PERCHLORATE REDUCTION USING ELECTROCHEMICALLY INDUCED PITTING CORROSION OF ZERO-VALENT TITANIUM

A Dissertation

by

CHUN WOO LEE

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

December 2007

Major Subject: Civil Engineering

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Approved by:

Chair of Committee,	Bill Batchelor
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ABSTRACT

Perchlorate Reduction Using Electrochemically Induced
Pitting Corrosion of Zero-Valent Titanium.
(December 2007)
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Perchlorate is a threat to public health through water but also food. However, there is no effective chemical treatment process which can destroy perchlorate found in groundwater and surface water. Thus, there is growing interest in developing effective technologies, especially chemical treatments, to completely destroy trace levels of perchlorate present in drinking and groundwater.

The research on perchlorate reduction by zero-valent titanium (Ti(0)) showed that perchlorate was effectively reduced to chloride using electrochemically developed pitting corrosion on Ti(0). Perchlorate reduction was believed to be caused by an active reductant (dissolved Ti(II)) during the pitting corrosion of Ti(0). The rate of perchlorate reduction was independent on the imposed potential as long as the potential was maintained above the pitting potential of Ti(0), but it was proportional to the applied current. The perchlorate reduction on the pitting developed Ti(0) was inhibited by the presence of chloride and bromide. Inhibition mechanism of perchlorate reduction inhibition was believed to be caused either by competitive adsorption of aggressive anions on bare Ti(0) surface or Ti(II) consumption by electrochemically produced chlorine. Kinetic models were developed based surface coverage of aggressive anions on bare Ti(0) and Ti(II) oxidation by chlorine. These kinetic models supported the perchlorate concentration change in the solution, but Ti(II) consumption model was not able to predict chloride concentration due to insufficient information describing complex nature of pitting on Ti(0).

These results shown in this research demonstrate that pitting corrosion developed Ti(0) has the capability to chemically reduce perchlorate present in natural water and engineered systems as well as possible problems associated with electric input. This research may be a starting point for development of a new treatment process that applies titanium or titanium metal ions as a chemical reductant to abate contaminants present in natural and engineering systems. Further developments can be achieved by alloying titanium metal with other metals such as iron and aluminum, and finding a methodology producing stable Ti(II) in ambient conditions.

DEDICATION

This dissertation is dedicated to late Dr. Timothy A. Kramer

who was an outstanding teacher,

gifted mentor and advisor.

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NOMENCLATURE

$\equiv Ti(0)^{dis}$ = oxidative dissolution of Ti(0) site

$\equiv Ti(0)^{ox}$ = chloride oxidation sites

μ = electric potential

a = geometric shape factor

A_p = surface area of pit

$C_{p,i}$ = anion concentration in the pit

$C_{s,i}$ = anion concentration in the solution

D_{Cl2} = diffusion coefficient of chlorine

D_i = diffusion coefficient

F = Faraday's constant (= 96,485 C/mole)

I = current (A)

j = current density

J_i = flux of i chemical speci

j_p = current density in the pit

k = second-order rate constant for perchlorate reduction

K_{Cl} = equilibrium constant for chloride

k_{Cl} = first-order rate constant for chloride oxidation

k_{Cl2} = second-order rate constant for Ti(II) oxidation by Cl_2 in the pit

K_{ClO4} = equilibrium constant for perchlorate

K_I = inhibition coefficient of chloride for perchlorate reduction in the pit

$K_{I,ox}$ = inhibition coefficient of perchlorate for chloride oxidation

k_{Ox} = rate constant of Ti(II) oxidation by an oxidizing agent

$k_{\mathrm{trans,Cl2}}$ = mass transfer coefficient for Cl_2 from the pit to solution

$M_{p\rightarrow s,Cl}$ = chloride mass flux from the pit to solution

$M_{p\rightarrow s,ClO4}$ = perchlorate mass flux from the pit to solution

$M_{s\rightarrow p,Cl}$ = chloride mass flux from solution to the pit

$M_{s\rightarrow p,ClO4}$ = perchlorate mass flux from solution to the pit

Mw_{Cl} = atomic weight of chlorine

Mw_{Ti} = atomic weight of titanium

n_{Cl} = number of electrons transferred per chlorine molecule that undergoes oxidation (= 1)

n_{Ti} = dissolution valence of titanium

Q_{Cl} = electrical charge consumption by Chloride oxidation

Q_{t} = total quantity of electric charge passed

R = gas constant

r = radius of pit

r_p = pit radius

t = time

T = temperature

v_{i} = stoichiometric factor of i specie

V_p = volume of the pit

x = distance

$\gamma_{\mathrm{loss},\equiv Ti(0)\cdot ClO4,dis}$ = rates of $\equiv Ti(0)^{dis}\cdot ClO_4^-$ loss

$\gamma_{\mathrm{loss,\equiv Ti(0)\cdot ClO4,ox}}$ = rates of $\equiv \mathrm{Ti(0)}^{\mathrm{ox}}\cdot \mathrm{ClO_4}^-$ loss

$\gamma_{\mathrm{loss,Cl,p}}$ = rate of chloride loss in the pit solution

$\gamma_{\mathrm{loss,ClO4,p}}$ = rate of perchlorate loss in the pit solution

$\gamma_{\mathrm{p,loss}}$ = rate of perchlorate loss

$\gamma_{\mathrm{p,loss,Cl}}$ = rate of Cl^- loss

$\gamma_{\mathrm{p,loss,Ti(II)}}$ = rate of Ti(II) loss in the pit

$\gamma_{\mathrm{p,prod}}$ = rate of perchlorate production

$\gamma_{\mathrm{p,prod,Cl}}$ = rate of Cl^- production in the pit

$\gamma_{\mathrm{p,prod,Ti(II)}}$ = rate of Ti(II) production in the pit

$\gamma_{\mathrm{prod,\equiv Ti(0)\cdot ClO4,dis}}$ = Rate of $\equiv \mathrm{Ti(0)}^{\mathrm{dis}}\cdot \mathrm{ClO_4}^-$ production

