × 1.5 mm × 1.5 mm, VWR) at 300 rpm. The gas evolved during the reaction was collected using a 12-mL syringe and stored in a graduated cylinder that had been filled with water and inverted in a water bath.

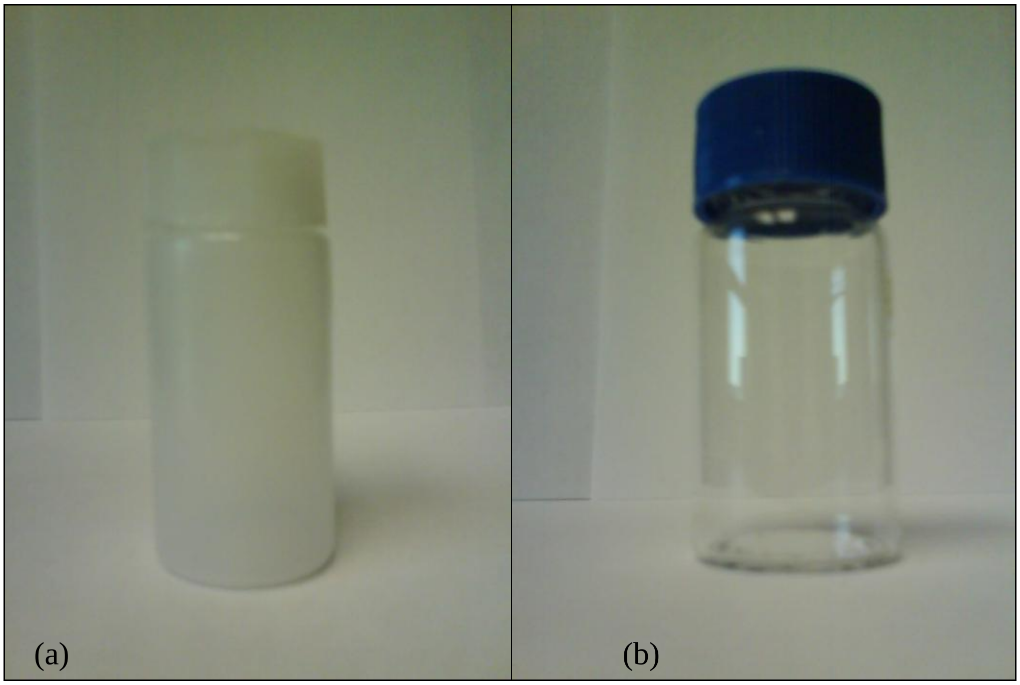

Figure 3.1 Reactors used to determine optimum conditions in pH-activated experiments. (a) 25-mL polypropylene bottle. (b) 25-mL glass bottle with a septum cap.

3.2.1.2 Kinetic Experiments

The kinetic experiments were conducted in 250-mL polypropylene bottles with an effective solution volume of 200 mL (Figure 3.2). An orbital shaker (Lab-Line Orbit Environ-Shaker, Model # 3948, Lab-Line Instruments Inc., Melrose Park, IL) with temperature control maintained the temperature of the solution in the reactor at 25 °C and kept the aluminum granules suspended by operating at 300 rpm.

Figure 3.2 Reactor (250-mL polypropylene bottles) used to determine kinetic parameters in the pH-activated experiments.

3.2.2 Electrochemically Induced Pitting Corrosion Experiments

A diagrammatic illustration of the reactor setup used in electrochemically induced pitting corrosion experiments is provided in Figure 3.3. All electrochemical experiments were conducted in a 1-L flat-bottom corrosion flask (Princeton Applied Research, TN) with an effective solution volume of 500 mL. The reactor incorporated a three-electrode configuration consisting of a working electrode, a counter electrode and a modified saturated calomel reference electrode that was guided by a salt bridge. The working electrode was an aluminum electrode (1 mm thick) and the counter electrode was a platinum mesh (2 cm × 2 cm).

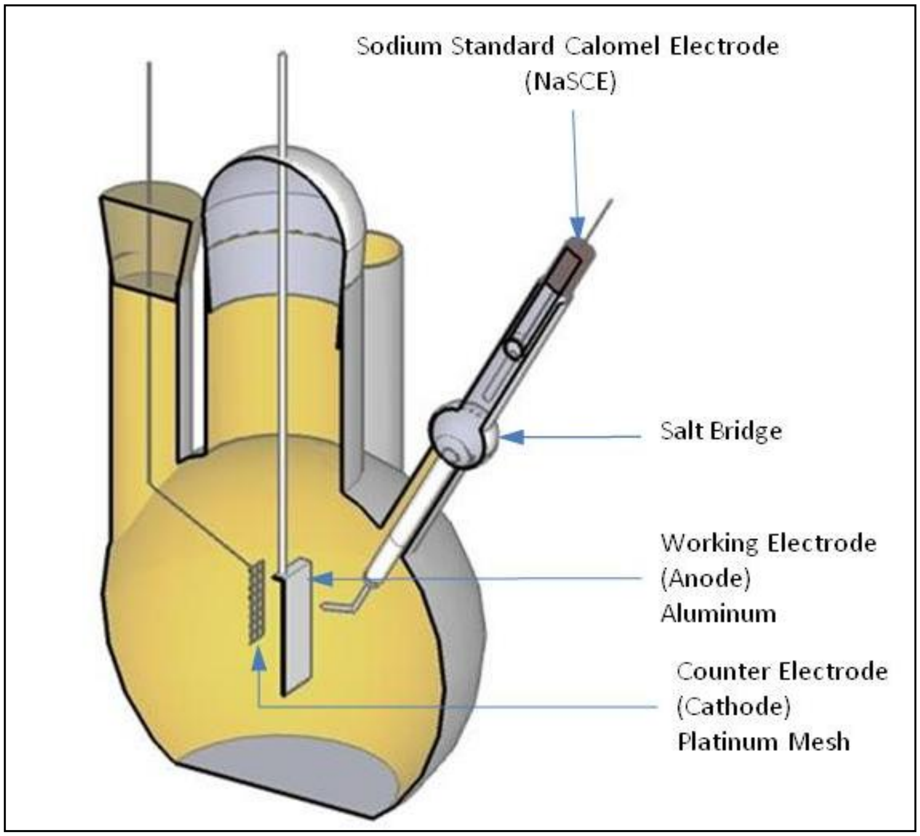

Figure 3.3 Diagrammatic illustration of the reactor setup used in electrochemically induced pitting corrosion experiments.

The salt bridge and reference electrode of the modified saturated calomel reference electrode were filled with saturated sodium chloride solution instead of potassium chloride to avoid possible precipitation of $KClO_4$ in the vycor tips (Bioanalytical Systems Inc., IN) of both the salt bridge and the reference electrode (Brown, 1986). The potential of the modified saturated calomel reference electrode, written as NaSCE, is 9 mV positive of SCE at 30 °C (Brown, 1986). The vycor tips for both the NaSCE and the salt bridge along with the saturated sodium chloride solution contained in them were replaced after each experiment. Electrochemical potential and current was measured and controlled using a potentiostat (Solartron Analytical, Model PW 18-1.8AQ). The cell was gently mixed (60 rpm) by a magnetic stir bar (25 mm × 5 mm × 5 mm, VWR) to reduce the accumulation of solid aluminum oxide or hydroxide on the anode surface.

3.3 Analytical Methods

Samples were collected from the reactors with 12-mL disposable syringes and filtered through 0.22-μm nylon membrane filter (MAGNA, GE Water & Process Technologies) before conducting any analytical procedures. The pH measurements were made using an Orion pH probe along with a pH meter (Orion model 720A) that was calibrated with a three-point method at pH 4, 7 and 10.

3.3.1 Perchlorate Analysis

Perchlorate and its degradation products (Cl^-, ClO_2^-, and ClO_3^-) were measured using a DX-500 ion chromatograph system (Dionex, Sunnyvale, CA) consisting of a GP-40 gradient pump, AS-40 automated sampler, CD-20 conductivity detector, and LC-10 chromatography enclosure equipped with a rear loading injection valve. Separations were carried out using a Dionex IonPac AS-16 (250×4.0 mm) anion-exchange analytical column, an IonPac AG-16 (50×4.0 mm) guard column, and an ASRS-Ultra 4-mm self-regenerating suppressor. The two eluents (10 mM NaOH and 50 mM NaOH) were prepared by mixing 2 mL and 11 mL, respectively, of 10 N NaOH with 2 L deionized water. The sodium hydroxide eluent flow rate was 1.25 mL min^{-1} with a concentration program of concentration being constant at 10 mM for 8 min, concentration increasing at a rate of 80 mM min^{-1} for 0.5 min, concentration being constant at 50 mM for 13 min, concentration decreasing at a rate of 80 mM min^{-1} for 0.5 min, and concentration held constant at 10 mM for 18 min to allow for equilibration before the next sample injection. A 25-μL injection loop was used to analyze the samples. All data were collected and analyzed using a Dionex PeakNet chromatography workstation.

3.3.2 Nitrate Analysis

A DX-80 IC system (Dionex, Sunnyvale, CA) was used for determining concentrations of nitrate, nitrite and chloride. Separations on this instrument were carried out using a Dionex IonPac AS14A (150×3.0 mm) analytical column and an IonPac AG14A (30×3.0 mm) guard column along with an AMMS-III 2mm suppressor. The system used a DS-5 model detection stabilizer. The eluent flow rate was 0.5 mL min^{-1} and a 10-μL injection loop was used. The eluent (8.0 mM Na_2CO_3/1.0 mM $NaHCO_3$) was prepared by diluting the AS14A eluent concentrate (Dionex) and the regenerant (50 mN H_2SO_4) was prepared by mixing 2.8 mL of concentrated sulfuric acid (10 N, Aldrich) in 2 L deionized water. All data were collected and analyzed using a Dionex PeakNet chromatography workstation.

3.3.3 Ammonia Analysis

The phenate method (APHA et al. 1995) was used to measure the concentration of ammonium produced by nitrate reduction. Ammonium stock solution was prepared by dissolving 3.819 g ammonium chloride in 1 L deionized water. Standards were prepared by diluting the stock ammonium solution to concentrations of 0.5, 0.3 and 0.1 mg/L of NH_3-N. The samples were diluted using deionized water to 5% of the original concentration. An aliquot (2.5 mL) of the diluted sample was mixed with 0.1 mL of phenol solution, 0.1 mL of sodium nitroprusside and 0.25 mL oxidizing solution. This mixture was allowed to sit in light for 2 hours to develop a stable color. The intensity of the color was measured using a UV-VIS spectrophotometer (Agilent Model 8453) at 640 nm.

3.4 Experimental Details

3.4.1 pH-Activated Oxide Layer Removal Experiments

Experiments were conducted to study the effect on reduction of perchlorate and nitrate of chemically removing the passivating oxide layer from the aluminum surface by changing the solution pH. First, some preliminary experiments were conducted to determine the type and concentration of acid that would be used for washing the aluminum granules and that could effectively remove the oxide layer from the surface. Separate studies were conducted to examine the reduction of perchlorate and nitrate.

3.4.1.1 Effect of Acid Washing on Reducing Ability of Aluminum

Hydrochloric acid, nitric acid, sulfuric acid and hydrofluoric acid were examined as possible alternatives for removing the oxide layer on aluminum granules. The procedure described in the next paragraph was carried out with each of the acids to obtain four separate batches of aluminum granules washed with hydrochloric acid, nitric acid, sulfuric acid or hydrofluoric acid. The control was provided by aluminum granules that were not acid washed.

Concentrated acid was slowly added to a 1,000-mL glass beaker containing aluminum granules (10 g) and the suspension was mixed with a magnetic stirrer in a fume hood under ambient conditions. Immediate evolution of fumes was observed. A small amount of distilled water was quickly added to dissipate heat and the suspension was stirred for 60 seconds. The acid washed aluminum granules were then rinsed 25 times with 1 L deionized water to remove any residual ions. The granules were then put in an aluminum dish, covered with a glass dish and dried in an oven at 100 ºC.

Fifteen reactors (250-mL, polypropylene bottles) were each filled with 200 mL of 1-mM nitrate solution that was adjusted to pH 12 using sodium hydroxide. Aluminum granules (approximately 1 g) from each of the four different acid washes were added to separate reactors. The aluminum granules that were not acid washed were added to a reactor for use as control. The reactors were stirred using magnetic stirrers and samples were collected from each of the reactors after 0, 10, 20, 30 and 60 minutes reaction and were analyzed for nitrate.

The results of these experiments are described in section 4.1.1 and they indicated that hydrochloric acid was best suited for acid washing of aluminum granules. Therefore, aluminum granules pretreated by washing with concentrated hydrochloric acid were used in other experiments to evaluate chemically induced oxide layer removal.

3.4.1.2 Perchlorate Reduction Experiments

This section describes the experiments conducted to determine the optimum pH and aluminum dosage and to determine the kinetic parameters for the reduction of perchlorate by aluminum granules.

3.4.1.2.1 Optimum pH

A bulk solution having a perchlorate concentration of 0.2 mM was prepared and the solution was adjusted to pH 1. The bulk solution was then divided into nine equal portions and the pH of each portion was adjusted using NaOH to achieve a range of values (2.8, 3, 3.5, 4, 5, 7, 9, 11 and 13). This ensured a uniform chloride concentration in all reactors. Approximately 1 g of acid-washed aluminum granules was added to each reactor and the reactors were placed in a shaker for 2 days. Samples were collected before adding the aluminum granules and after 2 days reaction and they were analyzed for pH, chlorite, chloride, chlorate and perchlorate. Four replicate runs were conducted, including one run to determine the amount of hydrogen gas evolved.

3.4.1.2.2 Optimum Aluminum Dosage

A perchlorate bulk solution (0.2 mM) was prepared and the solution was adjusted to pH 2.8. The aluminum dosages used during this experiment were 464, 695, 928, 1159, 1391, 1622, and 1855 mM. After acid-washed aluminum granules were added to the reactors, the reactors were placed in the orbital shaker for two days. Samples were collected before adding the aluminum granules and after 2 days reaction and analyzed for chlorite, chloride, chlorate and perchlorate. Four repetitions were conducted for each aluminum dosage, including one run to determine amount of hydrogen gas evolved.

3.4.1.2.3 Kinetic Experiments

These experiments were conducted in triplicates. A 0.2 mM perchlorate solution was prepared and the solution pH was adjusted to 2.8. An aluminum dosage of 2800 mM was attained by adding 15 g aluminum granules to each reactor. The reactors were placed in the orbital shaker for two days. The pH of the solution in the reactors was measured. Separate sampling intervals were used for each reactor. Samples were collected from the first reactor at t = 0, 1, 4, 7, 10, 13, 16, 20, 32, and 48 hours. Samples were collected from the second reactor at t = 0, 2, 5, 8, 11, 14, 17, 22, 32, and 48 hours. Samples were collected from the third reactor at t = 0, 3, 6, 9, 12, 15, 18, 24, 32, and 48 hours.

After observing the results of the first experiment, it was decided to repeat the experiment with shorter sampling intervals.

3.4.1.3 Nitrate Reduction Experiments

Experiments conducted to study the reduction of nitrate by aluminum granules are described in this section. The experiments to determine optimum pH and aluminum dosage for reduction of nitrate were conducted first and were followed by experiments to determine the kinetic parameters for the reduction of nitrate by aluminum granules.

3.4.1.3.1 Optimum pH

A bulk solution having a nitrate concentration of 1 mM was prepared and the solution was adjusted to pH 1 using concentrated hydrochloric acid. The bulk solution was then divided into thirteen equal portions and the pH of each portion was adjusted by addition of NaOH to achieve a range of values (0.9, 1.5, 2, 2.5, 3.1, 5.5, 7.3, 9.3, 11.2, 11.5, 12.1, 12.6, and 13). This ensured a uniform chloride concentration in all reactors. Approximately 0.2 g of acid-washed aluminum granules was added to each reactor and the reactors were placed in a shaker for 1 hour. Samples were collected before adding the aluminum granules and after 1 hour and analyzed for pH, nitrate, nitrite, ammonia and chloride. Four repetitions were conducted for each pH condition, including one run to determine the amount of hydrogen gas evolved.

3.4.1.3.2 Optimum Aluminum Dosage

Nitrate bulk solution (1 mM) was prepared and the solution was adjusted to pH 13. The aluminum dosages used during this experiment were 4, 19, 47, 70, 79, 94, 116, 139, and 380 mM. After addition of acid-washed aluminum granules, the reactors were placed in the orbital shaker for one hour. Samples were collected before adding the aluminum granules and after 1 hour and analyzed for nitrate, nitrite, ammonia and chloride. Four repetitions were conducted for each aluminum dosage, including one run to determine the amount of hydrogen gas evolved.

3.4.1.3.3 Kinetic Experiments

These experiments were conducted in triplicates. A 1 mM nitrate solution was prepared and the solution pH was adjusted to 13.2. An aluminum dosage of 185 mM was attained by adding 1 g aluminum granules to each reactor. The reactors were placed in the orbital shaker for two days and then the pH of the solution in the reactors was measured. Samples were collected from the first reactor at t = 0, 2, 8, 14, 20, 26, 32, 38, 44, 50, and 56 minutes. Samples were collected from the second reactor at t = 0, 4, 10, 16, 22, 28, 34, 40, 46, 52, and 58 minutes. Samples were collected from the third reactor at t = 0, 6, 12, 18, 24, 30, 36, 42, 48, 54, and 60 minutes.

3.4.2 Electrochemically Induced Pitting Corrosion Experiments

These experiments were conducted to study the reduction of perchlorate and nitrate by aluminum using electrochemically induced pitting corrosion of aluminum to remove the passivating oxide layer. Experiments were carried out to determine the critical pitting potential of aluminum in solutions with a range of concentrations of chloride, perchlorate and nitrate. Experiments were carried out to determine the kinetic parameters, as well as to determine the effect of current, electrode surface area and solution pH on the reduction of perchlorate and nitrate by aluminum.

The aluminum sheets that were used as the working electrode were washed with acetone to remove organic impurities, rinsed with deionized water, dried at room temperature in a desiccator and weighed before starting the experiments. The same procedure was repeated to obtain the weight of the electrode after completion of the experiment.

3.4.2.1 Critical Pitting Potential

Pitting potentials for aluminum were determined with different concentrations of chloride (0.1, 1, and 10 mM), perchlorate (0.2, 1, 2, 5, and 10 mM) and nitrate (1, 5, and 10 mM). Experiments were conducted in triplicate for each electrolyte concentration.

Pitting potential was measured by the potentiodynamic polarization method in which an open-circuit potential was applied for one minute followed by a potentiodynamic scan from -1 V to 3 V at a scan rate of 1 mV/s. Potential was measured between the aluminum working electrode and the modified saturated calomel reference electrode. Pitting potential was determined as the potential at which current began to increase rapidly. Aluminum sheets were cut to a size of 1.5 cm × 3 cm for the experiment. The working electrode had an effective surface area of 9 cm^2. The potentiodynamic scan took 1 hour. Samples of the electrolyte were collected before and after the scan, filtered and analyzed for chloride, perchlorate or nitrate. The pH of the sample collected from the reactor was measured.

3.4.2.2 Perchlorate Reduction Experiments

Effects of current, electrode surface area and initial solution pH on the reduction of perchlorate by aluminum were examined by conducting kinetic experiments.

3.4.2.2.1 Effect of Current

Three currents (10, 50, and 100 mA) were examined in this set of experiments. Aluminum sheets were cut to a size of 4.5 cm × 4 cm to give a working electrode with an effective surface area of 36 cm^2. The solution in the cell had an initial perchlorate concentration of 1 mM and was adjusted to pH 7. Experiments were conducted by applying the appropriate current between the working electrode and the counter electrode. The pH and concentrations of chlorite, chloride, chlorate and perchlorate in the reactor were monitored.

3.4.2.2.2 Effect of Electrode Surface Area

The effects of two effective surface areas (18 and 36 cm^2) for the working electrode were examined in this experiment. The solution in the cell had an initial perchlorate concentration of 1 mM and was adjusted to pH 7. A current of 50 mA was applied between the working and counter electrode for 24 hours. The pH and concentrations of chlorite, chloride, chlorate and perchlorate in the solution were monitored.

3.4.2.2.3 Effect of pH

The effect of initial solution pH at three values (3, 7, and 13) was examined in this set of experiments. The solution in the cell had an initial perchlorate concentration of 1 mM. Aluminum sheets were cut to a size of 4.5 cm × 4 cm to give a working electrode with an effective surface area of 36 cm^2. A current of 50 mA was applied between the working and counter electrode for 24 hours. The pH and concentrations of chlorite, chloride, chlorate and perchlorate in the reactor were monitored.

3.4.2.3 Nitrate Reduction Experiments

Effects of current, electrode surface area and initial solution pH on the reduction of perchlorate by aluminum were examined by conducting kinetic experiments.

3.4.2.3.1 Effect of Current

Three currents (10, 20, and 50 mA) were examined in these experiments. Aluminum sheets were cut to a size of 1.5 cm × 3 cm to give a working electrode with an effective surface area of 9 cm^2. The solution in the cell had an initial nitrate concentration of 1 mM and was adjusted to pH 7. Experiments were conducted by applying the appropriate current between the working electrode and the counter electrode. The pH and concentrations of nitrate, nitrite and ammonia in the reactor were monitored.

3.4.2.3.2 Effect of Electrode Surface Area

The effect of effective surface area (9 and 18 cm^2) for the working electrode was examined in this experiment. The solution in the cell had an initial nitrate concentration of 1 mM and was adjusted to pH 7. A current of 50 mA was applied between the working and counter electrode for 24 hours. The pH and concentrations of nitrate, nitrite and ammonia, in the reactor were monitored.

3.4.2.3.3 Effect of pH

The effect of initial solution pH (3, 7, and 13) was examined in this set of experiments. The solution in the cell had an initial perchlorate concentration of 1 mM.

A current of 50 mA was applied between the working and counter electrode for 24 hours. Aluminum sheets were cut to a size of 1.5 cm × 3 cm to give a working electrode with an effective surface area of 9 cm^2. The pH and concentrations of nitrate, nitrite and ammonia in the reactor were monitored.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter presents the results of the experiments described in Chapter III.

4.1 pH-Activated Oxide Layer Removal Experiments

4.1.1 Effect of Acid Washing on Reducing Ability of Aluminum

Pretreating zero-valent aluminum granules by washing them with a strong acid can cause damage to the oxide layer creating additional reaction sites for reducing perchlorate or nitrate. These experiments evaluated the ability of aluminum granules to reduce nitrate after being pretreated with different concentrated acids (hydrochloric, sulfuric, nitric, hydrofluoric). The control experiment used aluminum granules as provided by the manufacturer without any pretreatment.

A series of tests was performed for 1 hour in 250-mL reactors having an effective solution volume of 200 mL filled with 1 mM nitrate solution that was adjusted to pH 12 using sodium hydroxide. Aluminum granules (approximately 1 g) after pretreatment with each of the four different acids and the control were added to separate reactors. The reactors were stirred using magnetic stirrers and samples were collected from each of the reactors after 0, 10, 20, 30 and 60 minutes reaction and were analyzed for nitrate. Details of the experiment are provided in Section 3.4.1.1 of Chapter III. The ability of aluminum granules washed with each of the four acids to reduce a 1 mM solution of nitrate was used as an indicator of the damage done to the oxide layer and consequently the creation of additional reaction sites. The results of the experiment are presented in Figure 4.1.

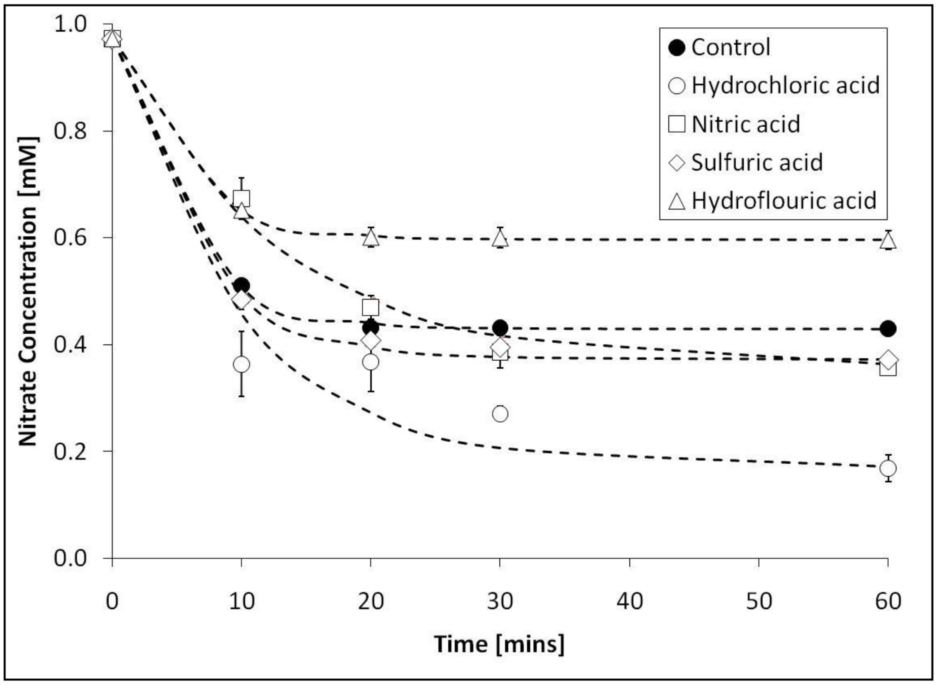

Figure 4.1 Change in nitrate concentration observed using aluminum granules pretreated with five different acids. Error bars indicate the standard deviation of replicate experiments. Some error bars are not visible because they are smaller than the symbol.