$\gamma_{\mathrm{prod,\equiv Ti(0)\cdot ClO4,ox}}$ = rate of $\equiv \mathrm{Ti(0)}^{\mathrm{ox}}\cdot \mathrm{ClO_4}^-$ production

$\gamma_{\mathrm{prod,Cl,p}}$ = rate of chloride production

$\gamma_{\mathrm{prod,ClO4,p}}$ = rate of perchlorate production

$\Delta\mu$ = potential drop in the pit

$\Delta \mathrm{M_{Cl}}$ = loss of mass of Cl (g)

$\Delta \mathrm{M_{Cl}} / \mathrm{Mw_{Cl}}$ = chlorine loss (mol)

$\Delta \mathrm{M_{Ti}}$ = loss of mass of Ti(0) (g)

θ_{ClO4} = surface coverage of bare Ti(0) surface by perchlorate

Θ^{dis} = adsorption site that is associated with oxidative dissolution of Ti(0)

θ^{ox} = adsorption site for chloride oxidation

κ = conductivity of solution in the pit

CHAPTER I

INTRODUCTION

1.1 Statement of Purpose

Perchlorate that originates from both natural and man-made sources has been found in surface and groundwater in many states in the United States. It has been known that perchlorate blocks uptake of iodide and inhibits normal production of thyroid hormones, which are critical for mature brain and central nervous system development in fetuses and infants. Thus, ingestion of perchlorate in food and water could result in deficiencies of thyroid hormone production and lead to mental retardation, delayed development and possibly thyroid tumors, which are a particular problem for iodine-deficient mothers.

In 2005, the U. S. Environmental Protection Agency (USEPA) established its official reference dose of perchlorate at 0.0007 mg/kg-day and this translates to a Drinking Water Equivalent Level (DWEL) of 24.5 μg/L. However, several states have adapted lower guidance or advisory levels of perchlorate than the DWEL of the USEPA. Moreover, recently Massachusetts promulgated a Maximum Contamination Level (MCL) of 2 μg/L for perchlorate in drinking water and this value is also used as a cleanup standard. Therefore, it is expected that the USEPA will establish drinking and groundwater clean up standards for perchlorate that are less than 24.5 μg/L.

This thesis follows the style of *Environmental Science and Technology*.

Perchlorate can be treated with ion exchange or biological processes. Ion exchange is very effective in removing perchlorate from water and is listed as Best Available Technology (BAT) for perchlorate treatment. However, ion exchangers need to be regenerated with brine that contains high concentrations of chloride. After regeneration, the brine contains high concentration of perchlorate and requires further treatment before disposal or reuse. Biological treatment is another way to effectively remove perchlorate from water. However, biological processes require the addition of electron donors and nutrients for biomass growth. Moreover, biological processes are highly susceptible to the presence of oxygen and other anions such as nitrate and sulfate. Besides, it is questionable whether the water industry will accept biological processes for treating drinking water. Other treatment technologies including tailored activated carbon, and chemical or electrochemical reduction, have been applied to remove perchlorate from water. However, these processes suffer from reduced efficiency caused by competition by other anions and organic contaminants for sorption sites, and from sluggish perchlorate reduction kinetics. Therefore, there is growing interest in developing effective technologies, especially chemical treatments, to completely destroy perchlorate present in drinking and groundwater.

Zero-valent metals, especially iron, are a popular reagent for the abatement of contaminants in drinking water and groundwater. However, as perchlorate reduction has a high activation energy, it is hard to chemically reduce perchlorate with commonly used zero-valent metals. However, titanium metal would be an attractive candidate for perchlorate treatment. Titanium has high thermodynamic reactivity and oxygen affinity that can stabilize transferred oxygen atom from perchlorate. Moreover, an ion formed by its oxidative dissolution (Ti(III)) can reduce perchlorate rapidly, compared to other common reductants. Therefore, it is worthy to investigate perchlorate reduction using titanium metal. However, titanium is always covered by an oxide film, which protects the underlying titanium from oxidants in natural environments. Thus, the surface oxide film must be removed to activate titanium metal as a chemical reductant and allow it to convert perchlorate to chloride.

In this study, electrochemically induced pitting corrosion is adapted as a methodology to remove the surface oxide film and dissolve titanium. In order to achieve the development of new perchlorate treatment technology, this study investigates not only the feasibilities of perchlorate reduction by titanium, but also perchlorate reduction mechanisms, perchlorate reduction kinetics and environmental and electrochemical conditions that can affect perchlorate reduction.

1.2 Research Objectives

The overall objective of this research is to develop an innovative treatment technology for the destruction of perchlorate in contaminated waters using Ti(0). The objectives of this study are: 1) to develop a method for using Ti(0) to produce active reductants in solution via the electrochemically induced pitting corrosion and determine electrochemical and environmental conditions that affect the rate of perchlorate reduction; 2) to generate and verify mechanisms that can explain perchlorate reduction at the pitting site of Ti(0); 3) to identify the influence of anions including nitrate, sulfate and phosphate on the rate of perchlorate reduction and to determine any mechanisms of inhibition; and 4) to develop a kinetic model that can predict perchlorate reduction at the pitting site on Ti(0).

1.2.1 Electrochemical and Environmental Conditions Affecting Perchlorate Reduction

The objectives of this phase of the study were: 1) to verify the hypothesis that electrochemically induced pitting corrosion of Ti(0) is responsible for the reduction of perchlorate, and 2) to determine how various factors affect on the rate of perchlorate reduction by Ti(0) during pitting corrosion. First, in order to verify the hypothesis, potential ranges that develop pitting corrosion on Ti(0) were measured as a function of perchlorate concentration. Based on these potential ranges, the hypothesis was verified by monitoring perchlorate and chloride concentrations with and without pitting corrosion. After verifying the hypothesis, influences of electrochemical and environmental parameters that affect on the rate of perchlorate reduction were determined. These parameters include current intensity, surface area, and solution pH. Additionally, reduction of trace levels of perchlorate using Ti(0) was investigated at different current intensities, surface areas, and initial chloride concentrations. Successful completion of this phase of the study provided the data needed to understand how effectively titanium can reduce perchlorate and how well it can remove trace levels of perchlorate such as found in natural environments.

1.2.2 Mechanism of Perchlorate Reduction During the Pitting Corrosion of Ti(0)

The objective of this phase of the study was to investigate the mechanism of perchlorate reduction at discrete sites on the Ti(0) surface developed by pitting corrosion.

Three possible scenarios were proposed based on literature studies and were investigated as mechanisms of perchlorate reduction at the pitting site of Ti(0): 1) ejection of metal particles, 2) production of high ohmic drops, and 3) formation of transitory titanium ions. The mechanism that assumed ejection of bare Ti(0) particle was investigated using optical microscopes, scanning electron microscope (SEM), and X-ray Diffraction (XRD) to identify the presence of bare Ti(0) particles. The mechanism based on a high ohmic potential drop was investigated using Ti(0) electrodes as the cathode to determine if perchlorate reduction were possible on surfaces of titanium oxide or hydroxide at the pitting site. Finally, the mechanism based on transitory titanium ions was investigated with measurements of perchlorate reduction by solutions of the transitory titanium ions, calculations of the dissolution valence of Ti(0), and the application of material balances to Ti and ClO_4^-. Based on these studies, a mechanism for perchlorate reduction at the pitting site of Ti(0) was proposed. Successful completion of this objective provided insights as to how perchlorate is reduced by Ti(0) during pitting corrosion.

1.2.3 Influence of Other Anions on Perchlorate Reduction During the Pitting Corrosion of Ti(0)

This phase of the study determined the influence of anions on perchlorate reduction during pitting corrosion of Ti(0). In general, perchlorate was present at trace levels ranging from several μg/L to hundreds μg/L in natural environments. Common anions such as nitrate, sulfate, and phosphate are found at concentrations that are high compared to perchlorate. Thus, the influences of these common anions on both high and trace levels of perchlorate were investigated by varying the anion concentration and current intensity. Possible reductions of these anions, especially nitrate, were monitored and any reduction products were examined. It is expected that nitrate would be reduced to nitrite and then to either ammonia or nitrogen gas. Additionally, a possible reduction of nitrate to titanium nitride (TiN) was investigated by analyzing solid products using XRD and XPS. Successful completion of this phase of the study demonstrated the effectiveness of the electrochemical Ti(0) process for the treatment of water contaminated with perchlorate. Additionally, it provided evidence for the potential applicability of the electrochemical Ti(0) process to other contaminants.

1.2.4. Kinetic Model Describing Rate of Perchlorate Reduction During the Pitting Corrosion of Ti(0)

The objective of this phase study was to develop kinetic models that can predict perchlorate reduction by electrochemically induced pitting corrosion of Ti(0). The kinetic models were developed to predict the rate of perchlorate reduction at both high and trace levels of perchlorate. Rate constants were determined based on results of experiments conducted for other purposes as well as experiments conducted to measure the rate of chloride oxidation and influence of initial chloride concentration on rates of perchlorate reduction. Successful completion of this phase of the study provided the data needed to understand how effectively titanium can reduce perchlorate and to predict rates of perchlorate reduction.

CHAPTER II

BACKGROUND

2.1 Perchlorate in Environments

The perchlorate (ClO_4^-) originates from anthropogenic and non-anthropogenic sources. Man-made perchlorate was first produced in Germany in 1816 by Stadion (*1*). He mixed potassium chlorate ($KClO_3$) with sulfuric acid (H_2SO_4) and found that the residue produced was a mixture of potassium perchlorate ($KClO_4$) and potassium sulfate (K_2SO_4). Later, many studies reported methodologies to produce perchlorate salts. Current perchlorate manufacturers use the electrochemical oxidation of sodium chloride (NaCl) for large-scale production of perchlorate salts, which are widely used in a variety of industries. Common products using perchlorate salts are electronic tubes, fireworks, air bag inflators and flares (*2, 3*). Beside, potassium perchlorate was once used to treat hyperthyroid patents that have Grave's disease (*3-5*). However, major consumers of perchlorate salts are defense and aerospace industries (*6*). As perchlorate has a high oxygen content and is a good oxidant, its salts, especially NH_4ClO_4, have been major components of solid rocket and missile propellants and are present in varying amounts in explosives.

Natural occurring perchlorate has been fund in the Atacama Dessert of northern Chile (*7*) and the Texas southern high plains (*8-10*). Several hypothetical mechanisms have been suggested to explain the formation of naturally occurring perchlorate in these areas. All of the potential mechanisms are linked to complex atmospheric processes involving photochemical and radical reactions. Simmonatis and Heicklen (*11*) proposed that the chlorine radical ($Cl\bullet$), which is generated by photodissociation of Cl_2 (*12*), undergoes an oxidation reaction with ozone (O_3) in the presence of O_2 to form $ClO_3\bullet$. The produced $ClO_3\bullet$ further reacts with reactive free radicals such as $\bullet OH$ to form $HClO_4$.

$$Cl\bullet + O_3 \xrightarrow{O_2} ClO_3\bullet \tag{2.1}$$

$$ClO_3\bullet + \bullet OH \longrightarrow HClO_4 \tag{2.2}$$

However, Prasad and Lee (*13*) discussed the fact that reactions (2.1) and (2.2) are kinetically slow due to the non-selective reactivity of $\bullet OH$ and they proposed an alternative pathway for the formation of $HClO_4$ via the following reactions.

$$ClO\bullet + O_2 \xrightarrow{M} ClO\bullet O_2 \tag{2.3}$$

$$ClO\bullet O_2 + O_3 \longrightarrow ClO\bullet O_3 + O_2 \tag{2.4}$$

$$ClO\bullet O_3 + HO_2\bullet \longrightarrow HClO_4 + O_2 \tag{2.5}$$

where M is an inert molecule that carries off the excessive energy of the reaction. A later study (*8*) expanded the possible atmospheric reactions that lead to formation of chlorine-oxygen compounds.