Aluminum granules pretreated with hydrochloric acid reduced nitrate to a greater extent as compared to the control. This indicates that a greater amount of aluminum surface was exposed when the aluminum granules were pretreated with hydrochloric acid, which consequently resulted in a larger number of available reaction sites. The enhanced nitrate removal by aluminum granules pretreated with hydrochloric acid can be attributed to chloride ions. Lampeas and Koutsoukos (1994) showed that the attack and consequent dissolution of the oxide film on aluminum is accelerated by the presence of chloride ions.

Nitrate has the ability to increase corrosion of aluminum (Khalil et al. 2003). Reduction of nitrate by aluminum granules pretreated with nitric acid seems to be slower than the control, although the concentration of nitrate at the end of one hour was nearly the same. The kinetics of nitrate reduction by aluminum granules pretreated with nitric acid was expected to be comparable to that observed using aluminum granules pretreated with hydrochloric acid. The results of the experiment could be misleading due to the interference of residual nitrate on the aluminum granules from the pretreatment process. Consequently, pretreating aluminum granules with nitric acid would not be advisable for such experiments due uncertainty in actual initial nitrate concentration.

Pretreating with hydrofluoric acid seemed to decrease the capacity of aluminum granules to reduce nitrate. A possible explanation for this inhibition is the incorporation of fluoride ions into the oxide layer followed by reaction with the aluminum to form stable complexes. Incorporation of anions into the native oxide film covering pure aluminum depends on the size of the anion, with smaller anions having a greater tendency to be incorporated into the oxide film (Khalil et al. 2003). Fluoride ion, which is smaller than chloride, nitrate and sulfate ion, has a higher tendency to be incorporated in the oxide layer.

No significant difference was observed between the nitrate reducing ability of aluminum granules pretreated with sulfuric acid and the control. Past studies have indicated that sulfate ions have negligible effect on the corrosion behavior of aluminum (Van Gheem et al. 2002, Khalil et al. 2003). Thus no additional benefits can be expected by pretreating aluminum granules with sulfuric acid.

It is interesting to note that the reaction involving aluminum granules washed with hydrofluoric acid, sulfuric acid and the control seems to have stopped after 60 minutes, while those washed with hydrochloric acid and nitric acid, seem to still have reaction sites for reduction of nitrate after 60 minutes. This can be explained by examining the change in solution pH during the experiment, as shown in Figure 4.2. Previously conducted trials indicated that the reduction reaction was accompanied by a decrease in pH, which is consistent with the observations of Luk and Au-Yeung (2002). A sufficiently high initial solution pH would ensure that the final solution pH remained above 10. Hence, an initial solution pH of 12 was used. However, as seen in Figure 4.2, the solution pH dropped below 10 in experiments involving aluminum granules pretreated with hydrofluoric acid and the control. As the pH approaches the range of 4 to 10, a stable protective oxide film would form on the aluminum surface and cover existing reaction sites. The final solution pH (at t=60 minutes) in experiments involving aluminum granules pretreated with hydrochloric acid and nitric acid was well above 10. The drop in solution pH could be attributed to interaction with the oxide layer of residual anions from the pretreatment. It has been proposed that chloride is chemisorbed onto the oxide surface forming oxide-chloride complexes that act as reactants (Garrigues et al. 1996). It is possible that fluoride, nitrate and sulfate also form oxide-anion complexes that interact with the solution producing hydrogen ions at different rates. A second possible explanation for the drop in solution pH could be reactions involving reduction of water, nitrate and nitrite by monovalent aluminum. These reactions are presented later on in this chapter (Equations 4.5 to 4.7) and they result in the production of hydrogen ions.

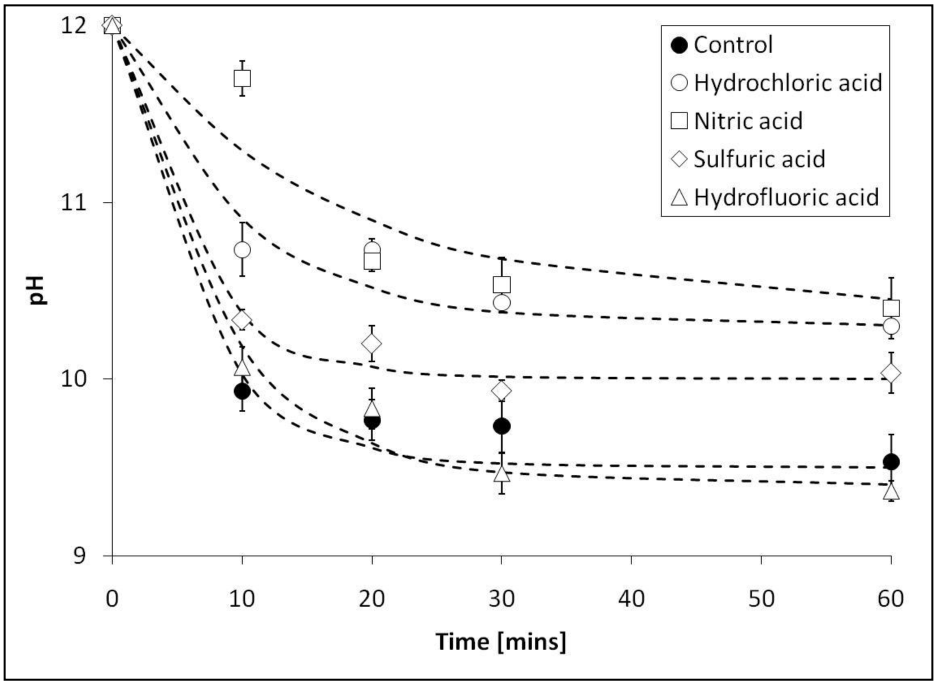

Figure 4.2 Change in pH observed using aluminum granules pretreated with five different acids. Error bars indicate the standard deviation of replicate experiments. Some error bars are not visible because they are smaller than the symbol.

Based on the results of these experiments hydrochloric acid is best suited for acid washing of aluminum granules. The rest of the experiments in this study used aluminum granules pretreated with hydrochloric acid.

4.1.2 Perchlorate Reduction Experiments

4.1.2.1 Optimum pH

This experiment was conducted to determine the optimum pH for reduction of perchlorate by aluminum. The experiment was performed for two days in 30-mL reactors having an effective solution volume of 20 mL with an initial perchlorate concentration of 0.2 mM and an aluminum dosage of 1.86 M. Details of the experiment are provided in Section 3.4.1.2.1 of Chapter III.

Figure 4.3 shows the pH measured in the reactors at the end of two days. The pH of the solutions in all the reactors tends to approach a value of 7 regardless of initial pH over the range of pH 2.8 to pH 11. Experiments were conducted at pH 13, but the results are not displayed, because perchlorate could not be measured at high pH due stabilization problems associated with the analytical system. The final pH measured in all the reactors was within the passive range ($4 \leq pH \leq 10$) for aluminum oxide, where dissolution of aluminum oxide is unlikely to occur. Consequently, no further decrease in perchlorate concentration can be expected. The results indicate that hydroxide ions were generated in systems with low initial pH and hydrogen ions were generated in systems with high initial pH. The pH change observed during these experiments can be explained by the speciation of trivalent aluminum, when zero-valent aluminum reduces water. Trivalent aluminum exists as Al^{3+} at $pH \leq 4$, as $Al(OH)_3$ between $4 < pH < 10$, and as $Al(OH)_4^-$ at $pH \geq 10$ (Hayden and Rubin 1974). Equations 4.1, 4.2 and 4.3 are the stoichiometric equations showing the reduction of water by zero-valent aluminum at acidic, near neutral and basic pHs, respectively. In highly acidic solutions, hydroxide ions are produced, while in highly basic solutions, hydrogen ions are produced by these reactions. This speciation of the trivalent aluminum ion could explain the tendency of the solution to approach the value of pH 7.

$$2Al^{0} + 6H_2O \leftrightarrow 2Al^{3+} + 3H_2 + 6OH^{-} \qquad (pH \leq 4) \qquad (4.1)$$

$$2Al^{0} + 6H_2O \leftrightarrow 2Al(OH)_3 + 3H_2 \qquad (4 \leq pH \leq 10) \qquad (4.2)$$

$$2Al^{0} + 8H_2O \leftrightarrow 2Al(OH)_4^{-} + 3H_2 + 2H^{+} \qquad (pH \geq 10) \qquad (4.3)$$

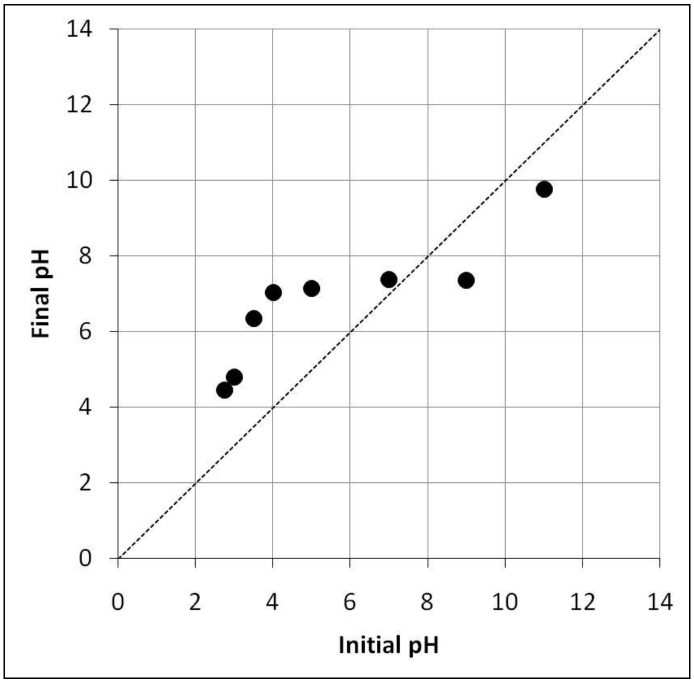

Figure 4.3 Final pH observed during experiments to determine optimum pH for perchlorate reduction. Error bars that would indicate the standard deviation of replicate experiments are not visible because they are smaller than the symbols.

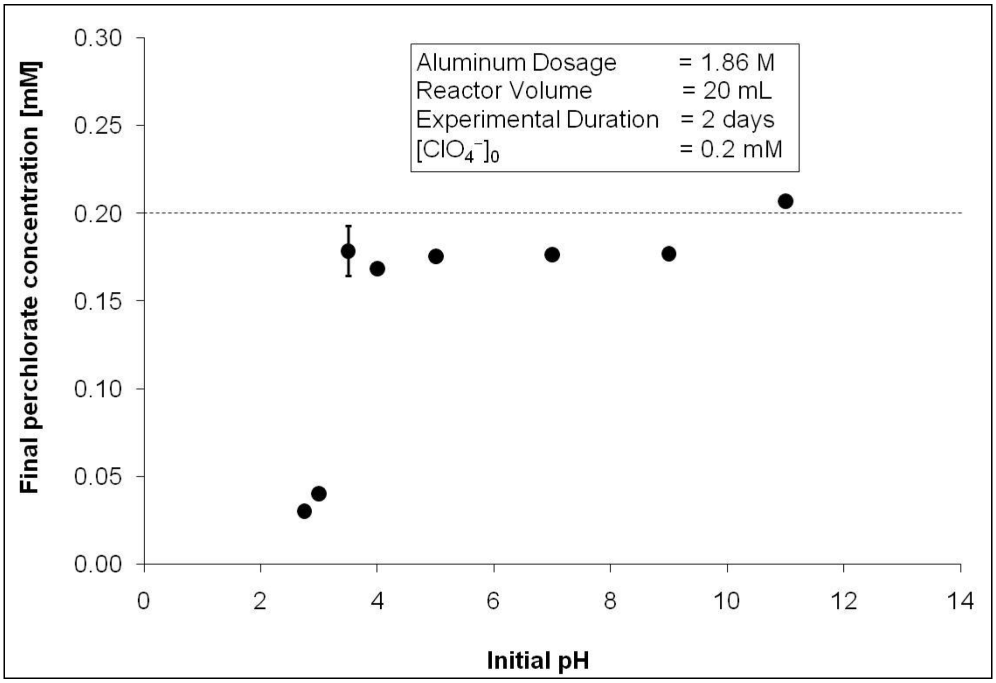

Figure 4.4 Final perchlorate concentration observed during experiments to determine the optimum pH for perchlorate reduction. Error bars that would indicate the standard deviation of replicate experiments are not visible because they are smaller than the symbols.

Figure 4.4 shows the perchlorate concentrations observed at the end of the experiments at different initial pH with the dotted line showing the initial perchlorate concentration. In reactors with initial pH ≤ 3, a large decrease in perchlorate concentration was observed. However, increases in chlorite, chlorate or chloride concentrations were not observed during the experiments conducted with initial pH ≤ 3. Although there is a possibility that perchlorate is being converted to hypochlorite in these experiments, the more likely explanation is that perchlorate was adsorbed onto the oxide layer. This explanation is supported by the results of the kinetic experiment presented in Section 4.1.2.3. The samples from experiments conducted at very high pH values (> 11) could not be analyzed using ion chromatography. The analytical system exhibited persistent stabilization problems when samples with pH > 11 were analyzed. However, if the samples could be analyzed then we would expect to observe perchlorate reduction.

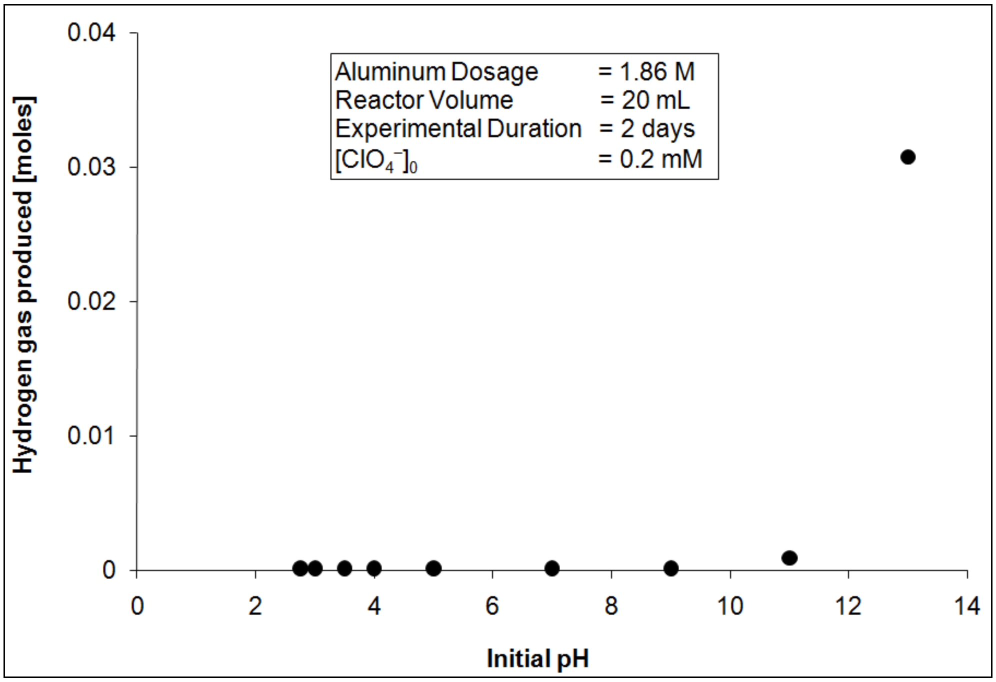

Figure 4.5 Hydrogen gas produced (mM) during the experiments to determine optimum pH for perchlorate reduction.

Figure 4.5 shows the amount of hydrogen gas generated during the experiment. Generation of hydrogen gas was observed only at pH ≥ 11 (Figure 4.5). The aluminum barrier oxide film is unstable below pH of 4 and above pH 10, which results in the underlying reactive aluminum to be exposed to the solution (Kolics et al. 2001). Kolics et al. (2001) also concluded that at pH > 11 a highly stable soluble complex, $Al(OH)_4^-$ is formed, while at acidic pHs aluminum hydrolysis is negligible. Hydrogen evolution during these experiments can be attributed to the reduction of water by aluminum. Therefore, there is a possibility that perchlorate may also be reduced by aluminum at pH > 11.

4.1.2.2 Optimum Aluminum Dosage

Although, the previous experiment did not provide conclusive evidence of perchlorate reduction, a decrease in perchlorate concentration was observed at low solution pH, which was attributed to adsorption of perchlorate on the oxide layer. It was, therefore, decided to conduct this experiment to determine the relationship between aluminum dosage and perchlorate removal. The experiment was conducted for two days in 30-mL reactors having an effective solution volume of 20 mL and with an initial perchlorate concentration of 0.2 mM and initial pH of 2.8. Details of the experiment are provided in Section 3.4.1.2.2 of Chapter III.

Figure 4.6 shows the solution pH in the reactors at the end of the experiment. It can be seen that the final pH observed in the reactor increased linearly with the aluminum dosage up to a dosage of 1 M, after which the slope decreases with increasing dosage. This experiment was conducted at an initial pH of 2.8, where the hypothesized mechanism of perchlorate removal is by adsorption on to the aluminum oxide surface layer. Reduction of water by zero-valent aluminum at low pHs (pH < 4) results in the formation of trivalent aluminum, hydrogen gas and hydroxide ion (Equation 4.1). The hydroxide ions formed by this process would increase the solution pH. Increasing the aluminum dosage could increase concentration of hydroxide ions generated, which would result in a greater increase in the solution pH.

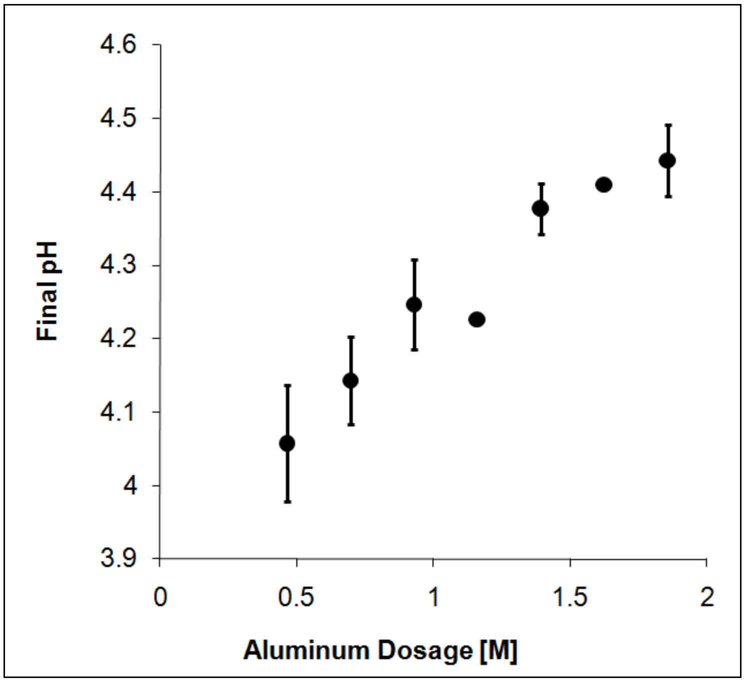

Figure 4.6 Final pH observed during experiments to determine optimum aluminum dosage for perchlorate reduction. Error bars indicate the standard deviation of replicate experiments. Some error bars are not visible because they are smaller than the symbol.

Figure 4.7 shows the perchlorate concentration at the end of the experiment for different aluminum dosages, with the dotted line showing the initial perchlorate concentration. These results indicate that increasing the aluminum dosage resulted in greater removal of perchlorate. However, equivalent amounts of chlorite, chlorate or chloride were not generated during these experiments, so perchlorate was probably not being chemically reduced. Increasing the aluminum dosage would generate more adsorption sites on the aluminum oxide surface layer, which in turn would result in greater removal of perchlorate by adsorption. Figure 4.8 shows the amount of hydrogen gas generated during the experiment. If monovalent aluminum, generated from zero-valent aluminum, has a tendency to reduce perchlorate then it is likely that monovalent aluminum also can reduce water to hydrogen gas. It is therefore reasonable to assume that hydrogen gas evolution should occur concurrently with perchlorate reduction. A much smaller amount of hydrogen gas was produced at all aluminum dosages in these experiments at initial pH 2.8, compared to what was observed at initial pH 13 (Figure 4.5), which indicates that very little reduction of water or perchlorate was occurring during these experiments.

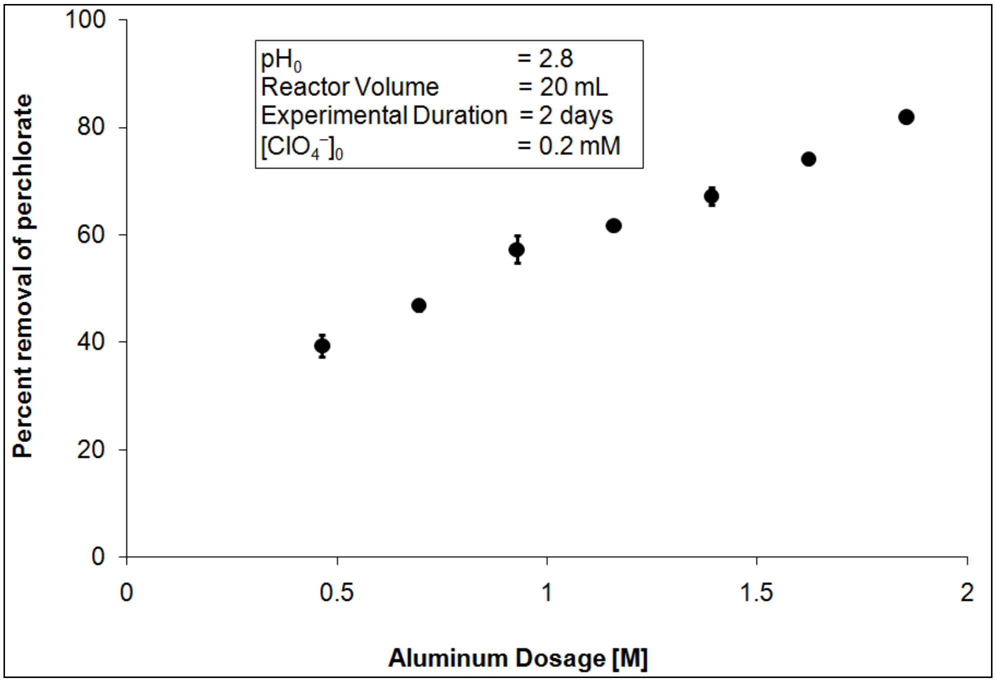

Figure 4.7 Percent removal of perchlorate observed during experiments to determine the optimum aluminum dosage for perchlorate reduction. Error bars indicate the standard deviation of replicate experiments. Some error bars are not visible because they are smaller than the symbol.

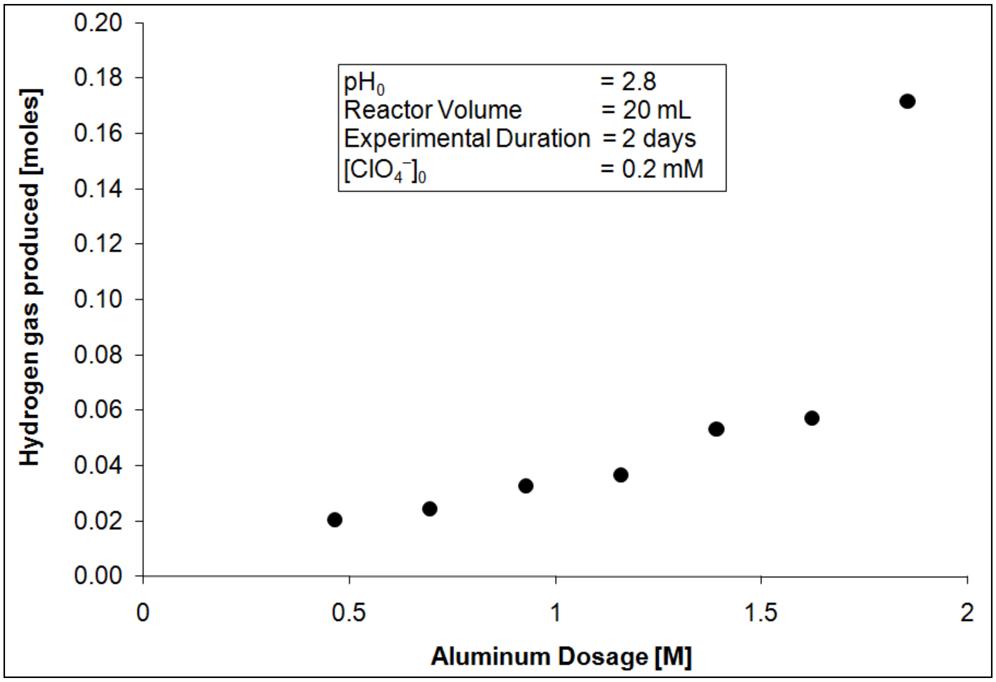

Figure 4.8 Hydrogen gas produced (mM) during the experiments to determine optimum aluminum dosage for perchlorate reduction.

4.1.2.3 Kinetic Experiments

Kinetic experiments to study the reduction of perchlorate at highly basic pH were not conducted, because perchlorate concentration could not be measured at high pH due stabilization problems associated with the analytical system. However, experiments were conducted to determine how fast perchlorate would be removed in highly acidic solutions (pH $\leq$ 3). The hypothesized mechanism for perchlorate removal in these experiments was by adsorption onto the oxide layer on the aluminum surface. Two experiments were conducted in 250-mL reactors having an effective solution volume of 200 mL with an initial perchlorate concentration of 0.2 mM, aluminum dosage of 1.86 M and an initial pH of 2.8. Details of the experiment are provided in Section 3.4.1.2.3 of Chapter III.

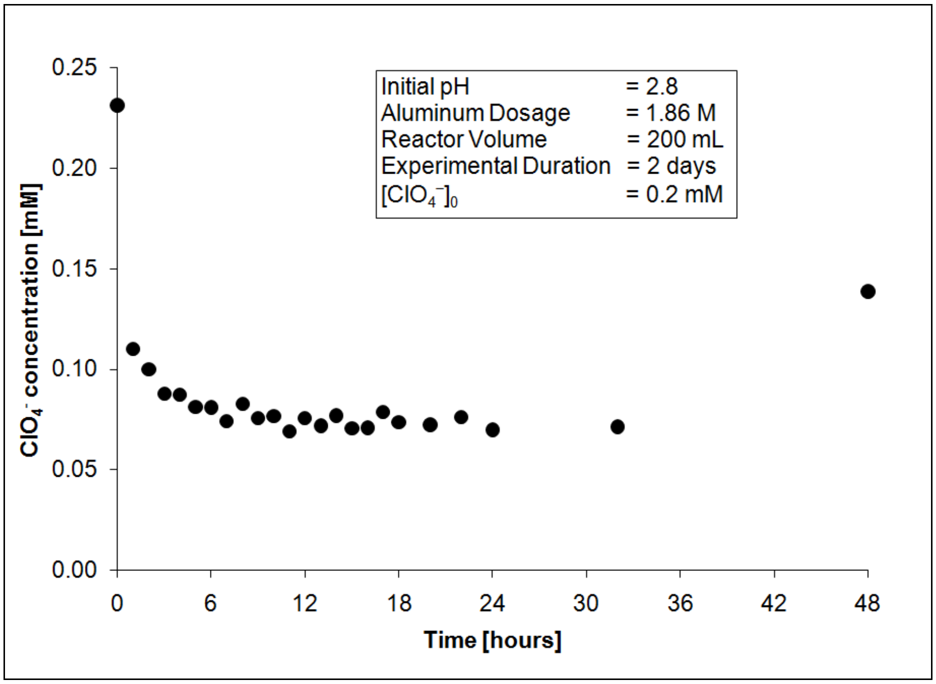

Figure 4.9 Change in perchlorate concentration with time observed during first kinetic experiment with perchlorate.

The first experiment was conducted for a period of two days. However, an instantaneous drop in perchlorate concentration was observed in the first hour of the experiment (Figure 4.9). Consequently, a second experiment was conducted with the same conditions for a period of one hour. Results indicate that the perchlorate concentration dropped immediately after adding the aluminum granules, after which no further drop in perchlorate concentration was observed (Figure 4.10). The decrease in perchlorate concentration was not accompanied by an equivalent increase in expected reduction by-products (chlorite, chlorate, chloride). No evolution of gas was observed during the experiments. All these conditions are indicative of an absorption reaction rather than a reduction reaction. The tendency of perchlorate ion to be incorporated into the oxide layer on aluminum has been suggested in several journal articles (Pyun et al. 2001, Khalil et al. 2003). However, adsorption studies of perchlorate on aluminum oxide have not been documented in the past. Although, a process indicative of perchlorate adsorption on the aluminum oxide surface layer was observed, a detailed study was not pursued as it was beyond the scope of this research. This is an interesting finding as aluminum oxide could be used in a packed-bed reactor to remove perchlorate from water.

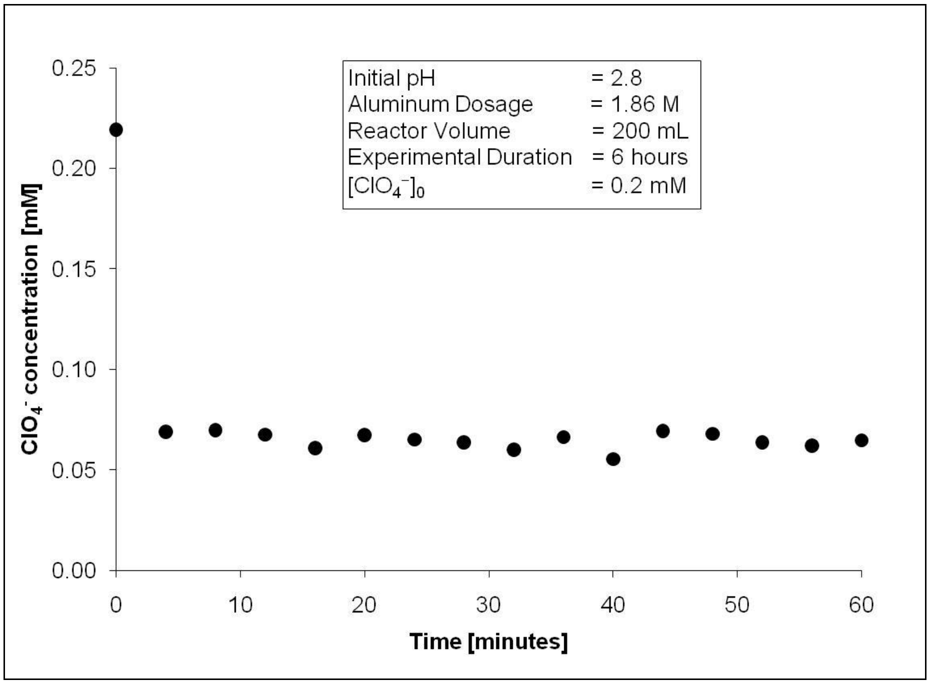

Figure 4.10 Change in perchlorate concentration with time observed during second kinetic experiment with perchlorate.

4.1.3 Nitrate Reduction Experiments

4.1.3.1 Optimum pH

This experiment was conducted to determine the optimum pH for reduction of nitrate by aluminum. The experiment was carried out for one hour in 30-mL reactors having an effective solution volume of 20 mL with an initial nitrate concentration of 1 mM and an aluminum dosage of 0.377 mM. Details of the experiment are provided in section 3.4.1.3.1 of Chapter III.

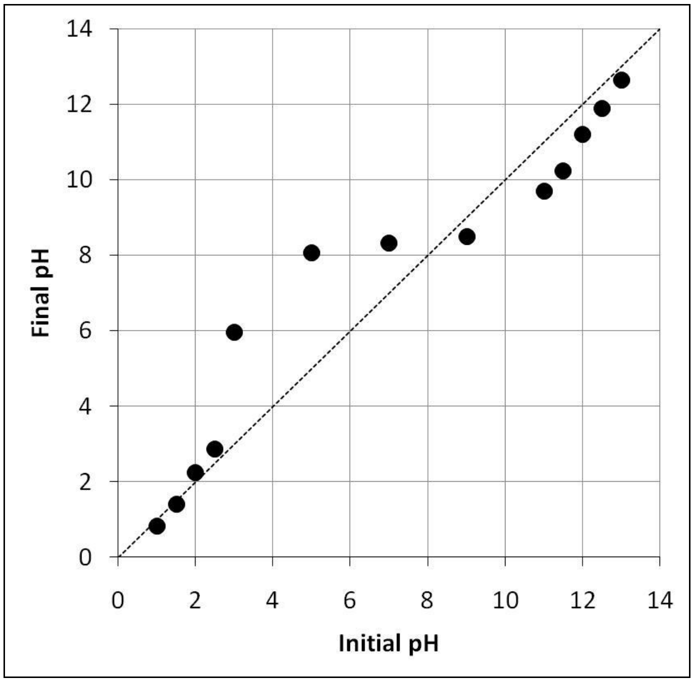

Figure 4.11 Final pH observed during experiments to determine optimum pH for nitrate reduction. Error bars that would indicate the standard deviation of replicate experiments are not visible because they are smaller than the symbols.

The final pH values observed at the end of the experiment are shown in Figure 4.11. The solutions in the reactors seem to approach a final pH value of 8. However, the final pH of the solutions in some reactors was not in the passive range for aluminum oxide film dissolution. Figure 4.12 shows the final nitrate concentrations observed at the end of experiments at different initial pH, with the dotted line showing the initial nitrate concentration. Similarly to the perchlorate experiments, the decrease in nitrate concentration observed in experiments conducted at initial pH 1 did not produce nitrite or ammonia. Furthermore, no evolution of gas was observed in the reactor with initial pH 1. This reinforces the theory that at low pH the predominant removal mechanism is by adsorption. At pH > 11, nitrate was completely converted into ammonia, which supports the hypothesis that perchlorate might be reduced at high pH. The results of the experiments show that the effect of solution pH on nitrate reduction is totally different than that reported by Luk and Au-Yeung (2002), who studied the reduction of nitrate by aluminum powder (200-325-mesh range, > 99%) that was finer is size than that used in this study. They reported that nitrate reduction was observed in the narrow range of 10.2 < pH < 11.5, while the results of our experiments show that nitrate reduction was observed for all pH that was tested above pH 11.

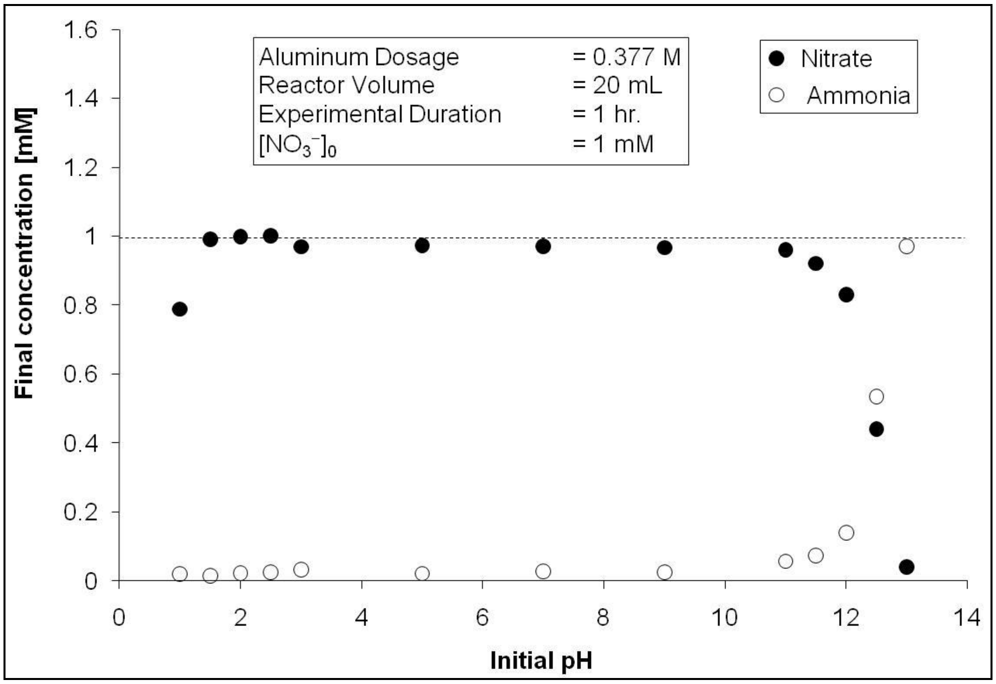

Figure 4.12 Final nitrate concentration observed in the experiments to determine optimum pH for nitrate reduction. Error bars that would indicate the standard deviation of replicate experiments are not visible because they are smaller than the symbols.

Figure 4.13 shows the amount of hydrogen gas produced during the experiment. Since all the nitrate was converted to ammonium, no nitrogen-containing gases would be produced. It is reasonable to assume that hydrogen is the only gas produced, because evolution of hydrogen gas has been reported in the literature for similar experiments (Murphy 1991). At pH > 12, reduction of nitrate to ammonia by aluminum granules was accompanied by strong hydrogen gas evolution. Below pH 12 very little hydrogen gas was produced. Hydrogen gas generation was observed during this experiment analogously to what was observed during the experiments with perchlorate. Hydrogen evolution during these experiments can be attributed to the reduction of water by aluminum.

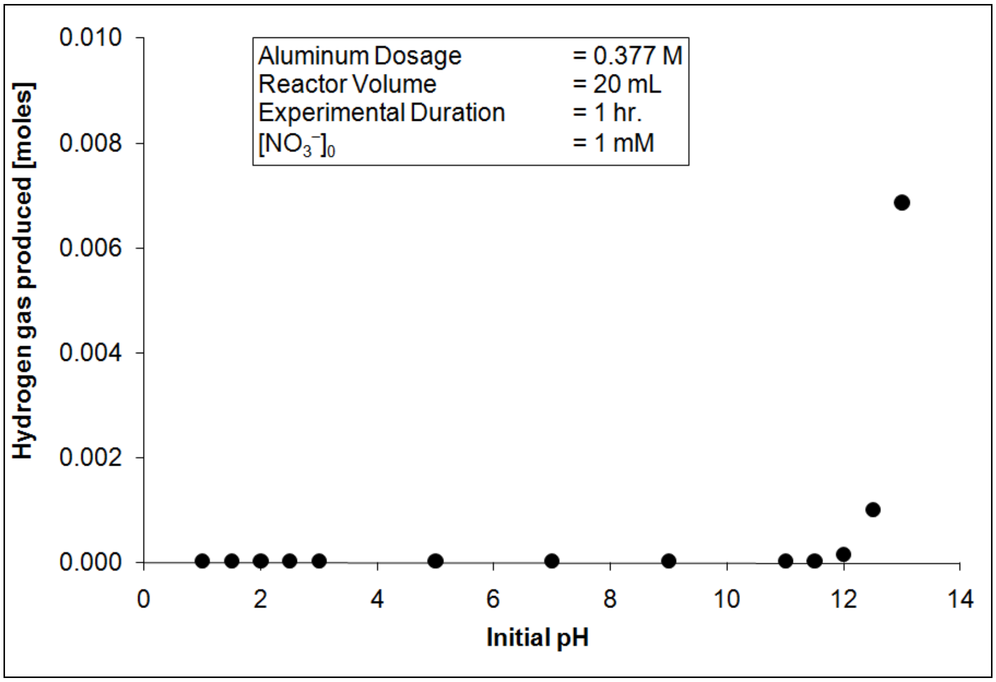

Figure 4.13 Hydrogen gas produced (mM) during the experiments to determine optimum pH for nitrate reduction.

4.1.3.2 Optimum Aluminum Dosage

This experiment was conducted with the intention of determining the optimum aluminum dosage for reduction of nitrate. The experiment was conducted for one hour in 30-mL reactors having an effective solution volume of 20 mL with an initial nitrate concentration of 1 mM and an initial pH of 13.1. Details of the experiment are provided in Section 3.4.1.3.2 of Chapter III.

Figure 4.14 shows the solution pH in the reactors at the end of the experiment. It can be seen that the final pH values observed in the reactors decrease linearly with the aluminum dosage. Figure 4.15 shows the final nitrate concentrations at the end of the experiments for different aluminum dosages with the dotted line showing the initial nitrate concentration. The final concentration of nitrate decreased with increasing aluminum dosage.

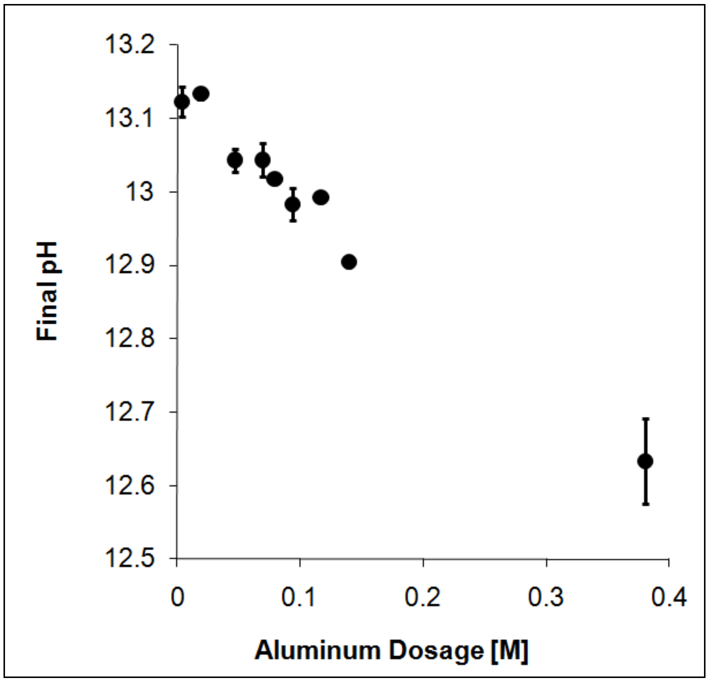

Figure 4.14 Final pH observed during experiments to determine optimum aluminum dosage for nitrate reduction. Error bars indicate the standard deviation of replicate experiments. Some error bars are not visible because they are smaller than the symbol.

Figure 4.16 shows the amount of hydrogen gas generated during the experiment. Increasing the aluminum dosage would result in more active sites for reduction of water and nitrate. Figure 4.17 shows the moles of hydrogen gas produced per mole of nitrate reduced. It can be seen that for every mole of nitrate reduced about 300 moles of hydrogen gas are produced.

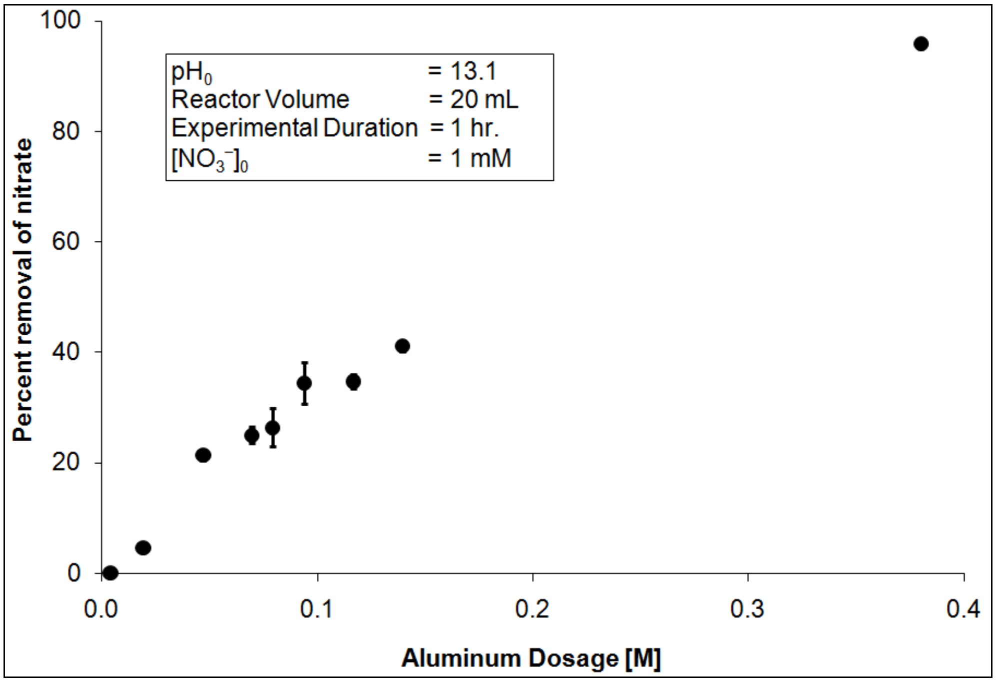

Figure 4.15 Percent removal of nitrate in the experiments to determine optimum aluminum dosage for nitrate reduction. Error bars indicate the standard deviation of replicate experiments. Some error bars are not visible because they are smaller than the symbol.

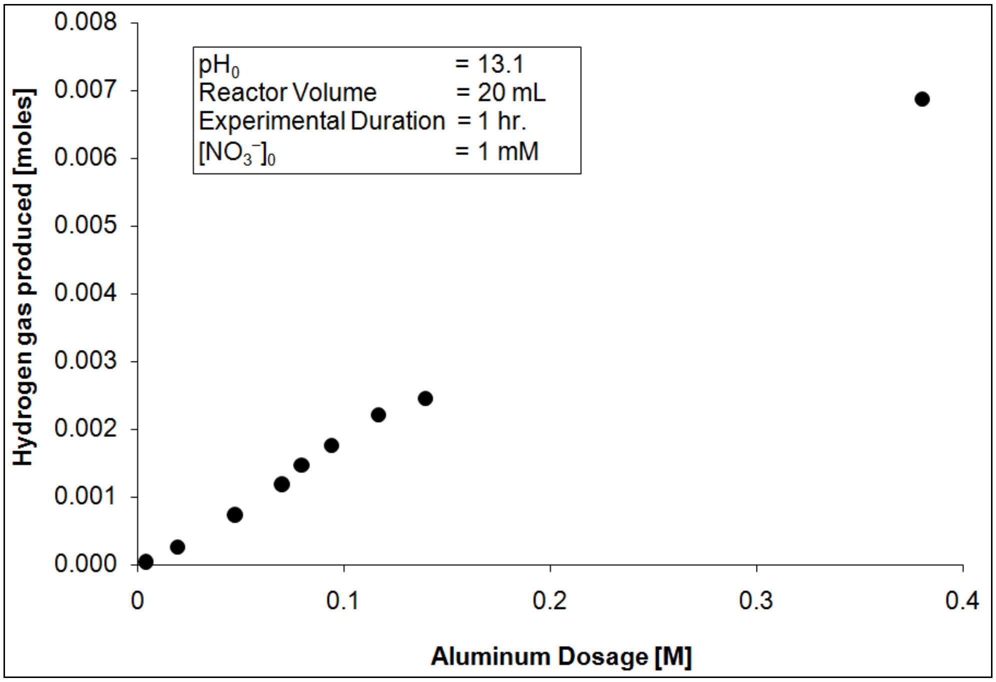

Figure 4.16 Hydrogen gas produced (moles) during the experiments to determine optimum aluminum dosage for nitrate reduction.

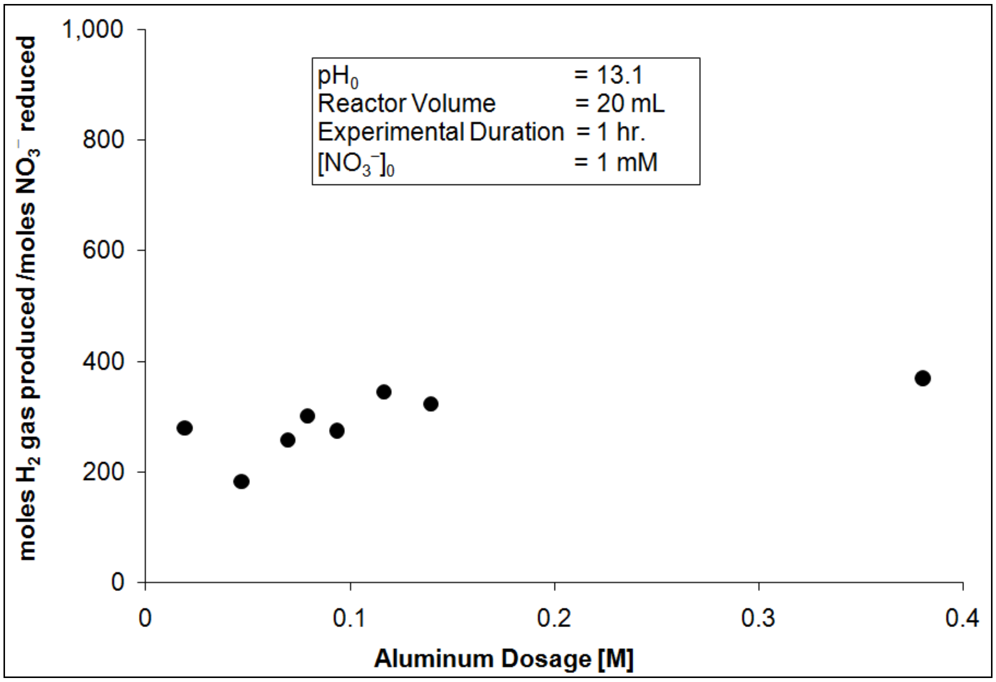

Figure 4.17 Hydrogen gas produced per mole of nitrate reduced during the experiments to determine optimum aluminum dosage for nitrate reduction.

4.1.3.3 Kinetic Experiments

Three experiments were simultaneously conducted to study the kinetics of nitrate reduction by pH-activated aluminum granules. The experiments were conducted for one hour in 250-mL reactors having an effective solution volume of 200 mL with an initial nitrate concentration of 1 mM and an aluminum dosage of 0.377 mM. Details of the experiment are provided in Section 3.4.1.3.3 of Chapter III.

The results of the three experiments are provided in Figures 4.21, 4.22 and 4.23. Experimental data indicates an initial lag in the conversion of nitrate to nitrite. This lag can be explained by the formation of an intermediate species of aluminum that participates in the reduction process. One such intermediate specie is monovalent aluminum, which could be formed by partial oxidation of zero-valent aluminum and then react with nitrate to form nitrite and finally ammonia. Nitrate was completely converted to ammonia during the three experiments. The rate-limiting step in this process is the first step of conversion of nitrate to nitrite, with the nitrite immediately being converted to ammonia. Very little accumulation of nitrite was observed during the experiment and no other intermediates were observed.