$$Cl\bullet + O_2 \xrightarrow{M} ClO_2 \tag{2.6}$$

$$Cl\bullet + O_3 \longrightarrow ClO_2 + O\bullet \tag{2.7}$$

$$Cl\bullet + O_3 \longrightarrow ClO\bullet + O_2 \tag{2.8}$$

$$ClO\bullet + O\bullet \xrightarrow{M} ClO_2 \tag{2.9}$$

$$ClO\bullet + O_2 \rightarrow ClO_2 + O\bullet \tag{2.10}$$

$$ClO\bullet + O_3 \xrightarrow{M} ClO_2 + O_2 \tag{2.11}$$

$$ClO\bullet + ClO\bullet \xrightarrow{M} Cl_2O_2 \tag{2.12}$$

$$Cl_2O_2 \rightarrow Cl\bullet + ClO_2 \tag{2.13}$$

$$ClO\bullet + O_2 \xrightarrow{M} ClO_3\bullet \tag{2.14}$$

$$Cl_2O_2 + O_3 \rightarrow ClO_3\bullet + ClO_2 \tag{2.15}$$

The ClO_2 and $ClO_3\bullet$ generated by atmospheric reactions are converted to $HClO_4$ by reaction with •OOH and •OH, respectively. Additionally, this study proved that perchlorate is formed under simulated complex atmospheric conditions using sonication, electrical energy discharge, UV irradiation and ozone exposure. All experiments showed the formation of perchlorate and support a hypothesis of atmospheric origin for naturally occurring perchlorate (*8, 14, 15*).

It has been known that perchlorate disrupts the ability of the thyroid gland to metabolize iodide ions and interferes with the production of thyroid hormones (*6, 16*). Iodide is an essential nutrient for the synthesis of thyroid hormones. However, perchlorate prevents iodide uptake by blocking the sodium-iodide symporter, which is the mechanism by which both sodium and iodide are simultaneously transported from the blood stream to the thyroid. In fetuses and infants, proper production of thyroid hormones is critical for mature brain and central nervous system development. A lack of these hormones can lead to mental retardation, delayed development and possibly thyroid tumors, particularly for iodine-deficient mothers. American Water Works Association (AWWA) reported that drinking water sources in 26 states of United State and Puerto Rico have been contaminated by perchlorate (*17*). Moreover, recent studies found perchlorate in bottled water, leaf vegetables, and fruits (*9, 18, 19*). Thus, perchlorate contamination is a nationwide problem and possibly threatens public health through ingestion of contaminated water and food. Moreover, recent studies found perchlorate in milk and breast milk (*15, 20, 21*), which indicates that many people, especially infants who are vulnerable, can be exposed to perchlorate contamination and its potential thyroid related health risks.

2.2 Perchlorate Regulations

The history of perchlorate regulation goes back to 1992. The USEPA proposed a provisional reference dose for perchlorate of 0.0001 mg/kg-day which is equivalent to a concentration of 4 μg/L in drinking water (*6, 22*). In 1995, USEPA reviewed the perchlorate toxicology studies and revised the provisional reference dose to be in a range from 0.0001 to 0.0004 mg/kg-day, which is equivalent to 4 to 18 μg/L in drinking water. Perchlorate was placed on the drinking water Contaminant Candidate List in 1998 and the USEPA proposed a draft reference dose of 0.0009 mg/kg-day in the same year (*23*). In 2002, the USEPA proposed an enhanced draft reference dose of 0.00003 mg/kg-day, which is equivalent to 1 μg/L in drinking water. The National Academy of Sciences (NAS) reviewed this draft reference dose and recommended a value of 0.0007 mg/kg-day in 2005 (*6*). The USEPA has established this value as the official reference dose for perchlorate in 2005. It translates to a Drinking Water Equivalent Level (DWEL) of 24.5 μg/L that represents the appropriate level of perchlorate when an adult body weight 70 kg consumes 2 L/day of tap water. However, several states have developed more strict advisory levels and Maximum Contamination levels (MCL) than the USEPA DWEL (*6*). California has set the notification level for perchlorate in drinking water at 6 μg/L andhas proposed a MCL of 6 µg/L. Maryland and New Mexico have set advisory and drinking water screening levels at values less than 1 µg/L. Other states, including Arizona, Nevada, New York, and Texas, have health-based goals for perchlorate ranging from 5 to 51 µg/L. Massachusetts is the first state in United State to promulgate a MCL of 2 µg/L for perchlorate in drinking water and it uses the same value as a cleanup standard (*24*). However, federal regulation of perchlorate in drinking water and during remediation at hazardous waste sites is still controversial and more toxicology effects of perchlorate are under investigations.

2.3 Chemistry of Perchlorate

Perchlorate has the same structure and electronic configuration as phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) (*2, 25*). The central chlorine atom has the highest oxidation state (+7) and it is tetrahedrally surrounded by four oxygen atoms. Perchlorate has highly delocalized monovalent anionic charge. This makes it hard to form complexes with metal ions and its salts have high solubility (*2*). Thermodynamically, perchlorate is a strong oxidizer and its reduction to chloride is a very favorable processes in both acid and alkaline solutions (*26*)

Acid solution

$$\begin{tikzcd} \mathrm{ClO_4^-} \arrow[r, "1.201\,\mathrm{V}"] \arrow[rrrrr, bend right, "1.287\mathrm{V}"'] & \mathrm{ClO_3^-} \arrow[r, "1.181\,\mathrm{V}"] & \mathrm{HClO_2^-} \arrow[r, "1.701\,\mathrm{V}"] & \mathrm{HClO} \arrow[r, "1.630\,\mathrm{V}"] & \mathrm{Cl_2} \arrow[r, "1.358\,\mathrm{V}"] & \mathrm{Cl^-} \end{tikzcd} \quad (2.16)$$

Alkaline solution

$$\begin{tikzcd} \mathrm{ClO_4^-} \arrow[r, "0.374\,\mathrm{V}"] \arrow[rrrrr, bend right, "0.560\mathrm{V}"'] & \mathrm{ClO_3^-} \arrow[r, "0.295\,\mathrm{V}"] & \mathrm{HClO_2^-} \arrow[r, "0.681\,\mathrm{V}"] & \mathrm{HClO} \arrow[r, "0.421\,\mathrm{V}"] & \mathrm{Cl_2} \arrow[r, "1.358\,\mathrm{V}"] & \mathrm{Cl^-} \end{tikzcd} \quad (2.17)$$

However, the reduction of perchlorate is kinetically hindered by high activation energy. Most common metal reductants have demonstrated sluggish reduction rates with perchlorate and they are virtually impossible to use as the basis for a treatment process for water contaminated by perchlorate (*27*). Some reductants have shown promising reduction rates that are high enough to possibly be applied in a treatment process (*28-31*). However, these results were obtained under extreme conditions such as strong acidity, high temperature, and high pressure.