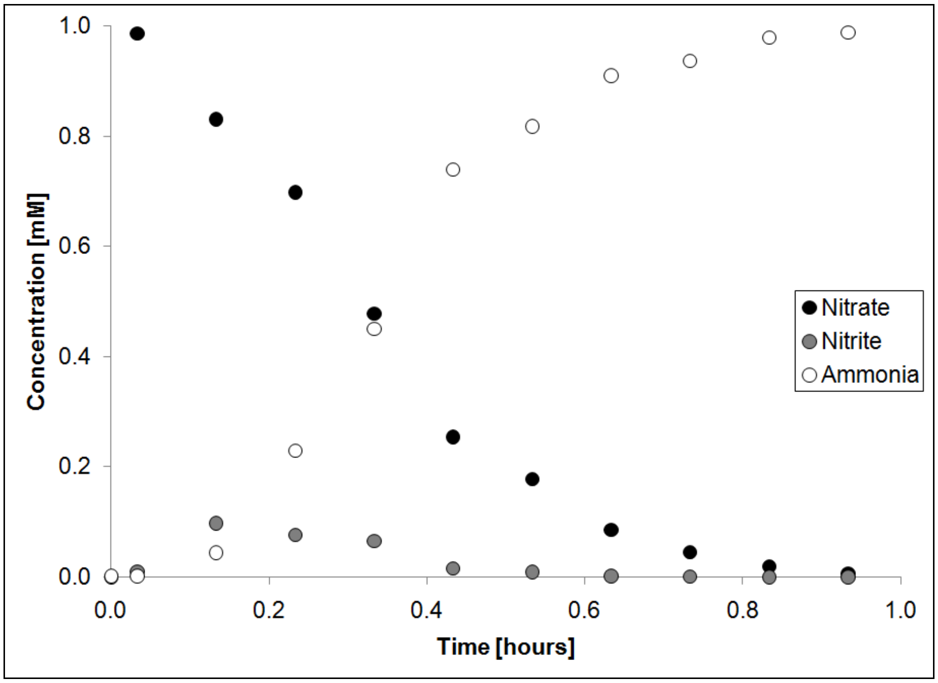

Figure 4.18 First kinetic experiment studying reduction of nitrate to ammonia.

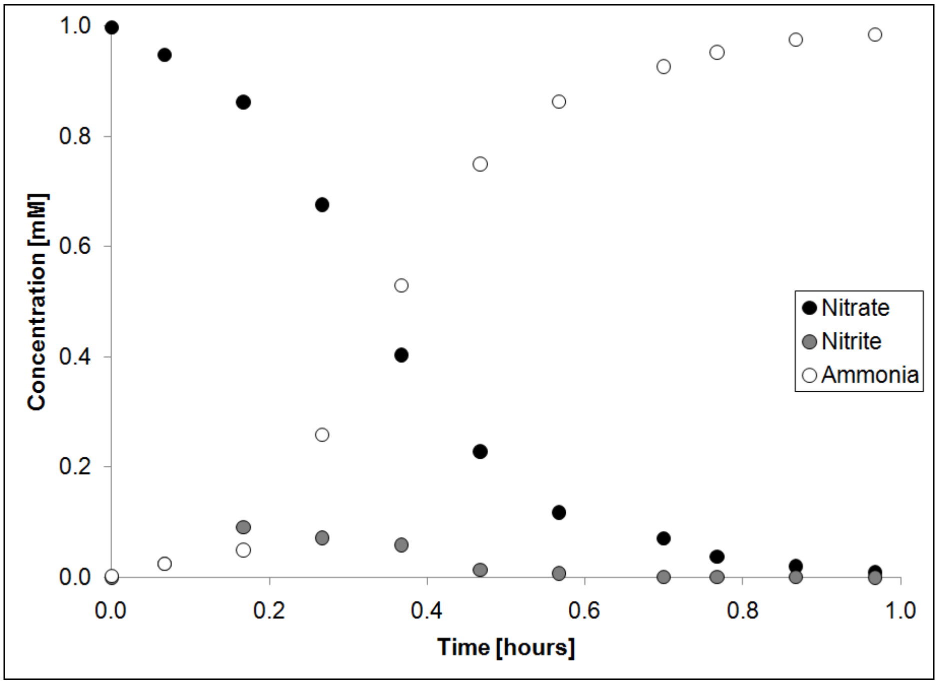

Figure 4.19 Second kinetic experiment studying reduction of nitrate to ammonia.

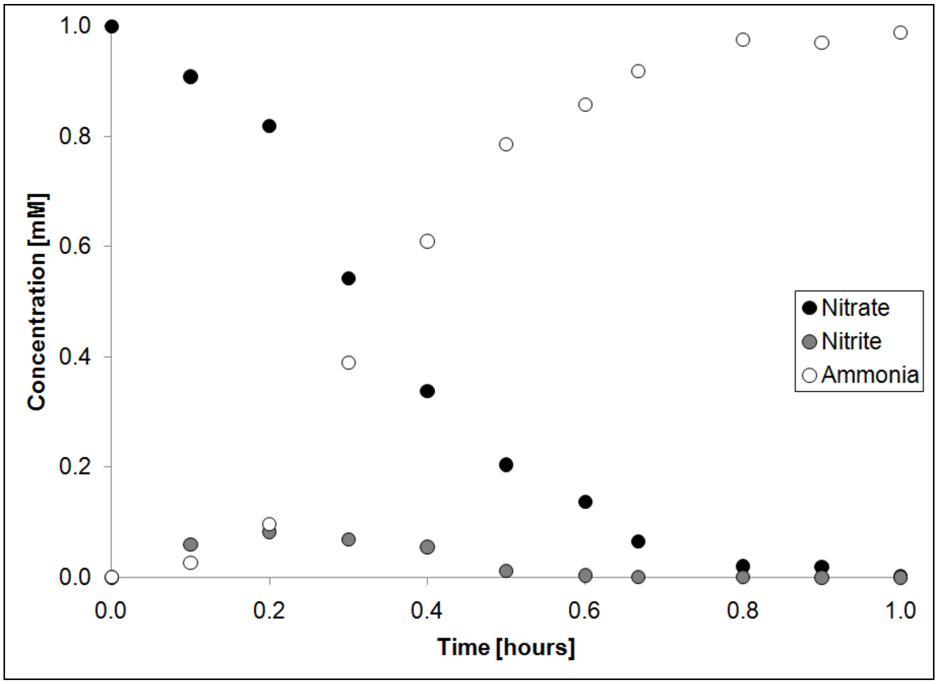

Figure 4.20 Third kinetic experiment studying reduction of nitrate to ammonia.

The results from this experiment were used to determine kinetic parameters in a model developed at the end of this chapter.

4.2 Electrochemically Induced Pitting Corrosion Experiments

4.2.1 Critical Pitting Potential

The critical pitting potential was determined by conducting a potentiodynamic scan using aluminum electrode from -1 V to 3 V at the rate of 1 mV/s and measuring the current. Pitting potential was determined as the potential at which a rapid rise in current was observed. The pitting potential of aluminum was determined in different concentrations of perchlorate, nitrate and chloride. Details of the experiment are provided in Section 3.4.2.1 of Chapter III.

Figure 4.21 shows that the pitting potential of aluminum depends on the concentration of perchlorate. The pitting potential of aluminum in a solution containing 0.2 mM perchlorate would about 0.15 V_{NaSCE}. The pitting potential of aluminum measured during these experiments is lower than that reported in the literature as shown in Figure 4.21 (Amin et al. 2006). The lower pitting potential could be because these experiments used a modified saturated calomel reference electrode that was filled with saturated sodium chloride solution instead of potassium chloride. The relationships between pitting potential and perchlorate concentration from the experiments conducted in this study and by Amin et al. (2006) are both linear and have similar slopes.

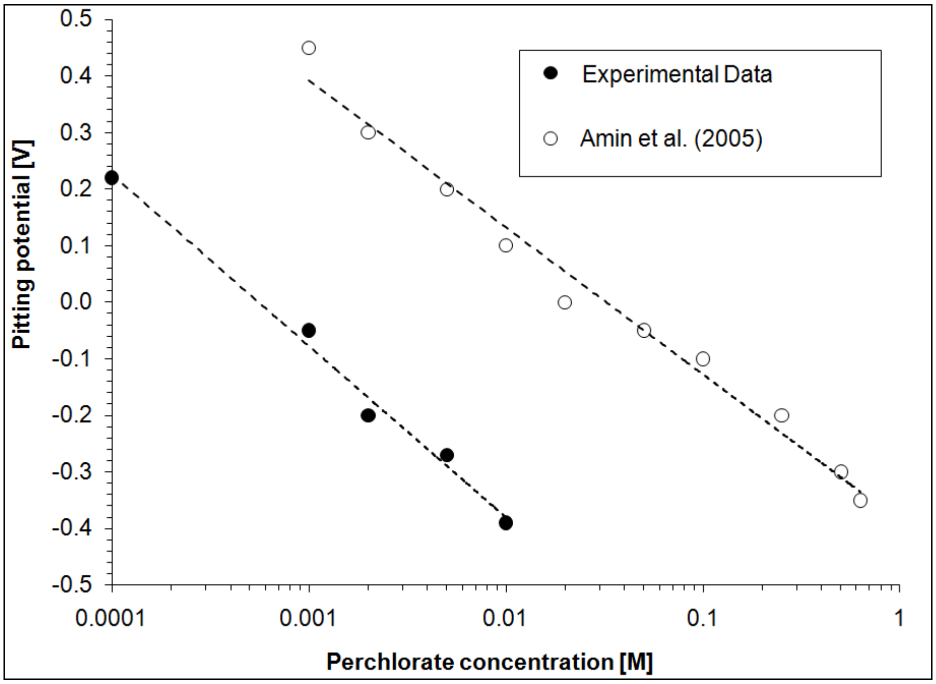

Figure 4.21 Pitting potential of aluminum as a function of perchlorate concentration. Error bars that would indicate the standard deviation of replicate experiments are not visible because they are smaller than the symbols.

Figure 4.22 shows that the pitting potential of aluminum depends on the concentration of nitrate. The pitting potential of aluminum in a solutions containing 1 mM nitrate would be about 1.9 V_{NaSCE}. The pitting potential of aluminum measured during these experiments is higher than that reported in the literature (Burstein and Organ 2005). Pitting potential of aluminum increased towards more positive value as the nitrate concentration was decreased which is similar to that observed by Burstein and Organ (2005).

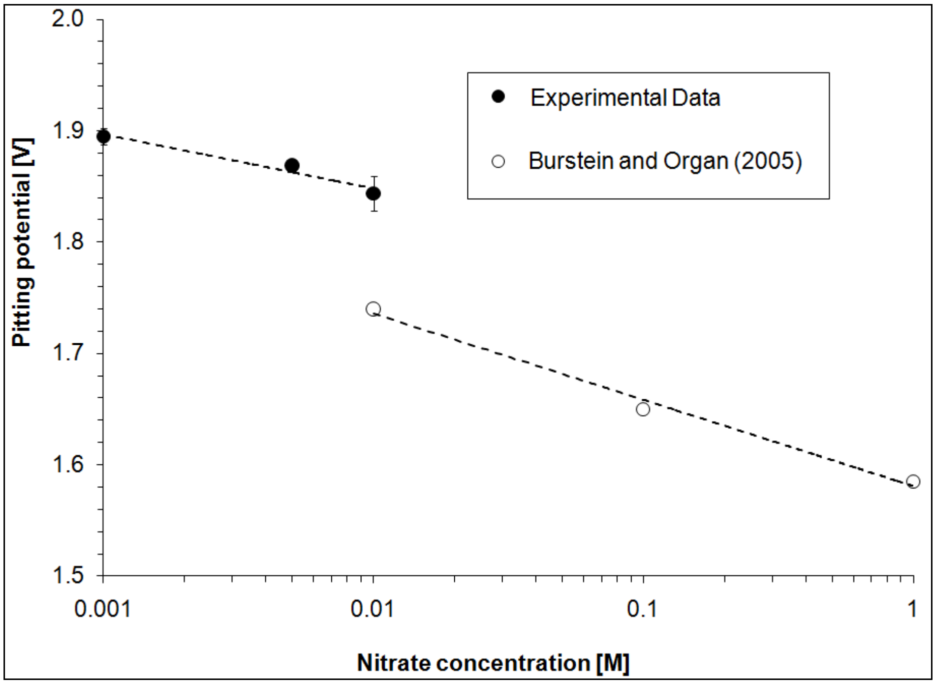

Figure 4.22 Pitting potential of aluminum as a function of nitrate concentration. Error bars indicate the standard deviation of replicate experiments. Some error bars are not visible because they are smaller than the symbol.

Figure 4.23 shows that the pitting potential of aluminum depends on the concentration of chloride. The pitting potential of aluminum in a solution containing 1 mM chloride would be about –0.35 V_{NaSCE}. The pitting potential of aluminum measured during these experiments is higher than that reported by McCafferty (2003), which can again be attributed to the modified saturated calomel reference electrode used in this study. Pitting potential of aluminum increased towards more positive values as the chloride concentration was decreased, which is similar to that observed by McCafferty (2003).

An increase in the pitting potential indicates that there is an increase in the resistance to pitting corrosion and vice versa. The pitting potentials measured during this experiment decreased in the order nitrate > perchlorate > chloride. This trend can be explained by the incorporation of ions into the oxide film. Incorporation of ions into the surface oxide film covering aluminum would depend on ionic size, with smaller ions being incorporated more easily than larger ions. Therefore, smaller ions would cause the pitting potential to drop more than larger ions by decreasing the resistance to pitting more effectively. The ionic radii of nitrate, perchlorate and chloride are 0.33 nm, 0.24 nm and 0.181 nm, respectively. Chloride, being the smallest of the three anions, will be the most effective in causing aluminum to corrode by causing the largest decrease in the resistance to pitting as measured by the pitting potential. Nitrate, being the largest to the three anions, will cause the smallest decrease in the resistance to pitting and the smallest decrease in pitting potential. Adding chloride to solutions with perchlorate and nitrate would result in shifting the pitting potential to more negative values which can be interpreted as an accelerating the pitting process.

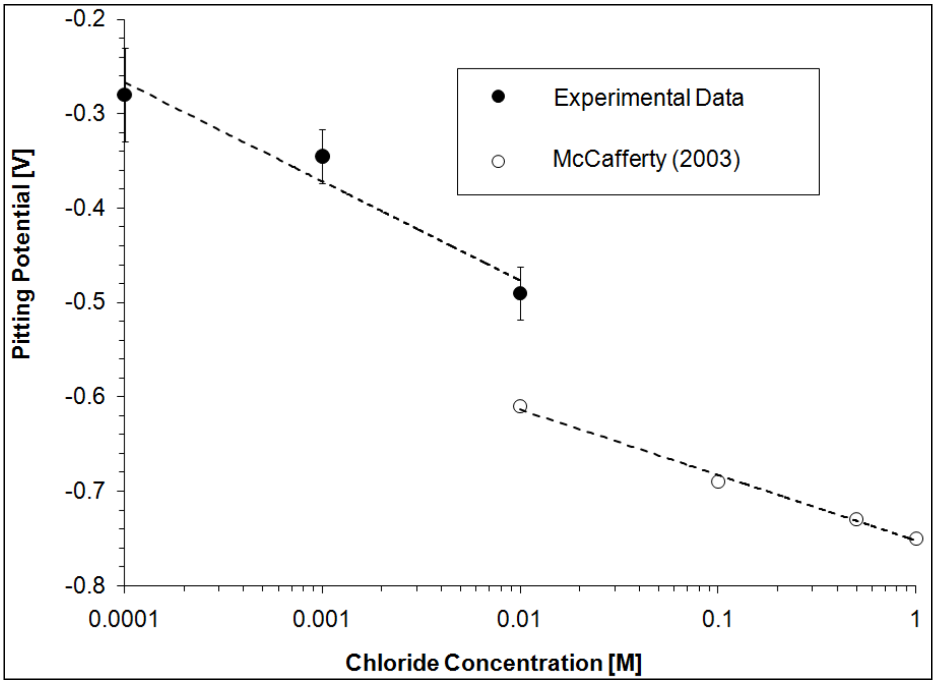

Figure 4.23 Pitting potential of aluminum as a function of chloride concentration. Error bars indicate the standard deviation of replicate experiments. Some error bars are not visible because they are smaller than the symbol.

4.2.2 Perchlorate Reduction Experiments

4.2.2.1 Effect of Current

This experiment was conducted to determine the effect of applied galvanostatic current on the rate of perchlorate reduction. The surface area concentration of the working electrode was 18 cm^2/L and the solution pH at the start of the experiment was 7. The changes in perchlorate and chloride concentrations with time were monitored for three currents (10 mA, 50 mA and 100 mA) by collecting samples and analyzing them using ion chromatography. The experiments were continued until the aluminum working electrode was completely consumed. Details of the experiment are provided in Section 3.4.2.3.1 of Chapter III.

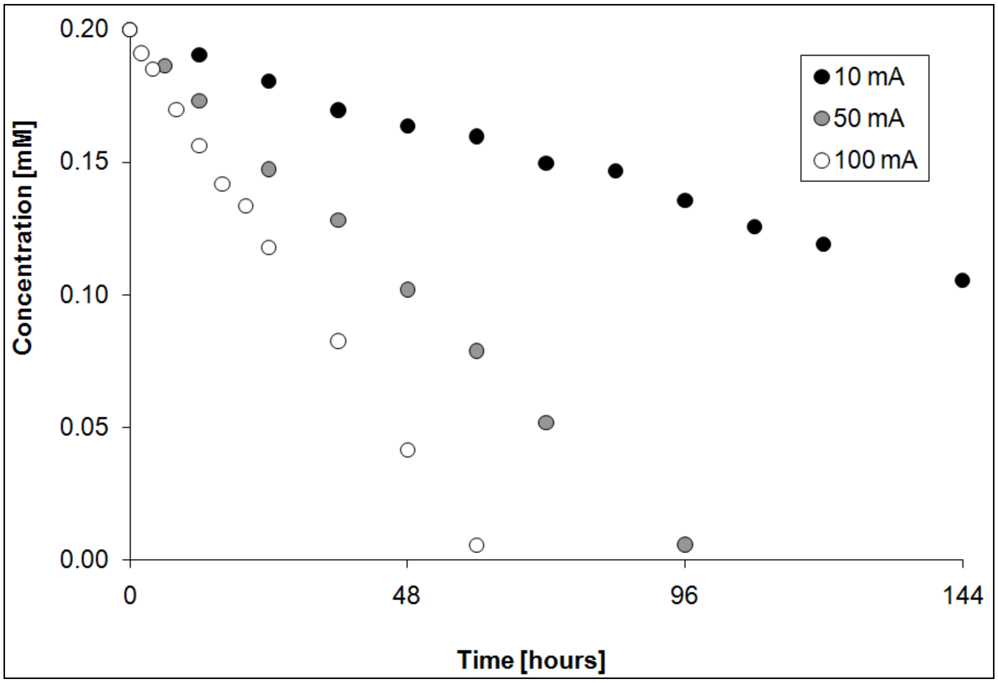

Figure 4.24 Effect of current on perchlorate reduction by aluminum during electrochemically induced pitting corrosion.

Figure 4.24 compares the changes in perchlorate concentrations with time for the three applied currents. The potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The potential at the working electrode, measured relative to the reference electrode, remained fairly constant during the length of the experiments conducted at 10 mA, 50 mA and 100 mA at approximately 0.11 V, 0.13 V and 0.19 V, respectively. A sharp increase in potential was observed at the end of the experiment when the electrode was significantly consumed. Increasing the current applied to the working electrode resulted in an increase in the rate of perchlorate reduction. Applying current to the electrode brings about pitting corrosion and consequent oxidation of zero-valent aluminum to form soluble monovalent aluminum. The effect of current on the rate of perchlorate reduction can be explained by Faraday's Law, which states that the rate liberation of a substance at an electrode is directly proportional to the rate of electric charge transferred at the electrode. Consequently, it follows that a higher galvanostatic current will cause larger rate of monovalent aluminum to be liberated at the electrode, which translates to a increase in the rate of perchlorate reduction. The experiment with 10 mA current resulted in about 50 percent decrease in perchlorate concentration before complete consumption of the working electrode. This may be because the rate of perchlorate generation is very slow resulting in the aluminum being consumed by reduction of water before it can react with all of the perchlorate that is present. The experiment with 50 mA and 100 mA reduced all the perchlorate to chloride in four and three days, respectively. The end-product of perchlorate reduction was chloride ions. The elemental balance for chlorine and associated chloride concentrations are presented in Section 4.3.2 along with the discussion of the model that was developed to describe reduction of perchlorate by aluminum activated by electrochemically induced pitting corrosion.

4.2.2.2 Effect of Electrode Surface Area

This experiment was conducted to determine the effect of electrode surface area on the rate of perchlorate reduction. Experiments were conducted with two working electrode surface areas (18 cm^2/L and 36 cm^2/L). A current of 100 mA was applied and the potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The solution had a pH of 7 at the start of the experiment. The experiments were conducted for a period of 60 hours during which time the perchlorate and chloride concentration in the reactor was monitored by collecting samples and analyzing them using ion chromatography. Details of the experiment are provided in Section 3.4.2.3.2 of Chapter III.

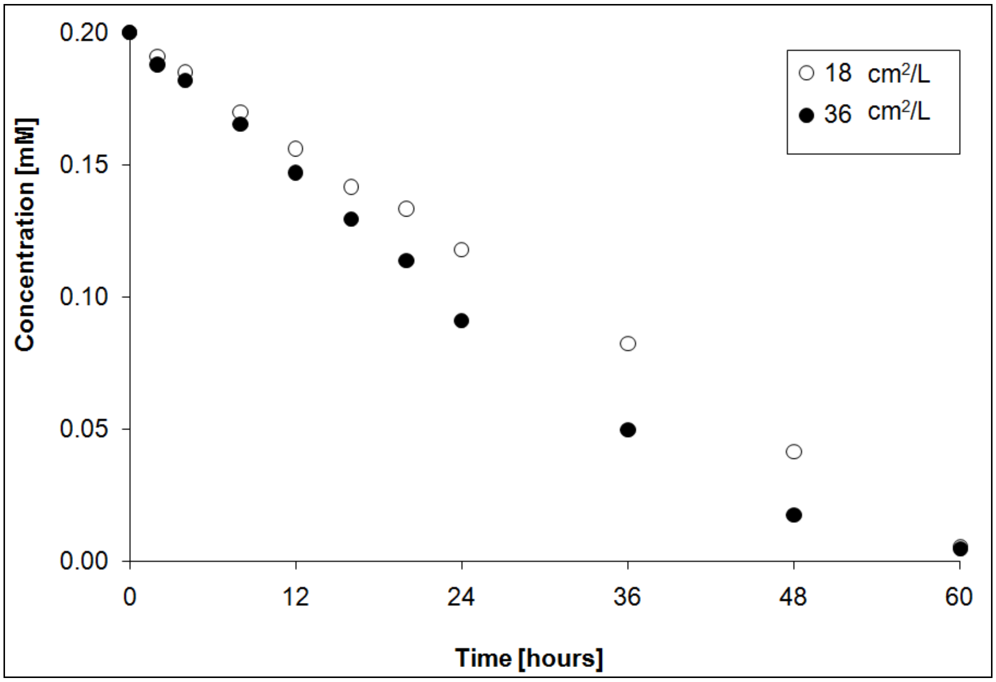

Figure 4.25 Effect of electrode surface area on perchlorate reduction by aluminum during electrochemically induced pitting corrosion.

Figure 4.25 shows the change in perchlorate concentration with time for experiments conducted with working electrode having surface area concentrations of 18 cm^2/L and 36 cm^2/L. The potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The potential at the working electrode, measured relative to the reference electrode, remained fairly constant during the length of both the experiments at approximately 0.19 V. A sharp increase in potential was observed at the end of the experiment when the electrode was significantly consumed. Increasing the electrode surface area of the working electrode seems to increase the rate of perchlorate reduction. However, the observed effect was very small compared to the increase in electrode surface area. During this experiment, perchlorate was reduced completely to chloride. The elemental balance on chlorine and associated chloride concentrations are presented in section 4.3.2, which discusses the model developed to describe reduction of perchlorate by aluminum activated by electrochemically induced pitting corrosion.

4.2.2.3 Effect of pH

This experiment was conducted to determine the effect of solution pH on the rate of perchlorate reduction, but experiments were not conducted with highly basic conditions ($pH \geq 10$), because of problems with analysis by ion chromatography. Hence, experiments were conducted at only acidic and neutral pH. A current of 100 mA was applied and the potential at the working electrode was monitored relative to the reference electrode during these experiments to ensure that it was above the required value to cause pitting. The working electrode had an effective surface area concentration of 18 cm^2/L. The experiments were conducted for a period of 60 hours, during which time the perchlorate and chloride concentrations in the reactor were monitored by collecting samples and analyzing them using ion chromatography. The experiment is explained in detail in Section 3.4.2.3.3 of Chapter III.

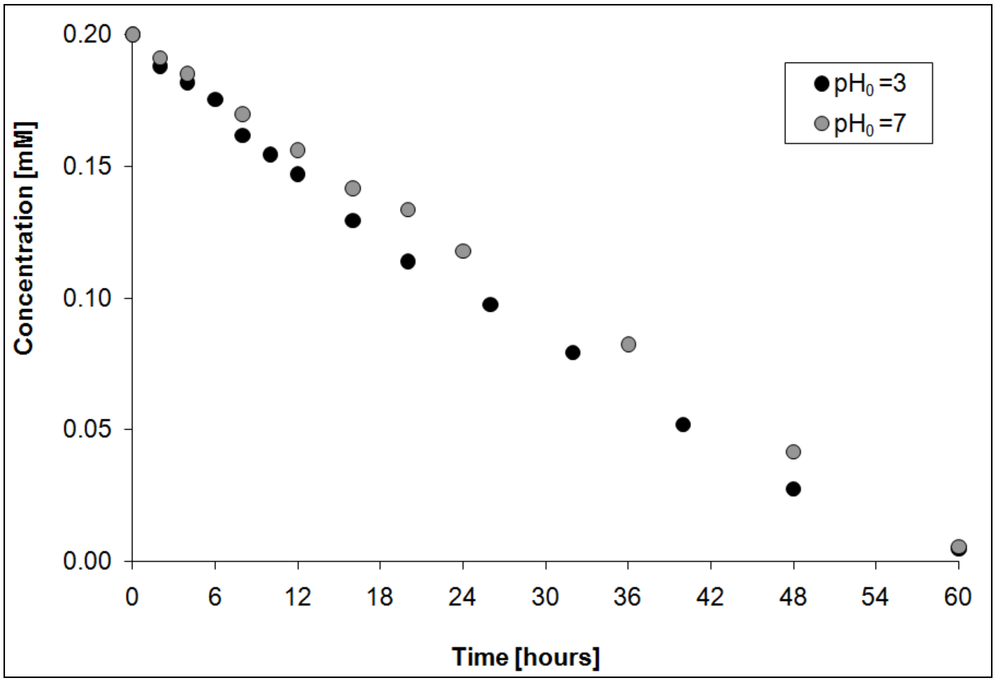

Figure 4.26 Effect of pH on perchlorate reduction by aluminum during electrochemically induced pitting corrosion.