2.4 Methods of Perchlorate Removal

Perchlorate has two distinctive chemical characteristics: delocalized negative charge distributions and high activation energy in reduction to chlorate (*2*). The delocalized negative charge distribution makes perchlorate a weak complexing agent and hinders the removal of perchlorate by precipitation and adsorption. The high activation energy prevents the application of chemical and electrochemical process to treat water contaminated with perchlorate by reducing it to chloride. The current Best Available Technology (BAT) for perchlorate is ion exchange (*32*). Ion exchange uses polymer-based resins that are charged with function groups. It has been reported that polystyrenic resins have a higher affinity for perchlorate than polyvinylpyridine and polyacrylic resins and they effectively remove perchlorate from water (*33, 34*). However, the higher affinity for perchlorate resulted in their being more difficult to regenerate than other resins. The major disadvantage of the ion exchange process is that regeneration of exhausted resin produces a brine that contains high concentrations of perchlorate, which requires additional treatment prior to disposal or reuse. Additionally, the presence of humic substances or other anions such as NO_3^-, SO_4^{2-}, or HCO_3^- greatly reduces bed volumes treated to breakthrough (*33, 35*). In order to overcome these disadvantages, perchlorate selective bifunctional resins (*33*) and disposable resin that are incinerated or disposed in landfill site after exhaustion (*36*) have been developed.

Other alternative technologies for perchlorate removal are biological and tailored activated carbon processes. Biological processes have successfully removed perchlorate at both trace levels in groundwater (*37-41*) and at high concentrations in brine waste (*14, 42*). However, it has been reported that biological processes are highly susceptible to environmental conditions such as concentrations of dissolved oxygen and other anions such as NO_3^- and SO_4^{2-} (*32, 43*) and require appropriate levels of carbon and nutrient supplies for growth of microorganisms (*32, 38, 43*). Besides, no large-scale biological drinking water treatment plant exists in the United States (*44*) and whether the water industry accepts biological process for drinking water treatment is still questionable, since the primary goal of drinking water treatment is removal of microorganisms that cause disease (*45*). It has been demonstrated that activated carbon can remove perchlorate by an ion exchange mechanism, but this process is limited by the low adsorption capacity of activated carbon for perchlorate (*37, 46*). Thus, several studies investigated methodologies develop tailored activated carbon by creating more ion exchange sites and thereby increasing its adsorption capacity for perchlorate (*47-49*). Tailored activated carbons have been produced by treatment with a quaternary amine or surfactants, and they have greatly increased adsorption capacities for perchlorate. However, the tailored carbon process is also limited by the presence of other anions and organic contaminants due to competition for ion exchange sites. Thus, it is recommended that the tailored activated carbons be combined with other processes such as ion exchange or standard activated carbon that can remove the interferences caused by anions and organic contaminants (*32*). Moreover, further treatment is required for the spent tailored activated carbon prior to disposal.

2.5 Titanium Chemistry

Titanium (Ti) is one of the elements of the first transition series in the periodic table and its atomic number is 22. Ti is the ninth most abundant element and the fourth most abundant metal on earth. Ti has silvery metallic color and exists in solid form at room temperature (*26*). Ti is not found as a free element, rather it is present as ilmentite ($FeTiO_3$) and rutile (TiO_2). Ti(0) cannot be produced by direct reduction of TiO_2 with C as Ti forms very stable titanium carbide (TiC) (*25, 50*). Thus, the rather expensive Kroll process is used on large scales. The Kroll process involves creating $TiCl_4$ by heating $FeTiO_3$ or TiO_2 with C and Cl_2. Then, Ti(0) metal is produced by reducing $TiCl_4$ with magnesium (Mg).

$$2TiFeO_3 + 7Cl_2 + 6C \xrightarrow{900\ ^{\circ}C} 2TiCl_4 + FeCl_3 + 6CO \qquad (2.18)$$

$$TiCl_4 + 2Mg \xrightarrow{1100\ ^{\circ}C} 2MgCl_2 + Ti \qquad (2.19)$$

However, a recent study suggested that Ti(0) can be produced by direct electrochemical reduction of TiO_2 in molten calcium chloride ($CaCl_2$) (*51*). Thermodynamically, Ti(0) is a very reactive material and the standard reduction potentials for it and other titanium species are shown below. (*26*)

Acid solution

$$TiO^{2+} \xrightarrow{0.1\,V} Ti^{3+} \xrightarrow{-0.37\,V} Ti^{2+} \xrightarrow{-1.63\,V} Ti^{0} \qquad (2.20)$$

$$TiO_2 \xrightarrow{-0.56\,V} Ti_2O_3 \xrightarrow{-1.23\,V} TiO \xrightarrow{-1.31\,V} Ti^{0} \qquad (2.21)$$

Alkaline solution

$$TiO_2 \xrightarrow{-1.38\,V} Ti_2O_3 \xrightarrow{-1.95\,V} TiO \xrightarrow{-2.13\,V} Ti^{0} \qquad (2.22)$$

It is known that Ti has three oxidation states: II, III, and IV. Ti(III) and Ti(IV) are present in violet and colorless aqueous solutions, respectively (*52*). The presence of Ti(II) has been identified in solids such as TiO, TiS, TiH_2, and $Ti(X)_{2,\ X=F^-,\ Cl^-,\ Br^-,\ I^-}$ (*50, 53*) and in nonaqueous media as $TiCl_4^{2-}$ (*25*). However, reports on the aquatic chemistry of Ti(II) are rare because it is easily oxidized. Only a few studies have reported on the possible presence of Ti(II) in aqueous solutions. They say that Ti(II) can be produced in strongly acidic conditions in the presence of excess F^- by disproportionation of Ti(III) to produce greenish-yellow or brownish-yellow solutions (*52-57*).

$$2Ti^{3+} \xrightarrow{\text{excess } F^-} Ti^{2+} + TiF_6^{2-} \qquad (2.23)$$

One important characteristic of Ti(0) is its high affinity toward nitrogen (N) and oxygen (O) (*25, 50*). It is known that Ti(0) is the only metal that burns in N_2. Ti(0) reacts with N_2 and is converted to titanium nitride (TiN) and with O_2 to titanium dioxide (TiO_2) as

$$2Ti(0) + N_{2(g)} \longrightarrow TiN_{(s)} \qquad (2.24)$$

$$Ti(0) + O_{2(g)} \longrightarrow TiO_{2(s)} \qquad (2.25)$$

Another important characteristic of Ti(0) is its high corrosion resistance (*26*). Thermodynamically, Ti(0) is very reactive, thus, reactions (2.24) and (2.25) would be favorable reactions under atmospheric conditions. However, an oxide film is rapidly formed on the Ti(0) surface and protects the underlying Ti(0) from oxidizing environments. This surface oxide film is mainly TiO_2, and it firmly adheres to the surface of Ti(0) and rapidly recovers from any physical attack. Ti(0) also shows strong resistance to other chemicals because its surface oxide coating (TiO_2) is inert to most acids and solvents (*58*).

2.6 Pitting Corrosion

Corrosion is defined as "the destruction or deterioration of a material under the chemical and electrochemical action of the surrounding environment" (*59*). This broad definition includes deterioration of metals and nonmetallic materials such as ceramics, plastics, and rubbers. However, the term corrosion generally is applied to metallic materials (*60*). Metal corrosion is a phenomenon that causes the metal to revert to its original state of being an ore and it accomplished by chemical and electrochemical oxidation (*61*). The oxidation of a metal is described by the following equation.

$$M \longrightarrow M^{n+} + ne^{-} \qquad (2.26)$$

The electrons produced by this half-reaction can be consumed by several different reduction half-reactions. The most common reduction half-reactions are shown below.

Hydrogen evolution

$$2H^{+} + 2e^{-} \longrightarrow H_2 \qquad (2.27)$$

Oxygen reduction

$$O_2 + 4H^{+} + 4e^{-} \longrightarrow 2H_2O \qquad (2.28)$$

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-} \qquad (2.29)$$

Metal ion reduction and deposition

$$M^{n+} + me^{-} \longrightarrow M^{n-m} \qquad (2.30)$$

Pitting corrosion is a localized corrosion in which a metal undergoes accelerated dissolution as the result of a damaged oxide film on the metal surface (*62*). Many metals are covered by thin oxide films that are formed naturally and protect it from oxidizing conditions in natural environments. However, this surface oxide film is often damaged and the underlying metal is exposed to oxidizing conditions, resulting in localized massive metal dissolution. Several hypothetical scenarios have been suggested to explain the break down of the surface oxide film (*63*). The penetration mechanism describes the break down of the surface oxide film as being caused by intrusion of aggressive anions such as halides and halide-containing ions. The adsorption mechanism describes the break down as being caused by a thinning of the film induced by adsorption of aggressive anions on the oxide surface. The film break down mechanism is based on the assumption that the damaged surface oxide film is in a continual state of breakdown and repair, but aggressive anions hinder the recovery of the oxide film. These surface oxide film breakdown and pit initiation mechanisms are based on one common requirement, which is the presence of aggressive anions. Other factors affecting pit initiation are potential, temperature, metal composition, and other presence of other anions (*60, 62*).

Many studies have applied pitting corrosion as a methodology to improve efficiency of treating contaminated groundwater and drinking water. Applications of zero-valent metals are familiar technologies for reducing organic and inorganic contaminants in natural water. Physicochemical sorption and chemical reduction are the mechanisms by which zero-valent metal technologies abate contaminants. In the chemical reduction mechanism, the contaminant is reduced by the dissolved metal and direct contact with metal surface. Several studies have reported that addition of Cl^- or pretreatment with acid improve the treatment efficiency by stimulating pitting corrosion. Moreover, studies have reported that pitting corrosion is involved in reduction of perchlorate by zero-valent metals. Prinz and Strehblow (*64*) reported perchlorate reduction by zero-valent iron at pitting sites during the measurement of iron's pitting potential. They measured the increase in the concentration of Cl^- over time at the pitting site using X-ray Photoelectron Spectroscopy (XPS). Aluminum was reported to reduce perchlorate by a mechanism involving an unstable aluminum ion (Al^+) that was formed during anodic dissolution of Al (references in (*62*)). Reduction of perchlorate was also observed during electropolishing of titanium in acetic acid solution that contained perchlorate (*65, 66*). Chloride, which is the final reduction product of perchlorate, was found in the oxide film and its concentration increased closer to the interface between titanium metal and the oxide film. The presence of Cl^- in the oxide film was explained by production during reduction of perchlorate at discreet sites on the metal surface formed through pitting corrosion.

Several studies have investigated pitting corrosion of Ti(0) (*58, 67-70*). Generally, titanium requires a higher potential to develop pitting corrosion than other metals. For example, in solutions containing Cl^-, Ti(0) requires 9.2 ± 0.3 V (SHE) to initiate pitting (*67*), but Fe (*71*), Al (*72*), and Zr (*73*) require 0.56 V (SHE), – 0.88 V (SHE), and – 0.01 V (SHE), respectively. This high pitting potential of Ti(0) is related to its surface oxide film. The surface oxide film of Ti(0) mainly consists of titanium dioxide (TiO_2), which is chemically inert in natural environments and is physically well attached to the Ti(0) surface (*67*). Moreover, the high affinity of Ti(0) for oxygen makes it possible to rapidly reform a damaged oxide film in air and in most aqueous solutions.