Figure 4.26 shows the change in nitrate concentration with time for the experiments with solution having initial pH values of 3 and 7. The potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The potential at the working electrode, measured relative to the reference electrode, remained fairly constant during the length of both the experiments at approximately 0.19 V. A sharp increase in potential was observed at the end of the experiment when the electrode was significantly consumed. Very little difference was observed between the two experiments. The pH of the solution in the reactors tended to shift towards alkaline values (pH ≈ 10) at the end on the experiment. Perchlorate was converted to chloride in this experiment. The elemental balance on chlorine and the associated chloride concentrations are presented in section 4.3.2, which also discusses the kinetic model developed to describe reduction of perchlorate by aluminum activated by electrochemically induced pitting corrosion.

4.2.3 Nitrate Reduction Experiments

4.2.3.1 Effect of Current

This experiment was conducted to determine the effect of applied galvanostatic current on the rate of nitrate reduction. The effective surface area concentration of the working electrode was 9 cm^2/L and the solution pH at the start of the experiment was 7. The potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The changes in nitrate-N, nitrite-N and ammonia-N concentrations with time were monitored for three currents (10 mA, 20 mA and 50 mA) by collecting samples and analyzing them using ion chromatography. The experiment was continued until the aluminum working electrode was completely consumed. The details of the experiment are provided in Section 3.4.2.3.1 of Chapter III.

Figure 4.27 shows the changes in nitrate concentrations with time for the three applied currents. The potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The potential at the working electrode, measured relative to the reference electrode, remained fairly constant during the length of the experiments conducted at 10 mA, 20 mA and 50 mA at approximately 2.0 V, 2.1 V and 2.3 V, respectively. A sharp increase in potential was observed at the end of the experiment when the electrode was significantly consumed. Increasing the current applied to the working electrode seems to increase the rate of nitrate reduction. The observed effect is similar to that observed with perchlorate reduction. Increasing the applied current brings about accelerated pitting and dissolution of aluminum causing more aluminum to be available for nitrate reduction. Reduction of nitrate produced equivalent amount of ammonium ions. The elemental balance on nitrogen and associated nitrate, nitrite and ammonia concentrations are presented in Section 4.3.2, which also discusses the kinetic model developed to describe reduction of nitrate by aluminum activated by electrochemically induced pitting corrosion.

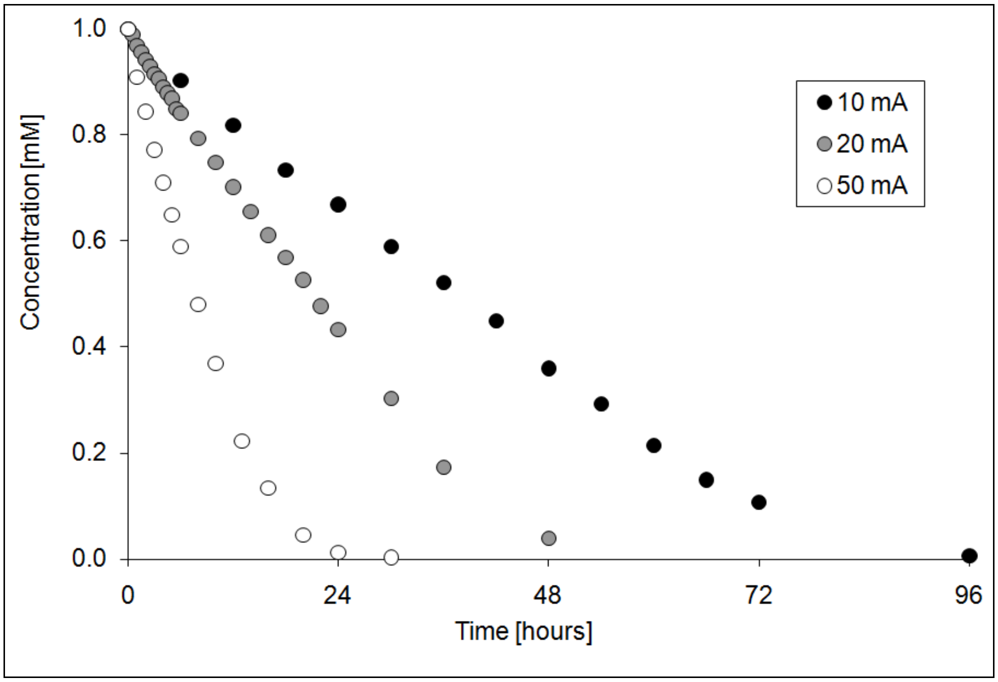

Figure 4.27 Effect of current on nitrate reduction by aluminum during electrochemically induced pitting corrosion.

4.2.3.2 Effect of Electrode Surface Area

This experiment was conducted to determine the effect of electrode surface area on the rate of nitrate reduction. Experiments were conducted with two working electrode surface areas (9 cm^2/L and 18 cm^2/L). A current of 50 mA was applied and the potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The solution had a pH of 7 at the start of the experiment. The experiments were conducted for a period of 30 hours during which time the nitrate-N, nitrite-N and ammonia-N concentrations in the reactor were monitored by collecting samples and analyzing them using ion chromatography. The experiment is explained in detail in Section 3.4.2.3.2 of Chapter III.

Figure 4.28 shows the change in nitrate concentration with time for the two experiments with different electrode surface areas. The potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The potential at the working electrode, measured relative to the reference electrode, remained fairly constant during the length of both the experiments at approximately 2.3 V. A sharp increase in potential was observed at the end of the experiment when the electrode was significantly consumed. Increasing the electrode surface area of the working electrode had little effect on the rate of nitrate reduction. The final product of nitrate reduction in this experiment was ammonium ions. The elemental balance on nitrogen and the associated nitrate, nitrite and ammonia concentrations are presented in Section 4.3.2, which also discusses the kinetic model developed to describe reduction of nitrate by aluminum activated by electrochemically induced pitting corrosion.

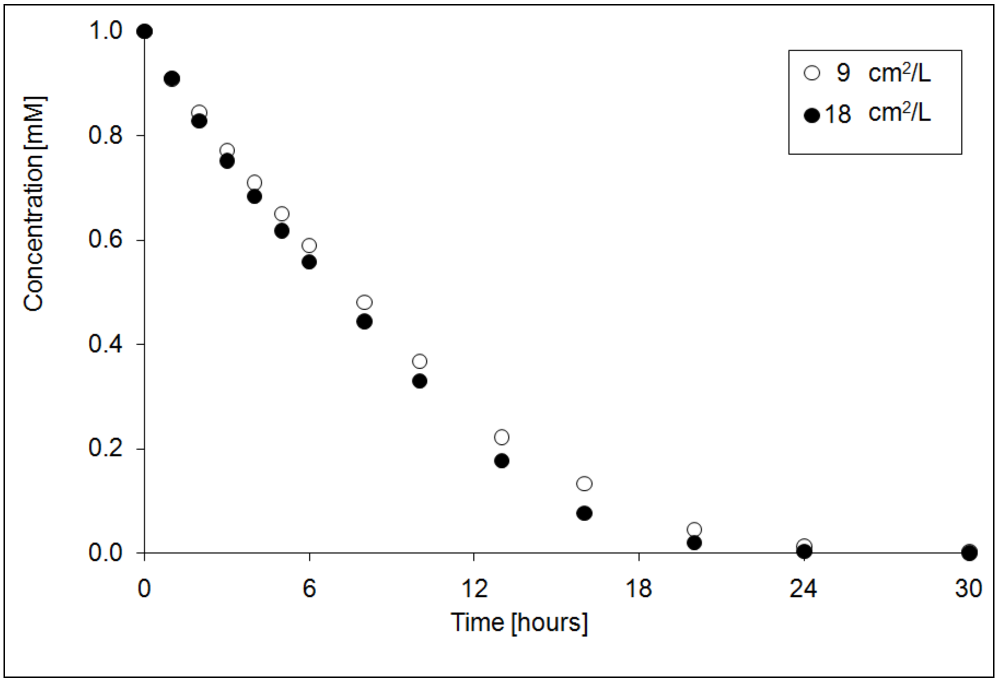

Figure 4.28 Effect of electrode surface area on nitrate reduction by aluminum during electrochemically induced pitting corrosion.

4.2.3.3 Effect of pH

This experiment was conducted to determine the effect of solution pH on the rate of nitrate reduction. Experiments were conducted at acidic, neutral and alkaline pH values. A current of 100 mA was applied and the potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The effective surface area concentration of the working electrode was 9 cm^2/L The experiments were conducted for a period of 30 hours, during which time the nitrate-N, nitrite-N and ammonia-N concentrations in the reactor were monitored by collecting samples and analyzing them using ion chromatography. The experiment is explained in detail in Section 3.4.2.3.3 of Chapter III.

Figure 4.29 shows the change in nitrate concentration with time for the experiments with solution having different initial pH values (3, 7 and 13). The potential at the working electrode relative to the reference electrode was monitored during these experiments to ensure that it was above the required value to cause pitting. The potential at the working electrode, measured relative to the reference electrode, remained fairly constant during the length of all three experiments at approximately 2.3 V. A sharp increase in potential was observed at the end of the experiment when the electrode was significantly consumed. Very little difference was observed between the experiments conducted at initial pH of 3 and 7. In the experiment conducted at initial pH of 13, a black oxide layer was formed on the electrode, which deteriorated after the first six hours. This coincides with anomalous behavior in the experiment at pH 13 between four and eight hours, where the rate of decrease in nitrate concentration slowed down. The pH of the solution in the reactors with initial pH values of 3 and 7 tended to shift towards alkaline values (pH $\approx$ 10) at the end on the experiment. For the experiment with initial pH of 13, the pH decreased to a final value of 10. Nitrate was completely converted to ammonium ion in the experiment with initial pH of 7. However, at initial pH 3 and 13, nitrate was only partially converted to ammonium ions and significant accumulation of nitrite was observed. The elemental balance on nitrogen and the associated nitrate, nitrite and ammonia concentrations are presented in Section 4.3.2, which also discusses the kinetic model developed to describe reduction of nitrate by aluminum activated by electrochemically induced pitting corrosion.

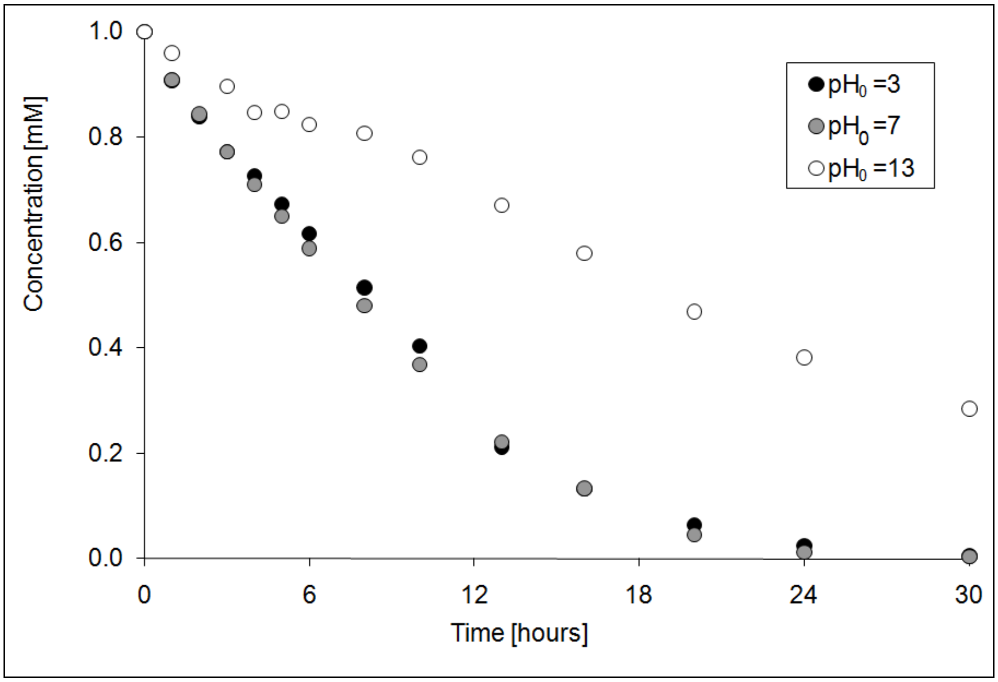

Figure 4.29 Effect of initial pH on nitrate reduction by aluminum during electrochemically induced pitting corrosion.

4.3 Model Results

4.3.1 Model for Reduction of Nitrate by pH-Activated Aluminum Granules

The results of experiments with pH-activated aluminum granules, presented in Section 4.1.3.3, show an initial lag in the conversion of nitrate to nitrite. This behavior suggests the formation of an intermediate species that reacts with nitrate in the reduction process. Since aluminum is the only reducing agent present in the system, monovalent aluminum, formed by the dissolution of zero-valent aluminum (Drazic 2005), could react with nitrate and bring about its reduction (Raijola and Davidson 1956). Pretreatment by washing aluminum granules with concentrated hydrochloric acid would generate defects in the surface oxide layer that could serve as active sites for conversion of zero-valent aluminum to monovalent aluminum.

The kinetics of nitrate reduction by pH-activated aluminum granules was described by a second-order rate model that depends on the concentrations of nitrate and monovalent aluminum ion (Al^+). The initial concentration of monovalent aluminum ion was assumed to be zero. As the experiment progressed monovalent aluminum ions were generated at the active sites on the surface of the aluminum granules. Nitrate reduction was assumed to be a two-step process with nitrite being the intermediate and ammonia being the final product. Initially, the process of nitrate reduction is limited by the conversion of Al^0 to Al^+; however, once sufficient Al^+ is produced, the rate limiting step would be the conversion of nitrate to nitrite. The relevant reactions involved in the reduction process are listed in Equations 4.4 to 4.7.

$$Al^0 + H^+ \leftrightarrow Al^+ + 1/2\ H_2 \tag{4.4}$$

$$Al^+ + 3H_2O \leftrightarrow Al(OH)_3 + H_2 + H^+ \tag{4.5}$$

$$Al^+ + NO_3^- + 2H_2O \leftrightarrow Al(OH)_3 + NO_2^- + H^+ \tag{4.6}$$

$$3Al^+ + NO_2^- + 7H_2O \leftrightarrow 3Al(OH)_3 + NH_4^+ + H^+ \tag{4.7}$$

The rate equations for the reactions shown in Equations 4.4 to 4.7 are given in Equations 4.8 to 4.11, respectively.

$$r_1 = k_1\ [Al^0] \tag{4.8}$$

$$r_2 = k_2\,[Al^+] \qquad (4.9)$$

$$r_3 = k_3\,[Al^+]\,[NO_3^-] \qquad (4.10)$$

$$r_4 = k_4\,[Al^+]\,[NO_2^-] \qquad (4.11)$$

where,

$[Al^0]$ is the zero-valent aluminum concentration (mM)

$[Al^+]$ is the mono-valent aluminum concentration (mM)

$[NO_3^-]$ is the nitrate concentration (mM)

$[NO_2^-]$ is the nitrite concentration (mM)

k_1, k_2, k_3 and k_4 are the rate constants

r_1, r_2, r_3 and r_4 are the reaction rates

Conducting material balances on $[Al^0]$, $[Al^+]$, $[NO_3^-]$, $[NO_2^-]$ and $[NH_4^+]$ generate Equations 4.12 to 4.16, respectively:

$$d[Al^0]/dt = r_{formation,\ Al^0} - r_{loss,\ Al^0} = (0) - (r_1)$$

$$d[Al^0]/dt = -\,r_1 \qquad (4.12)$$

$$d[Al^+]/dt = r_{formation,\ Al^+} - r_{loss,\ Al^+} = (r_1) - (r_2 + r_3 + 3r_4)$$

$$d[Al^+]/dt = r_1 - r_2 - r_3 - 3r_4 \qquad (4.13)$$

$$d[NO_3^-]/dt = r_{formation,\ NO_3^-} - r_{loss,\ NO_3^-} = (0) - (r_3)$$

$$d[NO_3^-]/dt = -\,r_3 \qquad (4.14)$$

$$d[NO_2^-]/dt = r_{formation,\ NO_2^-} - r_{loss,\ NO_2^-} = (r_3) - (3r_4)$$

$$d[NO_2^-]/dt = r_3 - 3r_4 \tag{4.15}$$

$$[NH_4^+]_t = [NO_3^-]_0 - [NO_3^-]_t - [NO_2^-]_t \tag{4.16}$$

The MATLAB program provided in Appendix A.1 was used to determine the rate constants. This program used the MATLAB ordinary differential equation solver named ode45 to solve the set of differential equations to provide model estimates of concentrations for a given set of rate constants. The MATLAB function named nlinfit was the nonlinear regression program used to fit the model data to the experimental data. The input data for the model is provided in Table B.1 in Appendix B.

The rate constants, k_1, k_2, k_3 and k_4 obtained by nonlinear regression are given in Table 4.1. Values are presented that were obtained using data from an individual experiment and from all of the data combined. Graphical outputs of the model simulations using data from individual experiments (1, 2, and 3) and all of the data combined are provided in Figures 4.30, 4.31, 4.32 and 4.33, respectively. The black, grey and white circles represent the measured nitrate, nitrite and ammonium concentrations, respectively. The dashed lines are the model approximations of nitrate, nitrite and ammonium concentrations.

The rate constant k_2 computed using Matlab for all four simulations was equal to zero, suggesting very little reaction between monovalent aluminum and water. The rate constants computed by nonlinear regression had very wide confidence intervals because there were no data points for zero-valent aluminum and monovalent aluminum concentrations with which to more closely specify the constants.

Table 4.1 Estimated rate constants for model for nitrate reduction by pH- activated aluminum granules.

	Kinetic experiment number			
	1	**2**	**3**	**All data**
k_1 (min^{-1})	0.0215	0.0279	0.0310	0.0038
95% CI	(-0.2461, 0.2892)	(-0.4737, 0.5294)	(-0.3244, 0.3863)	(-0.0043, 0.0120)
k_2 (min^{-1})	0.0000	0.000	0.0000	0.0000
95% CI	(-0.1353, 0.1353)	(-0.2935, 0.2935)	(-0.2133, 0.2133)	(-0.0142, 0.0142)
k_3 (min^{-1})	0.0068	0.0060	0.0063	0.0059
95% CI	(-0.0796, 0.0933)	(-0.1030, 0.1150)	(-0.0667, 0.0793)	(-0.0071, 0.0188)
k_4 (min^{-1})	0.0537	0.0444	0.0534	0.0491
95% CI	(-0.6250, 0.7325)	(-0.7612, 0.8501)	(-0.5640, 0.6708)	(-0.0588, 0.1571)
RSE	0.0853	0.0834	0.0539	0.0567

k_1, k_2, k_3 and k_4 are rate constant
RSE is the relative standard error of the estimate
CI is confidence interval

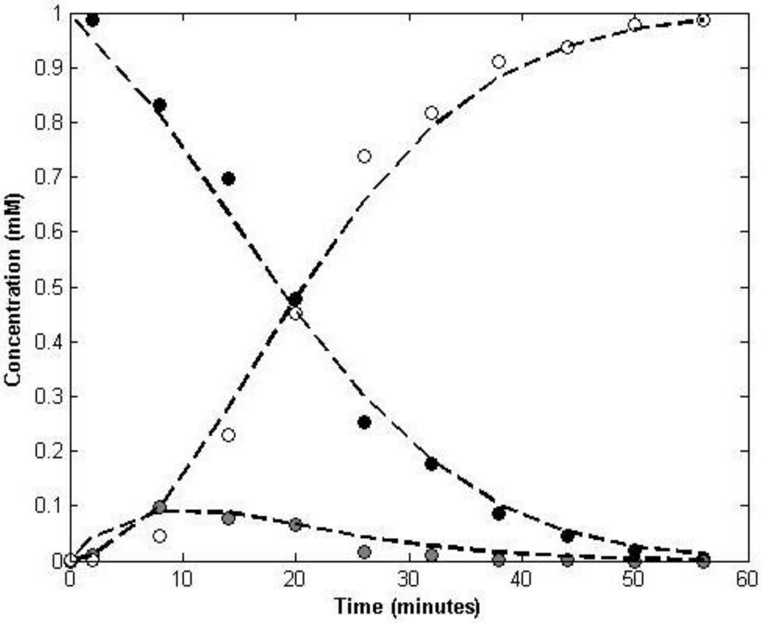

Figure 4.30 Model simulation results for nitrate reduction in kinetic experiment number 1.

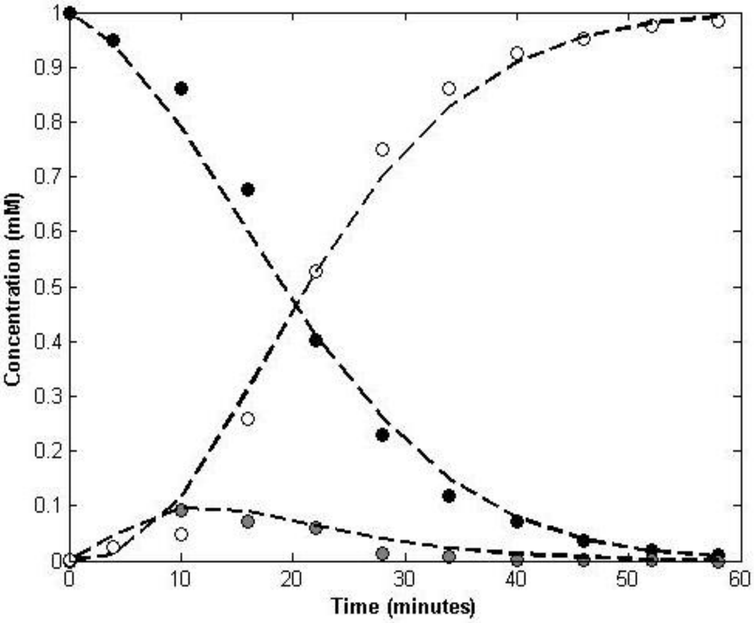

Figure 4.31 Model simulation results for nitrate reduction in kinetic experiment number 2.

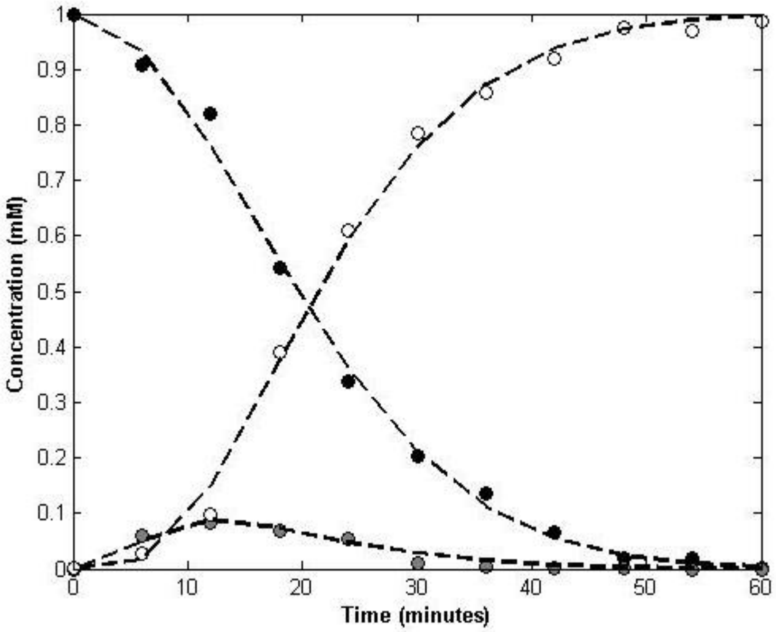

Figure 4.32 Model simulation results for nitrate reduction in kinetic experiment number 3.

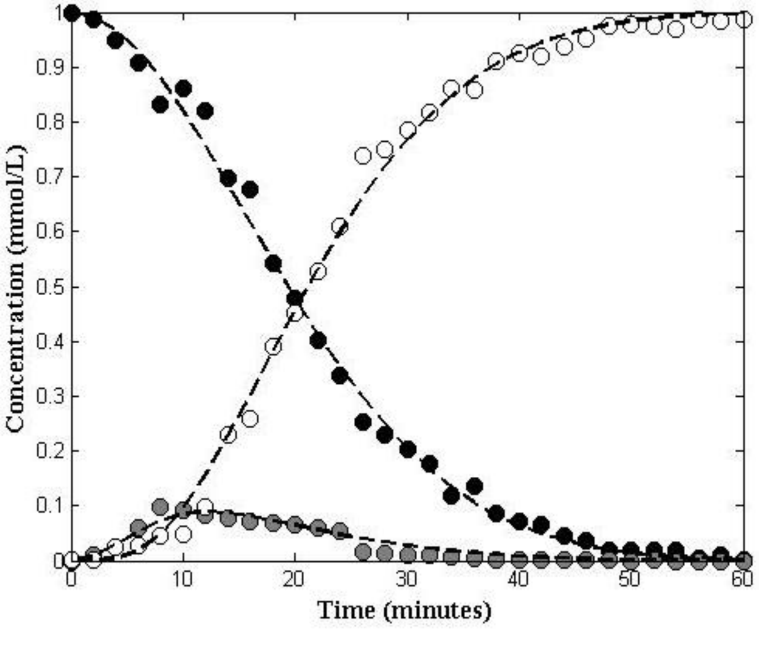

Figure 4.33 Model simulation results for nitrate reduction in kinetic experiment with all data.