CHAPTER III

ELECTROCHEICAL AND ENVIRONMENTAL CONDITIONS AFFECTING PERCHLORATE REDUCTION

3.1 Introduction

Reduction of perchlorate (ClO_4^-) has been attempted with transition metal ions (*74, 75*), zero-valent metals (*75-77*), and several metal electrodes (*78-80*). However, the perchlorate reduction occurs too slowly for use in remediation and water treatment processes under ambient conditions. A few studies have reported reduction of perchlorate at reasonable rates, but they were conducted under high temperature and pressure, or strongly acidic conditions, or both (*28-31*). It has been reported that the low reactivity of perchlorate is related to its high activation energy barrier in redox reactions (*2*). This high activation energy originates from its structure and electronic configuration (*2, 81, 82*). The structure of perchlorate is tetrahedron in which the chlorine atom is located at the center with four oxygen atoms surrounding and protecting it from direct attack of chemical reductants. Perchlorate has a stable electronic structure as indicated by the large energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (*81*). During a reduction by electron transfer, the electron is received by the LUMO. However, perchlorate cannot directly receive an additional electron to form ClO_4^{2-} because of the high energy level of its LUMO (*81*). As electron transfer is difficult to perchlorate, it is typically reduced by removing one of its oxygen atoms (*82*). However, this transfer can occur only when the electron-donor orbital of the reducing agent has appropriate symmetry and energy levels to effectively dissect oxygen atom from the perchlorate (*81*) or when the reducing agent forms a stable “yl” oxidized product by forming $M=O^{n+}$ (*82*). Therefore, the successful reduction of perchlorate is highly dependent on the ability of the reducing agent to effectively dissect the bond between chlorine and oxygen and to stabilize the transferred O^{2-}.

Zero-valent metals are strong chemical reducing agents and have been applied to abate contaminants in groundwater and wastewater. Zero-valent metals chemically reduce contaminants by direct contact of the contaminants with bare metal generally via pitting corrosion, by reaction with partially oxidized dissolved metal ions, and by reaction with elemental hydrogen produced by reaction of water with the metal (*76*), (*83*). Iron (*75*), (*76*), aluminum (*77*), zinc (*75*), and nickel (*74*) have been examined as reductants for perchlorate, but they showed very slow kinetics.

Titanium (Ti(0)) is the ninth most abundant element on earth and the fourth most abundant metal. It exists in four oxidation states 0, II, III, and IV. Ti(III) can reduce perchlorate rapidly compared to common metal reducing agents (*81*), (*27*) Moreover, titanium has a high oxygen affinity and forms a “yl” oxidized product by forming TiO^{2+} (*52*). This indicates that titanium compounds can effectively stabilize oxygen atoms transferred from perchlorate and promote perchlorate reduction. However, since titanium is always protected by a thick (0.5~7.0 nm) oxide film that spontaneously forms in air and aqueous solutions, its applications as a chemical reducing agent are rare. The oxide film is chemically inert in air and most aqueous solutions and rapidly recovers from chemical and mechanical attack (*58, 84-86*). One possible way to remove the oxide film from part of the Ti(0) surface would be by pitting corrosion.

Pitting corrosion is a localized breakdown of the oxide film in which holes or pits are formed on the metal surface. It is initiated by adsorption of aggressive anions at the defective surface oxide film, resulting in the local breakdown of the oxide on the surface. Halide ions, including perchlorate, act in this manner. This localized breakdown of the surface oxide film eventually exposes the underlying metal (*72, 87, 88*) and induces rapid metal dissolution at the localized pitting site. Recent studies support the idea of oxide film removal via pitting corrosion to expose underlying reactive metal. Gaspar et al., (*89*) exposed zero-valent iron (Fe(0)) to water containing carbon tetrachloride (CCl_4) and examined the surface with Auger electron spectroscopy (AES) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) to map chemical distributions on the surface. The chemical maps showed that high densities of elemental Cl and Cl^- existed at the area associated with pits on the surface of the Fe(0). This implies that pitting corrosion can effectively remove the oxide film and promote chemical reductions in localized areas. Other studies have shown that pretreatment of zero-valent metals with solutions containing acids or chloride, promotes pitting corrosion and enhances the reduction rates of contaminants (*90*) A similar effect is observed when the reactions occur in solutions with elevated concentrations of chloride (*90*). However, pitting corrosion, especially for Ti(0), is a very slow process even in the presence of high concentrations of chloride and sometimes the oxide film is regenerated and continues to protect the underlying Ti(0). However, application of an anodic potential can accelerate and maintain pitting corrosion.

In this work, Ti(0) was examined to produce active reductants for destroying perchlorate in water. Ti(0) was dissolved by eliminating the localized surface oxide film using electrochemically induced pitting corrosion. Pitting potentials of Ti(0) were determined with varying perchlorate concentrations. Various potentials, currents, surface areas of Ti(0), and solution pH were investigated in an effort to identify their influence on perchlorate reduction. Furthermore, removal of perchlorate at trace levels was examined in the presence of chloride. Experiments were conducted with various currents, chloride concentrations, and surface area concentrations of Ti(0) to identify possible application of this technology to remove perchlorate at the trace levels found in natural environments.

3.2 Materials and Methods

3.2.1Chemicals

Sodium perchlorate ($NaClO_4$) (98.0 +%, Aldrich) was used in this study as a source of ClO_4^-. However, in the experiments to evaluate the effect of pH, $HClO_4$ (60%, Alfa Aesar) was used as a ClO_4^- source instead $NaClO_4$ and pH was adjusted with NaOH (97%, Sigma). This was done to minimize effects of anions that would result from needing to use HCl, H_2SO_4 or HNO_3 to reduce pH. Ti(0) sheets (99.97 %) were purchased from ESPI Corp Inc and cut to appropriate sizes for the experiments. The

Ti(0) sheets were washed with acetone to remove organic impurities and rinsed several times with deionized water, then dried at room temperature and stored in a desiccator.