4.3.2 Model for Reduction of Perchlorate by Aluminum Activated by Electrochemically Induced Pitting Corrosion

The kinetics of perchlorate reduction by aluminum activated by induced pitting corrosion was expressed by a pseudo first-order rate model that depends on the concentration of perchlorate. Since the experiments were conducted at constant current (galvanostatically), we can assume that the concentration of monovalent aluminum is constant. This would allow for the use of a pseudo first-order rate model to determine the rate constants. In order to simplify the problem, perchlorate reduction was assumed to be a one-step process with chloride being the final product. The reaction involved in the reduction process is shown in Equation 4.17.

$$Al^{+} + ClO_4^{-} + 5H^{+} \leftrightarrow Al(OH)_3 + Cl^{-} + H_2O \qquad (4.17)$$

Writing the rate equation for the reactions shown in Equations 4.17 is given in Equations 4.18, which can be further simplified by assuming that the concentration of monovalent aluminum is constant.

$$r = k[Al^{+}]\,[ClO_4^{-}] = k'\,[ClO_4^{-}] \qquad (4.18)$$

Conducting a material balance on $[ClO_4^{-}]$ generates Equations 4.19, which can be integrated to get the concentration of perchlorate as a function of time (Equation 4.20).

$$d[ClO_4^{-}]/dt = k'\,[ClO_4^{-}] \qquad (4.19)$$

$$[ClO_4^{-}]_t = [ClO_4^{-}]_0 \times \exp(-k' \times t) \qquad (4.20)$$

Similarly, conducting a material balance on $[Cl^-]$, Equations 4.21 can be obtained to get the concentration of chloride as a function of time.

$$[Cl^-]_t = [Cl^-]_0 + [ClO_4^-]_0 - [ClO_4^-]_t \qquad (4.21)$$

where,

$[ClO_4^-]_0$ is the initial perchlorate concentration (mM)

$[ClO_4^-]_t$ is the perchlorate concentration (mM) at time t

$[Cl^-]_0$ is the initial chloride concentration (mM)

$[Cl^-]_t$ is the chloride concentration (mM) at time t

k' is the rate constant

The concentrations of perchlorate and chloride ion at any time can be determined using Equations 4.20 and 4.21, respectively.

The MATLAB program provided in Appendix A.2 was used to determine the rate constants. The program used nlinfit, a nonlinear fitting program to fit the model data to the experimental data. The input data for the model is provided in Tables B.2 and B.3 in Appendix B.

Figures 4.34 through 4.38 are the graphical outputs of the model simulation in Matlab. It should be noted that the concentration of chloride shown in the figures is computed by subtracting the initial concentration of chloride in the reactor from all the data points. The closed circles and open circles represent the measured perchlorate and chloride concentrations, respectively. The dashed lines are the model approximations of perchlorate and chloride concentrations. The figures show that perchlorate is completely converted to chloride.

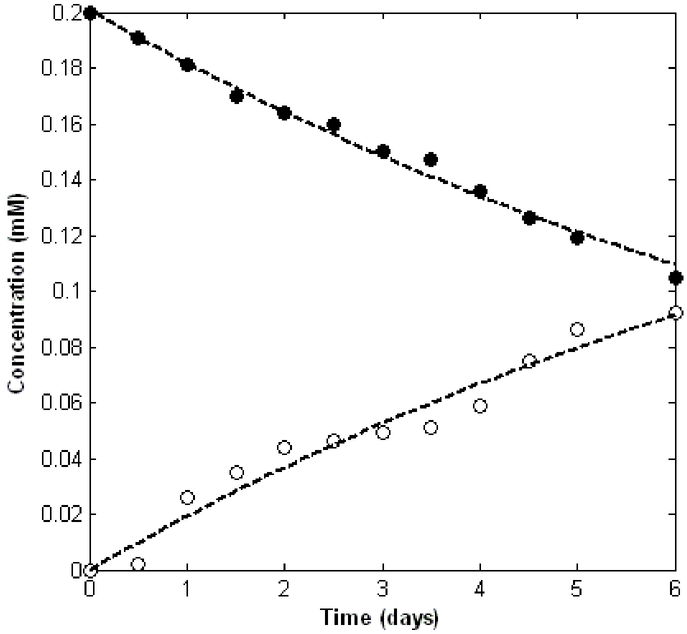

Figure 4.34 Model simulation results for perchlorate reduction at I = 10 mA, Electrode surface area = 18 cm^2/L and pH$_0$ = 7.

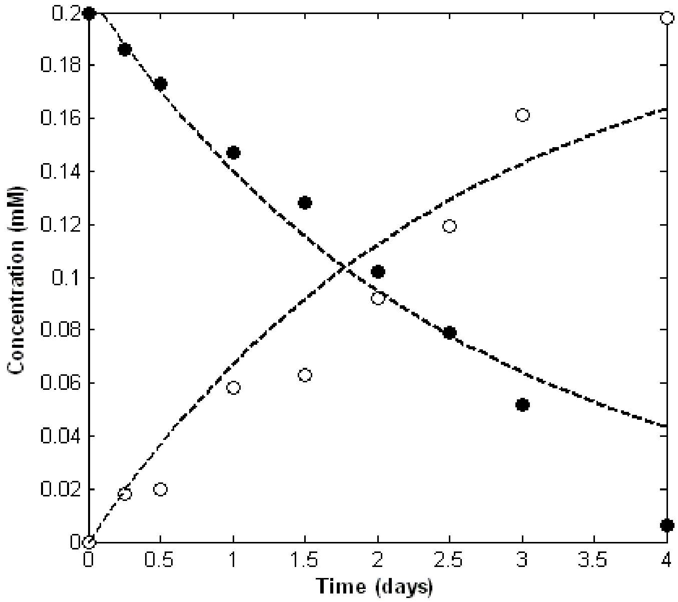

Figure 4.35 Model simulation results for perchlorate reduction at I = 50 mA, Electrode surface area = 18 cm^2/L and pH_0 = 7.

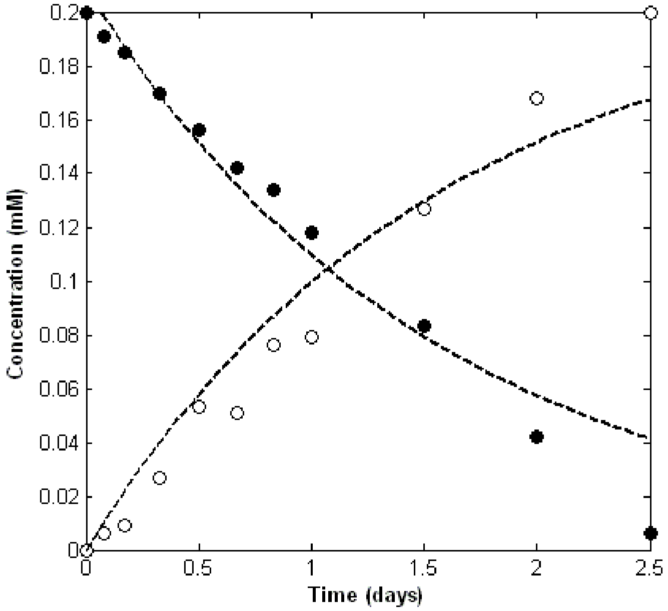

Figure 4.36 Model simulation results for perchlorate reduction at I = 100 mA, Electrode surface area = 18 cm^2/L and pH_0 = 7.

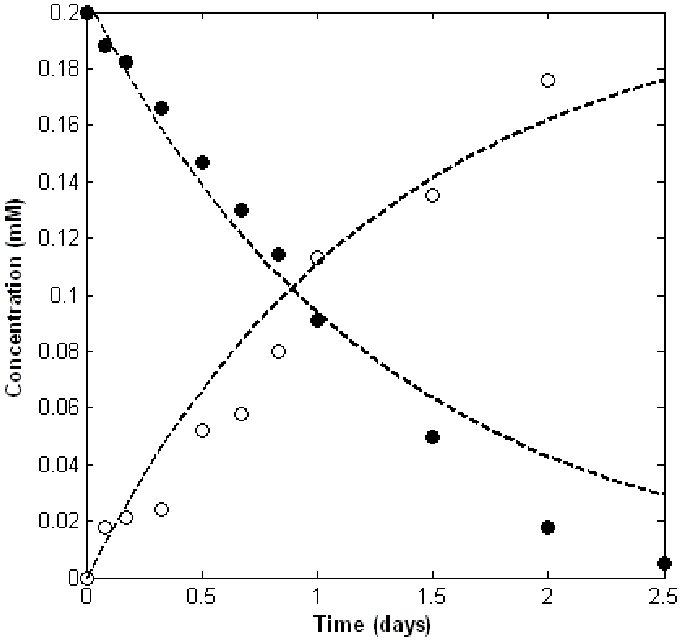

Figure 4.37 Model simulation results for perchlorate reduction at I = 100 mA, Electrode surface area = 36 cm^2/L and pH$_0$ = 7.

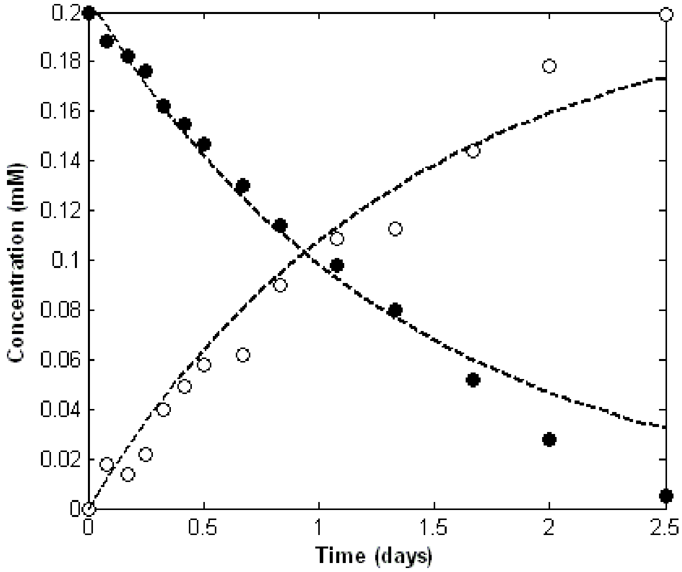

Figure 4.38 Model simulation results for perchlorate reduction at I = 100 mA, Electrode surface area = 18 cm^2/L and pH$_0$ = 3.

Table 4.2 shows the values of the rate constants estimated by nonlinear regression using Matlab. Figure 4.39 shows that the rate constant, ḱ, increases with increasing current. Increasing the electrode surface area increased the rate constants for perchlorate reduction to chloride by a small amount (Figure 4.40). The initial pH values of the solution in the reactor had very little effect on the rate constant for reduction of perchlorate to chloride (Figure 4.41).

Table 4.2 Estimated rate constants for model for perchlorate reduction by aluminum activated by electrochemically induced pitting corrosion.

	Experiment Number				
	1	**2**	**3**	**4**	**5**
I (mA)	10	50	100	100	100
ESA (cm^2/L)	18	18	18	36	18
Initial pH	7	7	7	7	3
ḱ (day^{-1})	0.10	0.39	0.65	0.78	0.74
95% CI	(0.10, 0.11)	(0.33, 0.45)	(0.57, 0.73)	(0.69, 0.87)	(0.68, 0.80)
RSE	0.0461	0.1730	0.1481	0.1451	0.1117

I is applied current
ESA is electrode surface area
ḱ is rate constant
RSE is the relative standard error of the estimate
CI is confidence interval

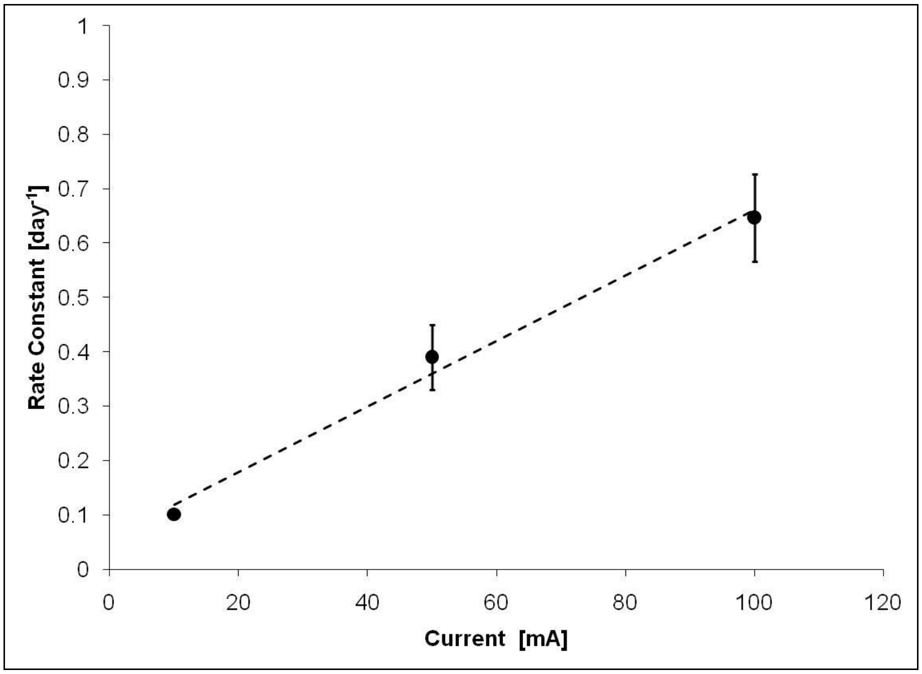

Figure 4.39 Effect of current on rate constant for perchlorate reduction by aluminum activated by electrochemically induced pitting corrosion. Error bars indicate the 95% confidence interval. Some error bars are not visible because they are smaller than the symbol.

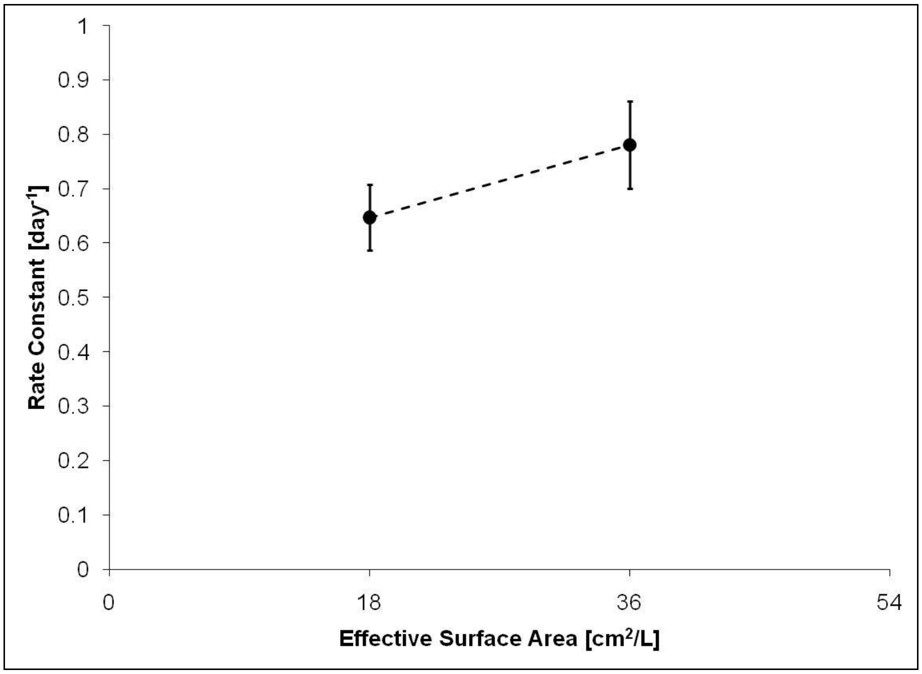

Figure 4.40 Effect of effective electrode surface area concentration on rate constant for perchlorate reduction by aluminum activated by electrochemically induced pitting corrosion. Error bars indicate the 95% confidence interval. Some error bars are not visible because they are smaller than the symbol.

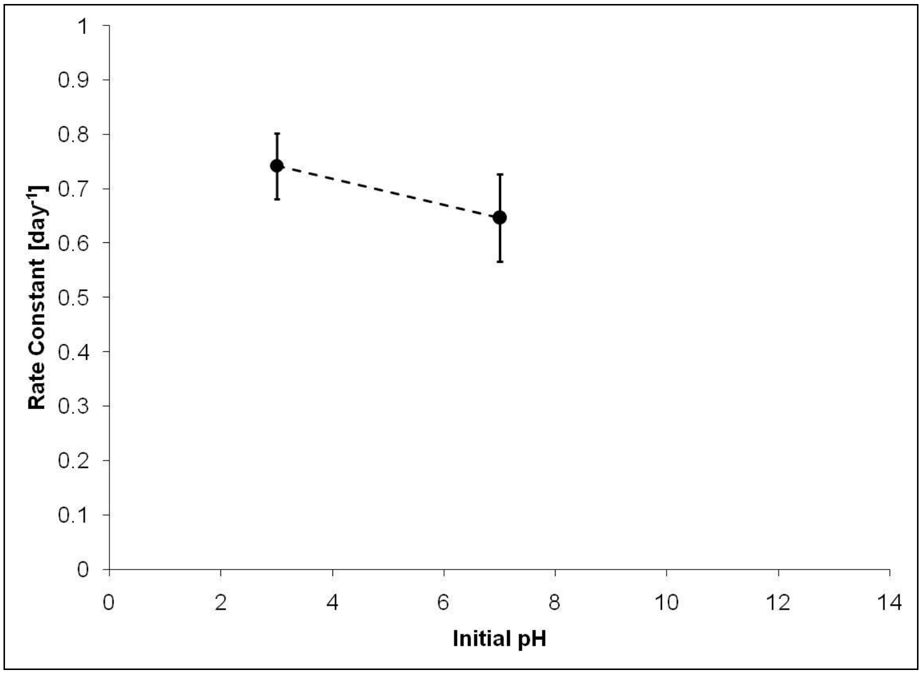

Figure 4.41 Effect of initial pH on rate constant for perchlorate reduction by aluminum activated by electrochemically induced pitting corrosion. Error bars indicate the 95% confidence interval. Some error bars are not visible because they are smaller than the symbol.

4.3.3 Model for Reduction of Nitrate by Aluminum Activated by Electrochemically Induced Pitting Corrosion

The kinetics of nitrate reduction by aluminum undergoing pitting corrosion was expressed by a pseudo first-order rate model that depends on the concentration of nitrate. Since the experiments were conducted at constant current (galvanostatically), we can assume that the concentration of monovalent aluminum is constant. Monovalent aluminum concentration was assumed to be constant to allow for the use of a pseudo first-order rate model. The reduction was assumed to be a two-step process with nitrite being the intermediate and ammonia being the final product. The relevant reactions involved in the reduction process are listed in Equation 4.22 and 4.23.

$$Al^{+} + NO_3^{-} + 2H_2O \leftrightarrow Al(OH)_3 + NO_2^{-} + H^{+} \qquad (4.22)$$

$$3Al^{+} + NO_2^{-} + 7H_2O \leftrightarrow 3Al(OH)_3 + NH_4^{+} + H^{+} \qquad (4.23)$$

Writing the rate equation for the reactions shown in Equations 4.22 and 4.23 and simplified by assuming that the concentration of monovalent aluminum is constant we get Equations 4.24 and 4.25.

$$r_1 = -k_1\,[Al^{+}]\,[NO_3^{-}] = k'_1\,[NO_3^{-}] \qquad (4.24)$$

$$r_2 = k_1\,[Al^{+}]\,[NO_3^{-}] - k_2\,[Al^{+}]\,[NO_3^{-}] = k'_1[NO_3^{-}] - k'_2[NO_2^{-}] \qquad (4.25)$$

Conducting a mass balance on nitrate and nitrite, we get Equations 4.26 and 4.27.

$$d[NO_3^{-}]_t\,/dt = -r_1 = -k'_1\,[NO_3^{-}] \qquad (4.26)$$

$$d[NO_2^{-}]_t\,/dt = r_1 - r_2 = k'_1[NO_3^{-}] - k'_2[NO_2^{-}] \qquad (4.27)$$

Integrating Equation 4.26, we get Equation 4.28.

$$[NO_3^{-}]_t = [NO_3^{-}]_0 \times \exp(-k' \times t) \qquad (4.28)$$

Substituting Equation 4.28 in Equation 4.27 and integrating, we get Equation 4.29.

$$[NO_2^{-}]_t = \frac{k' \times [NO_3^{-}]_t \times (\exp(-k' \times t) - \exp(-k_2 \times t))}{(k_2 - k')} \qquad (4.29)$$

Conducting a mass balance on ammonium, we get Equations 4.30.

$$[NH_4^{+}]_t = [NO_3^{-}]_0 - [NO_3^{-}]_t - [NO_2^{-}]_t \qquad (4.30)$$

where,

$[NO_3^-]_0$ is the initial nitrate concentration (mM)

$[NO_3^-]_t$ is the nitrate concentration (mM) at time t

$[NO_2^-]_t$ is the nitrite concentration (mM) at time t

$[NH_4^+]_t$ is the ammonium ion concentration (mM) at time t

k_1 and k_2, are the second-order rate constants for reactions 4.22 and 4.23, respectively

k'_1 and k'_2, are the pseudo-first-order rate constants for reactions 4.22 and 4.23, respectively

The concentrations of nitrate, nitrite and ammonium ion at any time can be determined using Equations 4.25 to 4.27, respectively.

The MATLAB program provided in Appendix B.3 was used to determine the rate constants. The program used nlinfit, a nonlinear fitting program to fit the model data to the experimental data. The input data for the model is provided in Tables B.4 to B.8 in Appendix B.

Figures 4.42 through 4.47 are the graphical outputs of the model simulation by the model using coefficients determined by non-linear regression and shown in Table 4.3. The black, grey and white circles represent the measured nitrate, nitrite and ammonium concentrations, respectively. The dashed lines are the model approximations of nitrate, nitrite and ammonium concentrations.

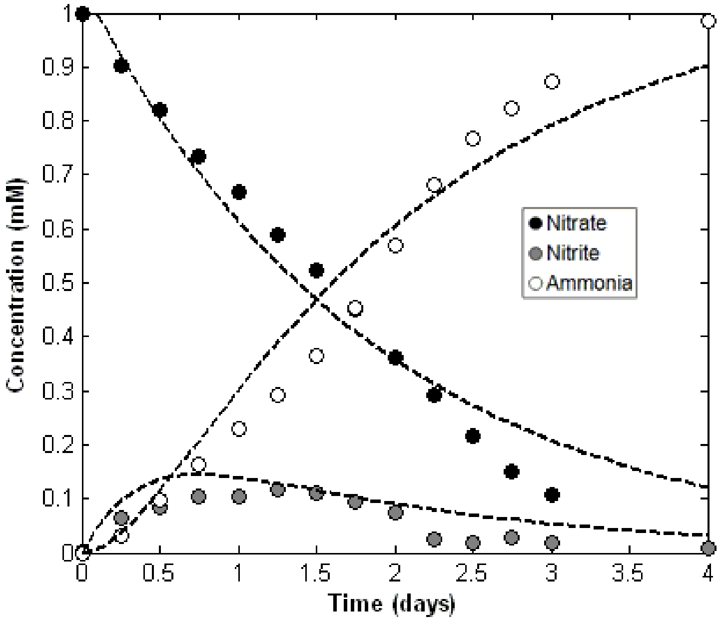

Figure 4.42 Model simulation results for nitrate reduction at I = 10 mA, Electrode surface area = 9 cm^2/L and pH_0 = 7.

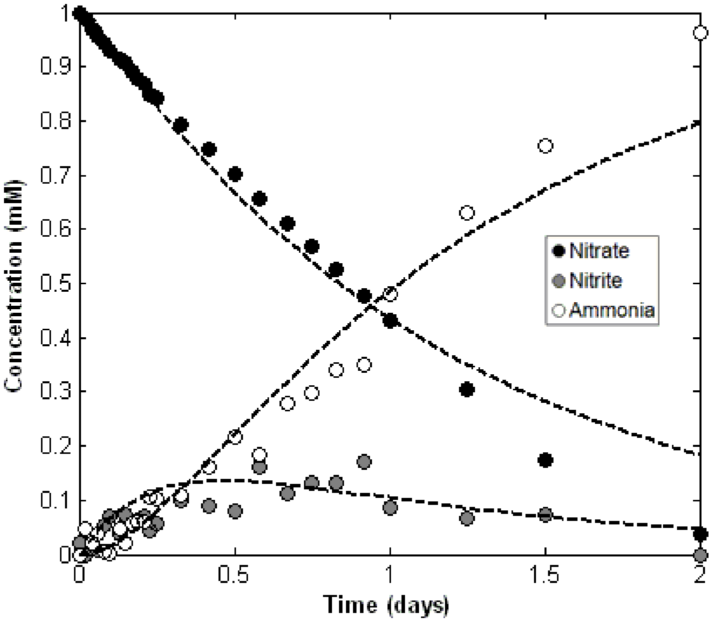

Figure 4.43 Model simulation results for nitrate reduction at I = 20 mA, Electrode surface area = 9 cm^2/L and pH_0 = 7.

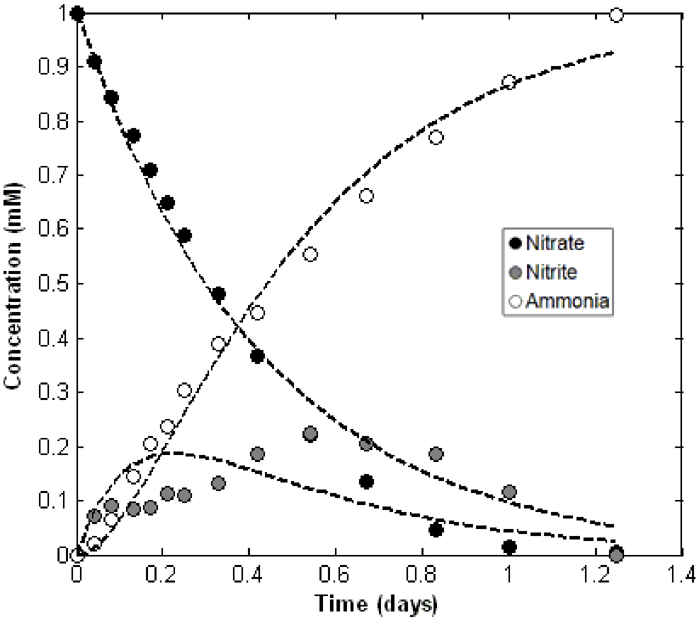

Figure 4.44 Model simulation results for nitrate reduction at I = 50 mA, Electrode surface area = 9 cm^2/L and pH$_0$ = 7.

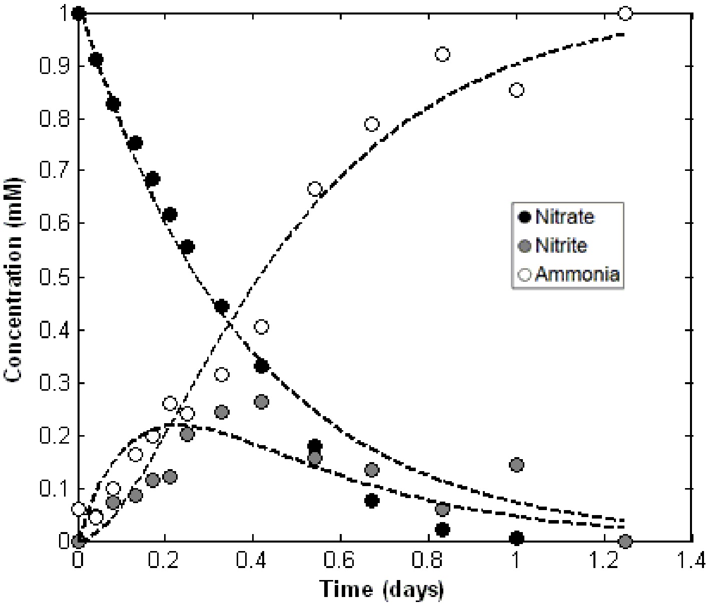

Figure 4.45 Model simulation results for nitrate reduction at I = 50 mA, Electrode surface area = 18 cm^2/L and pH$_0$ = 7.

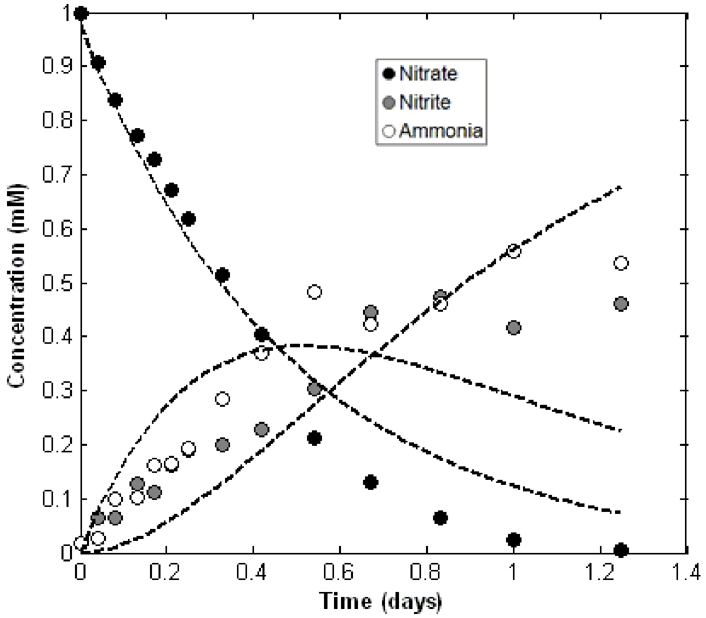

Figure 4.46 Model simulation results for nitrate reduction at I = 50 mA, Electrode surface area = 9 cm^2/L and pH$_0$ = 3.

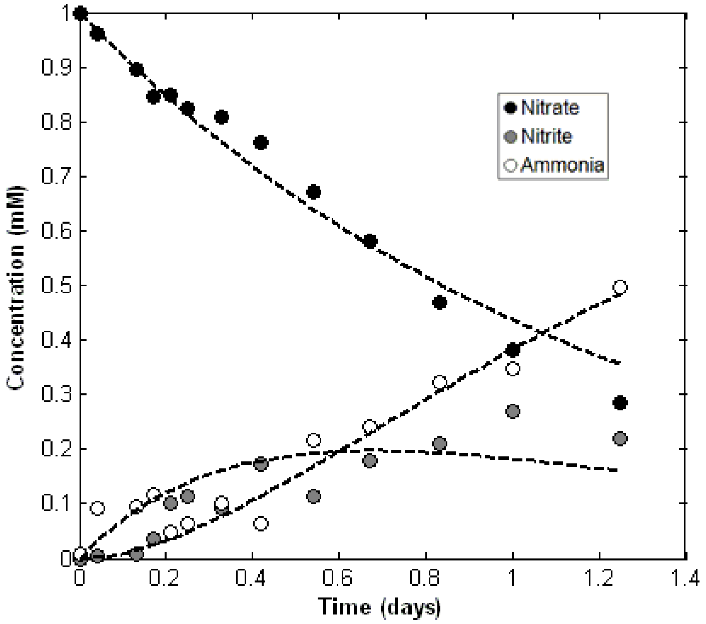

Figure 4.47 Model simulation results for nitrate reduction at I = 50 mA, Electrode surface area = 9 cm^2/L and pH$_0$ = 13.

Table 4.3 Estimated rate constants for model for nitrate reduction by aluminum activated by electrochemically induced pitting corrosion.

	Experiment Number					
	1	**2**	**3**	**4**	**5**	**6**
I (mA)	10	20	50	50	50	50
ESA (cm^2/L)	9	9	9	18	9	9
pH_0	7	7	7	7	3	13
$\acute{k}_1$ (day^{-1})	0.54	0.86	2.35	2.64	2.07	0.83
95% CI	(0.50, 0.58)	(0.80, 0.91)	(2.14, 2.56)	(2.40, 2.89)	(1.71, 2.42)	(0.75, 0.91)
$\acute{k}_2$ (day^{-1})	2.63	4.32	7.41	6.76	1.81	2.41
95% CI	(1.93, 3.32)	(3.54, 5.10)	(5.71, 9.11)	(5.34, 8.19)	(1.34, 2.29)	(1.92, 2.91)
RSE	0.1669	0.1345	0.1690	0.1750	0.3132	0.1420

I is applied current
ESA is electrode surface area
$\acute{k}_1$ and $\acute{k}_2$ are rate constant
RSE is the relative standard error of the estimate
CI is confidence interval

Table 4.3 shows the values of the rate constants estimated by nonlinear regression. Figure 4.48 shows the rate constants ($\acute{k}_1$ and $\acute{k}_2$) as a function of applied current and this figure shows that they increase linearly with increasing current. Increasing the electrode surface area had very little effect on the rate constant for nitrate reduction to nitrite and on the rate constant for nitrite reduction to ammonium

(Figure 4.49). Figure 4.45 shows the effect of initial solution pH on the rate constants (k'_1 and k'_2). The initial solution pH had very little effect on the rate constant for reduction of nitrate to nitrite (k'_1). However, the rate constant for reduction of nitrite to ammonium (k'_2), was considerably higher for the initial pH of 7. The inhibiting effect of pH was significantly greater for nitrite reduction to ammonium, which resulted in accumulation of nitrite in experiments at the extreme pH values.

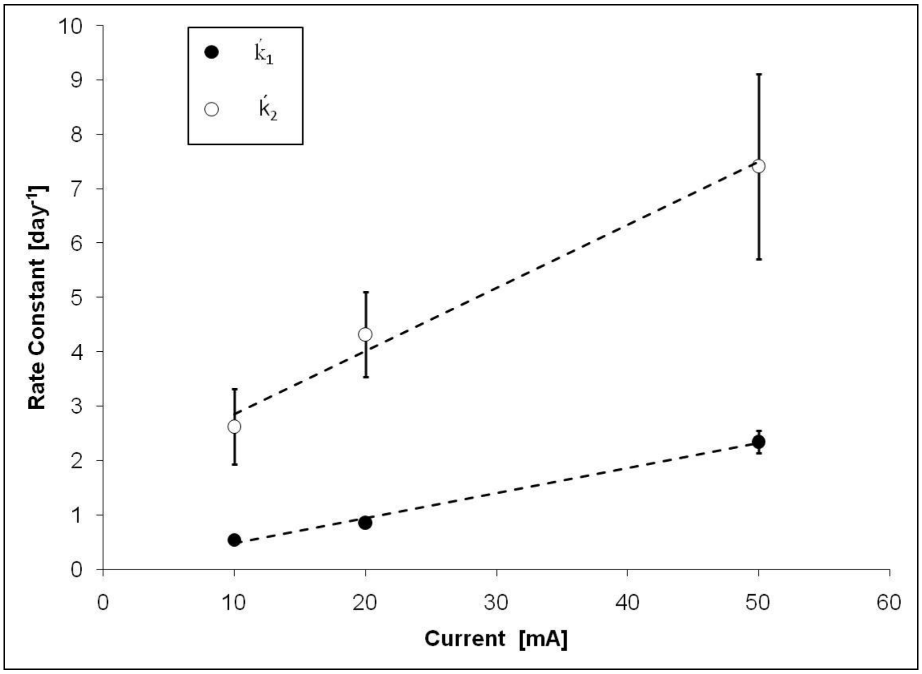

Figure 4.48 Effect of current on rate constants for reduction of nitrate and nitrite by aluminum activated by electrochemically induced pitting corrosion. Error bars indicate the 95% confidence interval. Some error bars are not visible because they are smaller than the symbol.

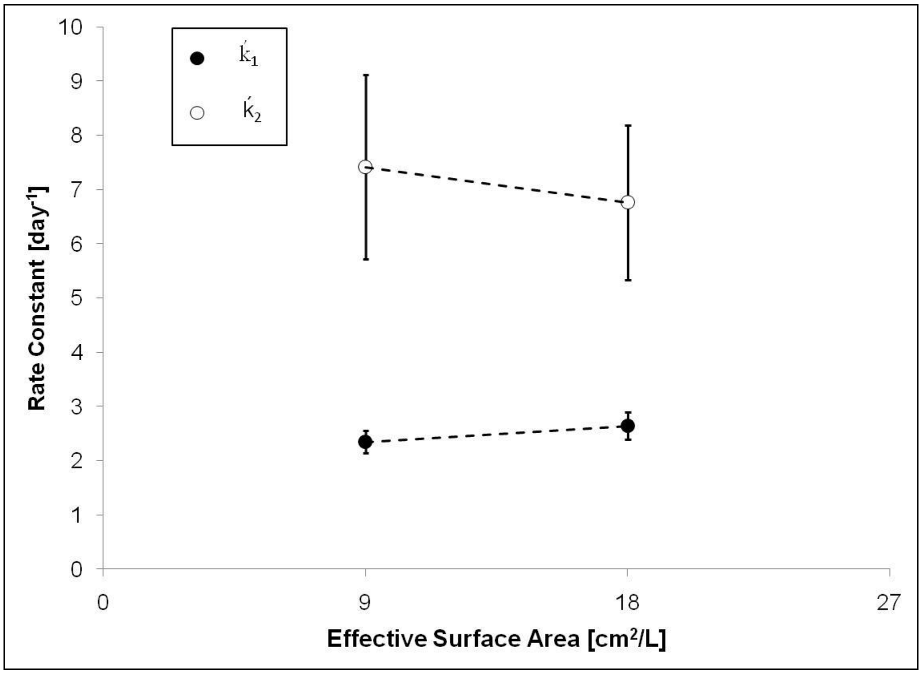

Figure 4.49 Effect of effective surface area concentration on rate constants for reduction of nitrate and nitrite by aluminum activated by electrochemically induced pitting corrosion. Error bars indicate the 95% confidence interval. Some error bars are not visible because they are smaller than the symbol.

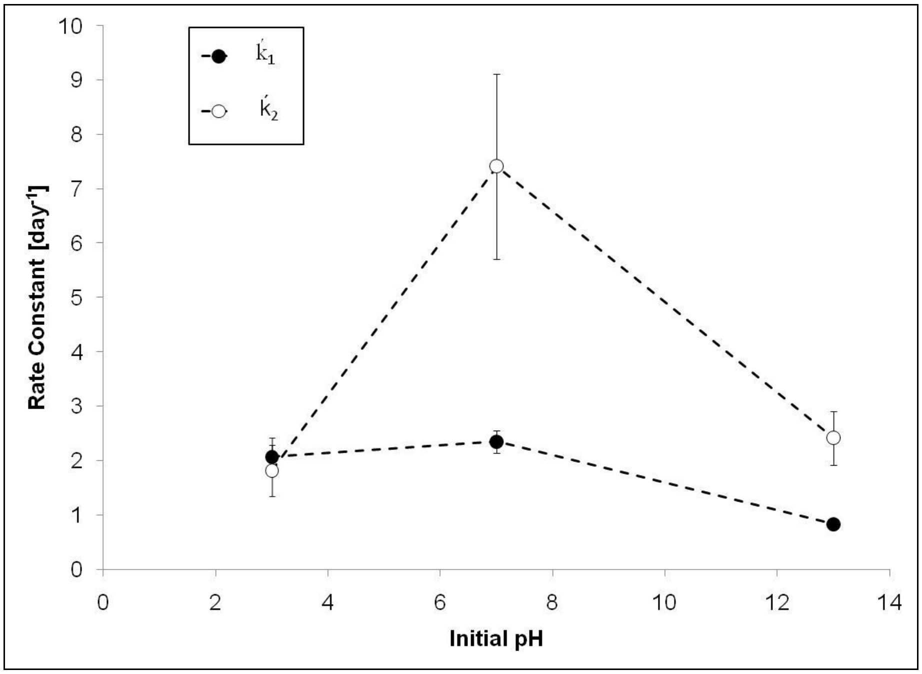

Figure 4.50 Effect of pH on rate constants for reduction of nitrate and nitrite by aluminum activated by electrochemically induced pitting corrosion. Error bars indicate the 95% confidence interval. Some error bars are not visible because they are smaller than the symbol.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

This chapter draws conclusions from the results of the experiments conducted during this dissertation study and presented in Chapter IV. The chapter concludes with recommendations for future research that could be performed to improve the understanding of the reduction of perchlorate and nitrate by aluminum.

5.1 Conclusions

While zero-valent aluminum has the thermodynamic ability to behave as a reducing agent, the presence of the passive oxide surface layer impedes any potential reduction processes from occurring. If the surface oxide layer is disrupted, potential sites could be created for the reduction of perchlorate and nitrate. Monovalent aluminum is believed to be generated at the sites by the partial oxidation of zero-valent aluminum. This study assumed that monovalent aluminum is the reducing agent that reacts with perchlorate and nitrate. The two potential methods of disrupting the surface oxide layer examined during the dissertation include activation of aluminum by controlling the solution pH and by applying an electrochemical potential.

The results of this research demonstrate that aluminum has the ability to reduce both perchlorate and nitrate. The conclusions based on results of experiments on the reduction of perchlorate and nitrate by aluminum that was activated by controlling the solution pH are presented in the section titled “Reduction by pH-Activated Aluminum

Granules". The conclusions based on results of experiments on the reduction of perchlorate and nitrate by aluminum activated by applying an electrochemical potential are presented in the section titled "Reduction by Aluminum Activated by Electrochemically Induced Pitting Corrosion". These sections are further divided into sub-sections addressing the conclusions related to perchlorate reduction or nitrate reduction.

5.1.1 pH-Activated Oxide Layer Removal Experiments

Zero-valent aluminum is able to either reduce or adsorb perchlorate or nitrate depending on the solution pH. The removal process is believed to be adsorption onto the surface oxide layer on the aluminum granules in highly acidic solutions, and reduction in highly alkaline solutions. The ability of the pH-activated aluminum to interact with perchlorate and nitrate is negligible in solutions having pH in the passive range for the aluminum oxide film ($4 \leq \mathrm{pH} \leq 10$). Pretreatment with concentrated hydrochloric acid is believed to disrupt the surface oxide layer producing defects or pits. Monovalent aluminum formed by the partial oxidation of zero-valent aluminum in the pits is believed to be the primary reducing agent. The following sub-sections summarize the conclusion drawn from the experiments studying reduction of perchlorate and nitrate by pH-activated aluminum granules.

5.1.1.1 Perchlorate

While perchlorate is a stable compound that is only slowly reduced by common chemical reducing agents under normal environmental conditions, monovalent aluminum has the potential to reduce perchlorate to chloride.

Changes in concentrations of perchlorate and possible degradation products during the preliminary experiments could not be measured in samples with pH ≥ 11 because of baseline stabilization problems associated with the DX-500 Ion Chromatography system. Therefore, the extents of removal and chemical reduction of perchlorate could not be quantified at very high pH. At pH ≥ 11, hydrogen gas evolution was observed that could be attributed to the reduction of water by aluminum. Therefore, there is a possibility that aluminum could also be reducing perchlorate in solutions having high pH (pH ≥ 11).Kinetic experiments were not conducted for perchlorate reduction in highly alkaline solution. A drop in solution pH was also observed during these experiments. The observed evolution of hydrogen gas and drop in solution pH, coupled with the observed reduction of nitrate to ammonia in highly alkaline solutions is indicative of the possibility for perchlorate reduction by pH-activated aluminum. Further experiments with reliable methods for measuring perchlorate concentration at high pH need to be conducted to evaluate whether perchlorate is reduced by pH-activated aluminum granules.

A decrease in perchlorate concentration was observed at highly acidic pH during the preliminary experiments conducted to determine the optimum pH and aluminum dosage. However, equivalent amounts of chlorite, chlorate or chloride were not generated during these experiments. Although, there is a chance that perchlorate could be converted to hypochlorite or other compounds that were not detectable by the analytical procedure, the more likely explanation is that perchlorate is being adsorbed on the surface oxide layer. Very little gas evolution was observed in preliminary experiments conducted at pH ≤ 11, which suggests that very little hydrogen or chlorine-containing gas was formed as an end-product. Since hydrogen is a byproduct in the reaction that generates monovalent aluminum, which is believed to bring about the reduction of perchlorate, it is unlikely that perchlorate is being reduced. The increase in solution pH during the preliminary experiments conducted at pH ≤ 4 could be attributed to the speciation of trivalent aluminum formed during the oxidization of zero-valent aluminum. Kinetic experiments conducted at initial pH of 2.8 showed that most of the decrease in perchlorate concentration occurred within the first four minutes of the experiment. These observations suggest that perchlorate may be adsorbing onto the surface oxide layer on aluminum granules in highly acidic solution. Investigation of the adsorption process was beyond the scope of this dissertation study and was therefore not conducted.

5.1.1.2 Nitrate

Nitrate, on the other hand, can be reduced with relative ease compared to perchlorate. The nitrate reduction reaction is extremely pH sensitive, with significant reduction occurring only when solution pH ≥ 11. At solution pH ≥ 11, monovalent aluminum is hypothesized to be produced from zero-valent aluminum in a reaction that also produces hydrogen gas. The reduction of nitrate by pH-activated aluminum granules is accompanied by a drop in pH to a value of approximately 10. A passive oxide film can form on the surface of the aluminum granules when the solution pH drops below 10, and prevent formation of the monovalent aluminum that is believed to be the active reducing agent for perchlorate. The kinetic experiments and modeling results provide evidence to suggest that an intermediate, like monovalent aluminum, formed by the partial oxidation of zero-valent aluminum has the potential to reduce nitrate to ammonia. Reduction of nitrate to ammonia is a two-step process with nitrite as the intermediate. The kinetic model for reduction of nitrate by pH-activated aluminum granules developed in this dissertation is able to predict the nitrate, nitrite and ammonia concentrations with reasonable accuracy. However, the rate constants derived from the model have uncertainties associated with the lack of data for concentrations of all the reactants and products. The rate constants (k_1, k_2, k_3, and k_4) had very wide confidence intervals, because no data was available on the concentrations of zero-valent and monovalent aluminum.

A decrease in nitrate concentration was observed at highly acidic pH during the preliminary experiments conducted to determine the optimum pH and aluminum dosage. However, equivalent amounts of nitrite and ammonia were not generated during these experiments. Also, very little gas evolution was observed in preliminary experiments conducted at pH ≤ 11, which suggests that very little hydrogen or nitrogen-containing gas as an end-product. Since hydrogen is a byproduct in the reaction that generates the monovalent aluminum that is believed to bring about the reduction of nitrate, it is unlikely that nitrate is being reduced in the absence of gas production. An increase in pH was observed during the experiments with nitrate at acidic pH, which is similar to that observed during experiments with perchlorate. These observed conditions, coupled with the observed adsorption of perchlorate at similar pH values, are indicative of nitrate adsorption onto the surface oxide layer on aluminum granules in highly acidic solution. Investigation of the adsorption process was beyond the scope of this dissertation study and was therefore not conducted.

5.1.2 Electrochemically Induced Pitting Corrosion Experiments

Electrochemically induced pitting corrosion of aluminum can disrupt the surface oxide layer creating stable pits on the aluminum surface. Stable pits will be formed on the aluminum electrode surface when the potential at the electrode is above the critical pitting potential for aluminum. The pitting potential is dependent on the concentration and type of anions in the bulk solution. Smaller ions are better incorporated into the oxide later than larger ions and therefore, decrease the resistance to pitting and lower the pitting potential to a greater degree. Chloride ion has an ionic radius of 0.181 nm, which is smaller than the ionic radii of both perchlorate and nitrate ions. Thus, presence of chloride in the solution would shift the pitting potential to more negative values more effectively than nitrate or perchlorate and this shift can accelerate the pitting process. Increasing the concentration of nitrate and perchlorate in the solution also accelerated the pitting process. Once the surface oxide layer is disrupted zero-valent aluminum is converted to monovalent aluminum in the stable pits. This monovalent aluminum has the potential for reducing perchlorate and nitrate.

5.1.2.1 Perchlorate

Aluminum activated by electrochemically induced pitting corrosion can effectively reduce perchlorate to chloride as long as the potential at the electrode is above the critical pitting potential for aluminum for the given perchlorate concentration. The rate of this reduction reaction was observed to be directly proportional to the applied current, which was explained by Faraday's Law. Applying a higher galvanostatic current would cause monovalent aluminum to be liberated at the electrode at a faster rate, which translates to an increase in the rate of perchlorate reduction. The rate of perchlorate reduction by aluminum activated by electrochemically induced pitting corrosion was independent of the electrode surface area when current was held constant. Faradays's Law states that the rate at which a substance is altered at an electrode is dependent on the rate at which charge passes through the electrode. The rate at which charge passes through the electrode is the galvanostatic current. Increasing the electrode surface area does not affect the current and consequently does not have an effect on the rate of perchlorate reduction. The initial pH of the solution had very little effect on the rate of perchlorate reduction. However, it must be noted that perchlorate reduction at high pH was not examined due to problems with the analytical system.

The kinetic model for reduction of perchlorate by aluminum activated by electrochemically induced pitting corrosion developed in this dissertation predicted the perchlorate and chloride concentrations with reasonable accuracy. The model was a simplified version that assumed a one-step process with chloride being the final product.

5.1.2.2 Nitrate

Aluminum activated by electrochemically induced pitting corrosion can effectively reduce nitrate to ammonia as long as the potential at the electrode is above the critical pitting potential for aluminum under conditions present in the solution. The rate of nitrate reduction was observed to be directly proportional to the applied current, which was explained by Faraday's Law. Applying a higher galvanostatic current would cause larger rate of monovalent aluminum production at the electrode, which translates to an increase in the rate of nitrate reduction. The rate of nitrate reduction by aluminum activated by electrochemically induced pitting corrosion was independent of the electrode surface area when current was held constant. Increasing the electrode surface area did not have an appreciable effect on the rate of the nitrate reduction by aluminum when current was held constant. Faradays's Law states that the rate at which a substance is altered at an electrode is dependent on the rate of charge transfer through the electrode, which is the galvanostatic current. Increasing the electrode surface area does not affect the current and consequently does not affect the rate of nitrate reduction. The initial pH of the solution did not have a significant effect on the rate of reduction of nitrite to ammonia. However, in solutions with initial pH near 7, acceleration in the rate nitrate reduction to nitrite was observed.

The kinetic model for reduction of nitrate by aluminum activated by electrochemically induced pitting corrosion developed in this dissertation predicted the nitrate, nitrite and ammonia concentrations with reasonable accuracy. The model was a simplified version that assumed a two-step process with nitrite being the intermediate and ammonia being the final product.

5.2 Recommendations

This research has demonstrated that perchlorate and nitrate can be effectively reduced by disrupting the passivating oxide film that prevents the underlying aluminum from participating in reactions. The two processes that were examined in this research to disrupt the oxide film were controlling the solution pH and by electrochemically induced pitting corrosion. Both of these methods seemed to effectively remove the oxide layer and in so doing, facilitated the reduction of perchlorate and nitrate. Removal of perchlorate and nitrate by adsorption on the oxide layer was also observed during experiments in which aluminum was treated by adjusting the solution to an acidic pH. However, before developing a practicable engineering system for future application of these processes, it is necessary to address some areas that need to further research. The following paragraphs discuss the areas of future research that need to be conducted to extend the work done during this study.

This research primarily focused on studying the phenomenon of perchlorate and nitrate reduction by aluminum and developing kinetic models for the reactions. However, little attention was directed to studying the mechanism of the reduction process. A detailed analysis of the oxide film by scanning electron microscopy (SEM) and X-ray diffraction (XRD) would provide further insight into the reduction process. Such a study would be necessary to improve the efficiency of the process and seek alternatives that would advance the development of a treatment system.

The reduction of perchlorate and nitrate by pH-activated aluminum studied in this dissertation resulted in a significant amount of aluminum being consumed by reaction with water to form hydrogen gas. This is evident from the Figure 4.13 in Chapter IV, where the amount of hydrogen gas released was substantially less at a solution pH of 12, when compared to the hydrogen gas released at a solution pH of 13. Murphy (1991) suggested that this loss can be minimized by carrying out this process in a narrow pH range ($9.5 \leq pH \leq 9.7$). However, in the experiments carried out in this dissertation study, reduction of nitrate was observed only at $pH \geq 11$. Reduction of nitrate, and possibly perchlorate, could be accomplished while simultaneously decreasing the amount of aluminum consumed by reaction with water by controlling the solution pH. The use of a buffering agent to maintain the solution pH above 11 would contribute to a cost-effective use of aluminum in the treatment process. One such buffering agent could be calcium oxide, which has a pKa value of 12.5. Calcium oxide or lime is commonly used in water and sewage treatment for water softening and removal of heavy metals. Such plants could easily incorporate lime to control solution pH for reduction process using pH-activated aluminum granules.

The process of perchlorate and nitrate adsorption on the oxide layer on aluminum granules in highly acidic solution was observed, but not studied. Further examination of this process might provide a viable alternative for removal of perchlorate and nitrate from highly concentrated waste streams, such as those generated from ion exchange.

In conclusion, the research on perchlorate and nitrate removal by aluminum discussed in this dissertation is necessarily a first step and is by no means complete. The potential for technological improvements possible in this treatment process are many and studying them would require an effort beyond the scope of this research. Understanding this treatment process and the challenges it could face is essential to developing an effective engineering system that will provide a solution to the problem of perchlorate and nitrate removal from water.

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APPENDIX A

MATLAB PROGRAMS

A.1MATLAB program to determine the rate constant for perchlorate reduction by aluminum activated by electrochemically induced pitting corrosion

```
disp('Pitting Corrosion Activated Perchlorate Reduction Model')
%Calculation of rate constant and 95% confidence limits
data=load('Input_perchlorate_100mA_small_7.txt');
% load the data stored in Input_perchlorate_100mA_small_7.txt
tmeas=data(:,1);
% measured values of time (days)
cmeas=data(:,2);
% measured values of perchlorate (mM), chloride (mM)
t=tmeas(1:11);
cclo4=cmeas(1:11);
% measured values of perchlorate (mM)
ccl=cmeas(12:22);
% measured values of chloride (mM)
plot(t, cclo4, 'o','MarkerEdgeColor','k','MarkerFaceColor','k','MarkerSize',6);hold on
plot(t, ccl, 'o','MarkerEdgeColor','k','MarkerFaceColor','w','MarkerSize',6);hold on
axis([0 2.5 0 0.2]);
xlabel('Time (days)','FontName','arial','fontsize',10,'fontweight','b');
% label the x-axis
ylabel('Concentration (mM)','FontName','arial','fontsize',10,'fontweight','b');
% label the y-axis
hold on

[beta,r,j]=nlinfit(tmeas, cmeas,@rateeqnperch_100mA_small_7,[ 0.2 3.1869]);
% nonlinear regression with ‘nlinfit’ function
ci=nlparci(beta,r,j);
% 95% confidential level
cclo40=beta(1)
k1=beta(2)
ci=ci'
sum_of_square=sum(r.^2)

dt=(max(tmeas)-min(tmeas))/50;
tp=min(tmeas):dt:max(tmeas);

for i=1:size(tp,2)
cclo40=beta(1);
k1=beta(2);
```

```
camodeltp(i)=cclo40*exp(-k1*tp(i));
% model values for perchlorate concentration (mM)
cbmodeltp(i)=cclo40-camodeltp(i);
% model values for chloride concentration (mM)
end
plot(tp,camodeltp,'--k','LineWidth',2);hold on
plot(tp,cbmodeltp,'--k','LineWidth',2);hold on
hold off

 ------------------------------------------------------------------------------------------------------
function cmodel=rateeqnperch_100mA_small_7(beta, t)
ccl40=beta(1);
k1=beta(2);
% ca0 is the inital perchlorate concentration
% k1 is the rate constant for perchlorate reduction to chloride

for i=1:11
camodela(i)=ccl40*exp(-k1*t(i));
% the model equation to calculate perchlorate concentration (mM)
end
camodela=camodela';

for i=12:22
camodelb(i)=ccl40*exp(-k1*t(i));
cbmodelb(i)=ccl40-camodelb(i);
% the model equation to calculate chloride concentration (mM)
end
cbmodelb=cbmodelb';

cmodel=[camodela(1:11);cbmodelb(12:22)];
```

A.2 MATLAB program to determine the rate constant for nitrate reduction by aluminum activated by electrochemically induced pitting corrosion

```
disp('Pitting Corrosion Activated Nitrate Reduction Model')
%Calculation of rate constant and 95% confidence limits
data=load("Input_Data.txt ');
% load the data stored in 'Input_Data.txt
tmeas=data(:,1);
% measured values of time (days)
cmeas=data(:,2);
% measured values of nitrate (mM), nitrite (mM), ammonium (mM)
t=tmeas(1:14);
cno3=cmeas(1:14);
% measured values of nitrate (mM)
cno2=cmeas(15:28);
% measured values of nitrite (mM)
cnh3=cmeas(29:42);
% measured values of ammonium (mM)

plot(t, cno3, 'o','MarkerEdgeColor','k','MarkerFaceColor','k','MarkerSize',6);
hold on
plot(t, cno2, 'o','MarkerEdgeColor','k','MarkerFaceColor',[.5 .5 .5],'MarkerSize',6);
hold on
plot(t, cnh3, 'o','MarkerEdgeColor','k','MarkerFaceColor','w','MarkerSize',6);
hold on
axis([0 4 0 1]);
% h=axes('XTickLabel','0|10|20|30|40|50|60','FontName','arial','FontSize',12);
xlabel('Time (days)','FontName','arial','fontsize',10,'fontweight','b');
% label the x-axis
ylabel('Concentration (mM)','FontName','arial','fontsize',10,'fontweight','b');
% label the y-axis
hold on

 [beta,r,j]=nlinfit(tmeas, cmeas,@rateeqnnitrate, [ 1 3.1869 19.6423] );
% nonlinear regression with ‘nlinfit’ function
ci=nlparci(beta,r,j);
% 95% confidential level
cno30=beta(1)
k1=beta(2)
k2=beta(3)
ci=ci'
sum_of_square=sum(r.^2)

dt=(max(tmeas)-min(tmeas))/50;
```

```
tp=min(tmeas):dt:max(tmeas);

for i=1:size(tp,2)
cno30=beta(1);
k1=beta(2);
k2=beta(3);
camodeltp(i)= cno30*exp(-k1*tp(i));
% model values for nitrate concentration (mM)
cbmodeltp(i)=(k1* cno30)*(exp(-k1*tp(i))-exp(-k2*tp(i)))/(k2-k1);
% model values for nitrite concentration (mM)
ccmodeltp(i)= cno30-camodeltp(i)-cbmodeltp(i);
% model values for ammonium concentration (mM)
end
plot(tp,camodeltp,'--k','LineWidth',2);hold on
plot(tp,cbmodeltp,'--k','LineWidth',2);hold on
plot(tp,ccmodeltp,'--k','LineWidth',2);hold on
hold off
 ----------------------------------------------------------------------------------------------------
function cmodel=rateeqnnitrate (beta, t)
cno30=beta(1);
k1=beta(2);
k2=beta(3);
% ca0 is the inital nitrate concentration
% k1 is the rate constant for nitrate reduction to nitrite
% k2 is the rate constant for nitrite reduction to ammonium

for i=1:14
camodela(i)= cno30*exp(-k1*t(i));
% the model equation to calculate nitrate concentration (mM)
end
camodela=camodela';

for i=15:28
cbmodelb(i)=( cno30*k1)./(k2-k1)*(exp(-k1*t(i))-exp(-k2*t(i)));
% the model equation to calculate nitrite concentration (mM)
end
cbmodelb=cbmodelb';

for i=29:42
camodelc(i)= cno30*exp(-k1*t(i));
cbmodelc(i)=( cno30*k1)./(k2-k1)*(exp(-k1*t(i))-exp(-k2*t(i)));
ccmodelc(i)= cno30-camodelc(i)-cbmodelc(i);
% the model equation to calculate ammonium concentration (mM)
ccmodelc=ccmodelc';
```

```
cmodel=[camodela(1:14);cbmodelb(15:28);ccmodelc(29:42)];
```

A.3 MATLAB program to determine the rate constant for nitrate reduction by by pH-activated aluminum granules

```
disp('Nitrate pH-Activated Reduction Model')
% Calculation of rate constant and 95% confidence limits
data=load('Input_nitrate_chemical_1.txt');
% load the data stored in Input_nitrate_chemical_1.txt
tmeas=data(:,1);
% measured values of time (minutes)
cmeas=data(:,2);
% measured values of nitrate (mM), nitrite (mM), ammonium (mM)
t=tmeas(1:11);
cno3=cmeas(1:11);
% measured values of nitrate (mM)
cno2=cmeas(12:22);
% measured values of nitrite (mM)
cnh3=cmeas(23:33);
% measured values of ammonium (mM)

plot(t, cno3, 'o','MarkerEdgeColor','k','MarkerFaceColor','k','MarkerSize',6);
hold on
plot(t, cno2, 'o','MarkerEdgeColor','k','MarkerFaceColor',[.5 .5 .5],'MarkerSize',6);
hold on
plot(t, cnh3, 'o','MarkerEdgeColor','k','MarkerFaceColor','w','MarkerSize',6);
hold on
axis([0 60 0 1]);
xlabel('Time (minutes)','FontName','arial','fontsize',10,'fontweight','b');
% label the x-axis
ylabel('Concentration (mM)','FontName','arial','fontsize',10,'fontweight','b');
% label the y-axis
hold on

beta0=[0.004 0.004 0.004 0.004];
% initial guesses for rate constants
[beta,r,j]=nlinfit(tmeas, cmeas,@calcmod_ode, beta0);
% nonlinear regression with ‘nlinfit’ function
ci=nlparci(beta,r,j);
% 95% confidential level
k=beta;
k
ci=ci'
sum_of_square=sum(r.^2)

load('cmodel.mat');
```

```
plot(t,cmodel(1:11),'--k','LineWidth',2);hold on
plot(t,cmodel(12:22),'--k','LineWidth',2);hold on
plot(t,cmodel(23:33),'--k','LineWidth',2);hold on
 ---------------------------------------------------------------------------------------------------------
function cmodel=calcmod_ode(beta,t)
data=load('ExperimentalData.txt');
% load the data stored in ExperimentalData.txt
tmeas=data(:,1);
% measured values of time (minutes)
tspan=tmeas(1:11);

[tout,cmod]=ode45(@deriv_ode,tspan,[185 0 1 0],[],beta);
cmodel=[cmod(:,3); cmod(:,4); 1-(cmod(:,3)+ cmod(:,4))];
save cmod.mat cmod
save cmodel.mat cmodel
   function dcdt=deriv_ode(t,c,beta)
      beta=abs(beta);
      r=[beta(1)*c(1) beta(2)*c(2) beta(3)*c(2)*c(3) beta(4)*c(2)*c(4)];
      dcdt(1)=-r(1);
      dcdt(2)=r(1)-r(2)-r(3)-3*r(4);
      dcdt(3)=-r(3);
      dcdt(4)=r(3)-r(4);
      dcdt=dcdt';
      c=c';
   end
end
```

APPENDIX B

INPUT DATA USED IN MATLAB

Table B.1 Matlab data in to determine the rate constant for nitrate reduction by pH-activated aluminum granules.

First Experiment		Second Experiment		Third Experiment	
Time (minutes)	**C (mM)**	**Time (minutes)**	**C (mM)**	**Time (minutes)**	**C (mM)**
0	1.0013	0	0.9975	0	0.9990
2	0.9862	4	0.9475	6	0.9082
8	0.8308	10	0.8621	12	0.8194
14	0.6984	16	0.6763	18	0.5419
20	0.4783	22	0.4034	24	0.3374
26	0.2543	28	0.2286	30	0.2043
32	0.1778	34	0.1176	36	0.1366
38	0.0861	40	0.0707	42	0.0654
44	0.0449	46	0.0374	48	0.0203
50	0.0196	52	0.0198	54	0.0192
56	0.0058	58	0.0088	60	0.0014
0	0.0000	0	0.0000	0	0.0000
2	0.0102	4	0.0241	6	0.0594
8	0.0973	10	0.0910	12	0.0825
14	0.0768	16	0.0717	18	0.0690
20	0.0654	22	0.0590	24	0.0550
26	0.0156	28	0.0131	30	0.0115
32	0.0090	34	0.0069	36	0.0034
38	0.0017	40	0.0011	42	0.0006
44	0.0002	46	0.0004	48	0.0002
50	0.0000	52	0.0002	54	0.0000
56	0.0000	58	0.0000	60	0.0000
0	0.0015	0	0.0023	0	0.0003
2	0.0017	4	0.0248	6	0.0270
8	0.0439	10	0.0495	12	0.0965
14	0.2295	16	0.2585	18	0.3896
20	0.4505	22	0.5292	24	0.6097
26	0.7395	28	0.7496	30	0.7852
32	0.8182	34	0.8625	36	0.8579
38	0.9098	40	0.9264	42	0.9182
44	0.9364	46	0.9524	48	0.9755
50	0.9787	52	0.9751	54	0.9695
56	0.9880	58	0.9840	60	0.9870

C includes measured concentrations of nitrate, nitrite and ammonium

Table B.2 Matlab data in to determine the rate constant for perchlorate reduction by aluminum activated by electrochemically induced pitting corrosion - Part 1.

I = 10 mA
ESA = 18 cm^2/L
pH = 7

Time (days)	C (mM)
0.00	0.200
0.50	0.191
1.00	0.181
1.50	0.170
2.00	0.164
2.50	0.160
3.00	0.150
3.50	0.147
4.00	0.136
4.50	0.126
5.00	0.119
6.00	0.105
0.00	0.000
0.50	0.002
1.00	0.026
1.50	0.035
2.00	0.044
2.50	0.046
3.00	0.049
3.50	0.051
4.00	0.059
4.50	0.075
5.00	0.086
6.00	0.092

I = 50 mA
ESA = 18 cm^2/L
pH = 7

Time (days)	C (mM)
0.00	0.200
0.25	0.186
0.50	0.173
1.00	0.147
1.50	0.128
2.00	0.102
2.50	0.079
3.00	0.052
4.00	0.006
0.00	0.000
0.25	0.018
0.50	0.020
1.00	0.058
1.50	0.063
2.00	0.092
2.50	0.119
3.00	0.161
4.00	0.198

I = 100 mA
ESA = 18 cm^2/L
pH = 7

Time (days)	C (mM)
0.00	0.200
0.08	0.191
0.17	0.185
0.33	0.170
0.50	0.156
0.67	0.142
0.83	0.134
1.00	0.118
1.50	0.083
2.00	0.042
2.50	0.006
0.00	0.000
0.08	0.006
0.17	0.009
0.33	0.027
0.50	0.053
0.67	0.051
0.83	0.076
1.00	0.079
1.50	0.127
2.00	0.168
2.50	0.200

C includes measured concentrations of perchlorate and chloride

Table B.3 Matlab data in to determine the rate constant for perchlorate reduction by aluminum activated by electrochemically induced pitting corrosion - Part 2.

I = 100 mA ESA = 36 cm^2/L pH = 7		I = 100 mA ESA = 18 cm^2/L pH = 3	
Time (days)	C (mM)	Time (days)	C (mM)
0.00	0.200	0.00	0.200
0.08	0.188	0.08	0.188
0.17	0.182	0.17	0.182
0.33	0.166	0.25	0.176
0.50	0.147	0.33	0.162
0.67	0.130	0.42	0.155
0.83	0.114	0.50	0.147
1.00	0.091	0.67	0.130
1.50	0.050	0.83	0.114
2.00	0.018	1.08	0.098
2.50	0.005	1.33	0.080
0.00	0.000	1.67	0.052
0.08	0.018	2.00	0.028
0.17	0.021	2.50	0.005
0.33	0.024	0.00	0.000
0.50	0.052	0.08	0.018
0.67	0.058	0.17	0.014
0.83	0.080	0.25	0.022
1.00	0.113	0.33	0.040
1.50	0.135	0.42	0.049
2.00	0.176	0.50	0.058
2.50	0.202	0.67	0.062
		0.83	0.090
		1.08	0.109
		1.33	0.113
		1.67	0.144
		2.00	0.178
		2.50	0.199

C includes measured concentrations of perchlorate and chloride

Table B.4 Matlab data in to determine the rate constant for nitrate reduction by aluminum activated by electrochemically induced pitting corrosion - Part 1.

I = 10 mA ESA = 9 cm^2/L pH = 7		**I = 10 mA ESA = 9 cm^2/L pH = 7**		**I = 20 mA ESA = 9 cm^2/L pH = 7**	
Time (days)	**C (mM)**	**Time (days)**	**C (mM)**	**Time (days)**	**C (mM)**
0.00	0.999	2.00	0.568	0.00	1.000
0.25	0.902	2.25	0.682	0.02	0.989
0.50	0.819	2.50	0.766	0.04	0.969
0.75	0.733	2.75	0.823	0.06	0.956
1.00	0.669	3.00	0.874	0.08	0.942
1.25	0.590	4.00	0.986	0.10	0.930
1.50	0.522			0.13	0.915
1.75	0.449			0.15	0.906
2.00	0.360			0.17	0.890
2.25	0.293			0.19	0.879
2.50	0.215			0.21	0.869
2.75	0.150			0.23	0.849
3.00	0.107			0.25	0.841
4.00	0.007			0.33	0.794
0.00	0.002			0.42	0.748
0.25	0.066			0.50	0.702
0.50	0.084			0.58	0.655
0.75	0.105			0.67	0.611
1.00	0.104			0.75	0.569
1.25	0.117			0.83	0.527
1.50	0.112			0.92	0.477
1.75	0.095			1.00	0.433
2.00	0.073			1.25	0.303
2.25	0.026			1.50	0.174
2.50	0.019			2.00	0.039
2.75	0.027			0.00	0.022
3.00	0.018			0.02	0.000
4.00	0.007			0.04	0.011
0.00	0.000			0.06	0.007
0.25	0.031			0.08	0.053
0.50	0.097			0.10	0.069
0.75	0.162			0.13	0.037
1.00	0.228			0.15	0.073
1.25	0.293			0.17	0.054
1.50	0.366			0.19	0.062
1.75	0.455			0.21	0.070

C includes measured concentrations of nitrate, nitrite and ammonium

Table B.5 Matlab data in to determine the rate constant for nitrate reduction by aluminum activated by electrochemically induced pitting corrosion - Part 2.

I = 20 mA ESA = 9 cm^2/L pH = 7		I = 20 mA ESA = 9 cm^2/L pH = 7		I = 50 mA ESA = 9 cm^2/L pH = 7	
Time (days)	C (mM)	Time (days)	C (mM)	Time (days)	C (mM)
0.23	0.045	1.25	0.629	0.00	1.000
0.25	0.056	1.50	0.754	0.04	0.909
0.33	0.098	2.00	0.962	0.08	0.844
0.42	0.091			0.13	0.772
0.50	0.081			0.17	0.710
0.58	0.161			0.21	0.650
0.67	0.112			0.25	0.589
0.75	0.132			0.33	0.481
0.83	0.133			0.42	0.368
0.92	0.172			0.54	0.222
1.00	0.085			0.67	0.134
1.25	0.068			0.83	0.045
1.50	0.072			1.00	0.013
2.00	0.000			1.25	0.004
0.00	0.000			0.00	0.000
0.02	0.048			0.04	0.070
0.04	0.020			0.08	0.092
0.06	0.037			0.13	0.085
0.08	0.004			0.17	0.086
0.10	0.001			0.21	0.112
0.13	0.048			0.25	0.108
0.15	0.021			0.33	0.132
0.17	0.056			0.42	0.186
0.19	0.059			0.54	0.224
0.21	0.061			0.67	0.205
0.23	0.107			0.83	0.186
0.25	0.103			1.00	0.117
0.33	0.108			1.25	0.000
0.42	0.161			0.00	0.000
0.50	0.217			0.04	0.021
0.58	0.184			0.08	0.064
0.67	0.277			0.13	0.143
0.75	0.298			0.17	0.205
0.83	0.340			0.21	0.238
0.92	0.351			0.25	0.303
1.00	0.482			0.33	0.388

C includes measured concentrations of nitrate, nitrite and ammonium

Table B.6 Matlab data in to determine the rate constant for nitrate reduction by aluminum activated by electrochemically induced pitting corrosion - Part 3.

I = 50 mA ESA = 9 cm^2/L pH = 7		I = 50 mA ESA = 18 cm^2/L pH = 7		I = 50 mA ESA = 18 cm^2/L pH = 7	
Time (days)	**C (mM)**	**Time (days)**	**C (mM)**	**Time (days)**	**C (mM)**
0.42	0.445	0.00	1.000	0.42	0.406
0.54	0.554	0.04	0.910	0.54	0.666
0.67	0.661	0.08	0.828	0.67	0.788
0.83	0.769	0.13	0.752	0.83	0.920
1.00	0.870	0.17	0.684	1.00	0.852
1.25	0.996	0.21	0.618	1.25	1.000
		0.25	0.558		
		0.33	0.444		
		0.42	0.331		
		0.54	0.178		
		0.67	0.077		
		0.83	0.020		
		1.00	0.004		
		1.25	0.000		
		0.00	0.000		
		0.04	0.046		
		0.08	0.072		
		0.13	0.086		
		0.17	0.116		
		0.21	0.121		
		0.25	0.202		
		0.33	0.242		
		0.42	0.263		
		0.54	0.156		
		0.67	0.135		
		0.83	0.060		
		1.00	0.144		
		1.25	0.000		
		0.00	0.059		
		0.04	0.044		
		0.08	0.100		
		0.13	0.162		
		0.17	0.200		
		0.21	0.261		
		0.25	0.240		
		0.33	0.314		

C includes measured concentrations of nitrate, nitrite and ammonium

Table B.7 Matlab data in to determine the rate constant for nitrate reduction by aluminum activated by electrochemically induced pitting corrosion - Part 4.

I = 50 mA **ESA = 9 cm^2/L** **pH = 3**		**I = 50 mA** **ESA = 9 cm^2/L** **pH = 3**		**I = 50 mA** **ESA = 9 cm^2/L** **pH = 13**	
Time (days)	**C (mM)**	**Time (days)**	**C (mM)**	**Time (days)**	**C (mM)**
0.00	1.000	0.42	0.368	0.00	1.000
0.04	0.908	0.54	0.483	0.04	0.960
0.08	0.839	0.67	0.424	0.13	0.897
0.13	0.772	0.83	0.462	0.17	0.847
0.17	0.727	1.00	0.557	0.21	0.849
0.21	0.672	1.25	0.535	0.25	0.823
0.25	0.617			0.33	0.808
0.33	0.514			0.42	0.762
0.42	0.403			0.54	0.671
0.54	0.213			0.67	0.580
0.67	0.132			0.83	0.469
0.83	0.064			1.00	0.382
1.00	0.025			1.25	0.284
1.25	0.005			0.00	0.000
0.00	0.016			0.04	0.004
0.04	0.064			0.13	0.007
0.08	0.063			0.17	0.036
0.13	0.126			0.21	0.101
0.17	0.111			0.25	0.113
0.21	0.163			0.33	0.091
0.25	0.190			0.42	0.173
0.33	0.200			0.54	0.113
0.42	0.229			0.67	0.178
0.54	0.304			0.83	0.210
0.67	0.444			1.00	0.270
0.83	0.474			1.25	0.219
1.00	0.418			0.00	0.008
1.25	0.460			0.04	0.091
0.00	0.016			0.13	0.096
0.04	0.028			0.17	0.117
0.08	0.098			0.21	0.049
0.13	0.102			0.25	0.063
0.17	0.163			0.33	0.101
0.21	0.165			0.42	0.065
0.25	0.193			0.54	0.216
0.33	0.285			0.67	0.242

C includes measured concentrations of nitrate, nitrite and ammonium

Table B.8 Matlab data in to determine the rate constant for nitrate reduction by aluminum activated by electrochemically induced pitting corrosion - Part 5.

I = 50 mA
ESA = 9 cm^2/L
pH = 7

Time (days)	C (mM)
0.83	0.321
1.00	0.348
1.25	0.497

C includes measured concentrations of nitrate, nitrite and ammonium

VITA

Name: Aditya Babu Raut Desai

Address: Department of Civil Engineering
Texas A&M University
3136 TAMU
College Station, Texas 77843-3136
c/o Bill Batchelor

Email Address: adityabrd77@neo.tamu.edu

Education: B.E., Civil Engineering, 1998
Goa University, Farmagudi, Goa, India

M.S., Civil Engineering, 2004
Texas A&M University, College Station, TX

Ph.D., Civil Engineering, 2010
Texas A&M University, College Station, TX