3.2.2 Pitting Potential and Potentiostatic (constant potential) Experiments

All experiments were conducted in a 1-L corrosion reactor (Princeton Applied Research, TN) with an effective solution volume of 500 mL. The reactor incorporates a three-electrode configuration with a saturated calomel reference electrode that is guided by a bridge tube. To avoid possible precipitation of $KClO_4$ in the Vycor tip (Bioanalytical Systems, Inc) of both the bridge tube and the reference electrode (*91*), both were filled with a saturated sodium chloride solution. The potential of the sodium chloride saturated calomel reference electrode is written as NaSCE and its potential is 9 mV positive of SCE at 30 ˚C (*91*). Throughout all experiments, the working Ti(0) electrode had an effective surface area of 5.0 cm^2 and the counter electrode was Pt mesh with dimensions of 2 cm× 2 cm. Electrochemical potential was controlled using a potentiostat (Solartron Analytical, Model 1287A) and constant current was achieved with a DC power supply (Kenwood, Model PW18-1.8AQ).

Pitting potentials of Ti(0) were measured by the potentiodynamic polarization method in which the open-circuit potential (OCP) was swept to 14.5 V (NaSCE) at a 1 mV/s rate. Pitting potential was determined as the potential at which current began to increase rapidly. At lower perchlorate concentrations, oscillations were observed in the polarization curve and introduced considerable variability in measured pitting potentials. Moreover, at concentrations of perchlorate less than 1 mM, the pitting potential was affected by the small amount of chloride that leaked from the bridge tube and resulted in pitting potentials lower than would be observed in a solution that contained only 1 mM perchlorate. In order to minimize the influence of chloride, the vycor was replaced after each pitting potential measurement. However, a small amount of chloride continued to leak in subsequent experiments, resulting in concentration of approximately 0.1 ~ 0.2 mM.

3.2.3 Galvanostatic (constant current) Experiments

Electrochemical experiments were carried out in a lab-scale electrochemical cell with two electrodes (anode and cathode) that had an effective volume of 800 mL. Both the anode and cathode used were Ti(0) sheets (99.97 %) and constant current was supplied by a DC power supply (Kenwood, Model PW18-1.8AQ). The electrochemical potential was not monitored during the experiments, but preliminary experiments were conducted to ensure that it would be above the pitting potential under all experimental conditions. The geometry of the cathode was 0.05 cm × 5.1 cm × 7.25 cm and the surface area of the anode varied. The cell was gently mixed (60 rpm) by a magnetic stir bar (2.5 cm long x 8 cm diameter, VWR) to prevent the accumulation of solid titanium oxide or hydroxide on the anode surface. A 6-mL sample was taken at each time interval and filtered by 0.22-µm nylon membrane filters (Magna). The samples were kept in refrigerator without any treatment until analysis and most samples were analyzed within two weeks.

3.2.4 Analytical Methods

ClO_4^-, ClO_3^-, ClO_2^-, and Cl^- concentrations were analyzed using a Dionex 500 ion chromatograph equipped with a 4-mm Dionex AS–16 analytical and guard column.

The eluent concentration, gradient operation, and injection sample loop size were the same as in a previous study (*76*), except that NaOH was used instead of KOH. Concentrations of perchlorate less than 1 mg/L were analyzed isocratically with a 1.00 mL min^{-1} flow of 50 mM NaOH as eluent and a 1000-μL injection sample loop.

3.3 Results and Discussions

3.3.1 Pitting Potential of Titanium

Figure 3.1 shows that the pitting potential depends on the concentration of perchlorate. The pitting potential for a 100 mM solution of perchlorate is 12.53 ± 0.04 V_{NaSCE}. Basame and White (*67*) reported that the pitting potential for 100 mM chloride is 9.35 ± 0.43 V_{NaSCE}, for 100 mM iodide (I^-) is 7.45 ± 0.71 V_{NaSCE} and for 100 mM bromide (Br^-) is 1.35 ± 0.28 V_{NaSCE}. This higher pitting potential for perchlorate than other halide ions is consistent with what has been reported for Al, Fe, and Zr (*62, 64, 92*)

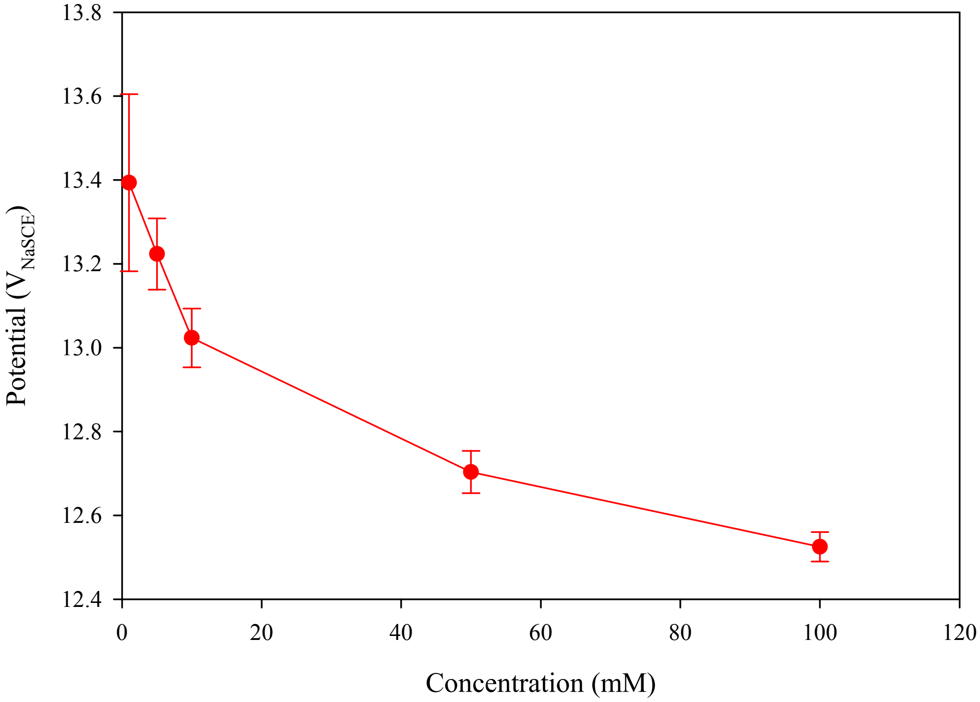


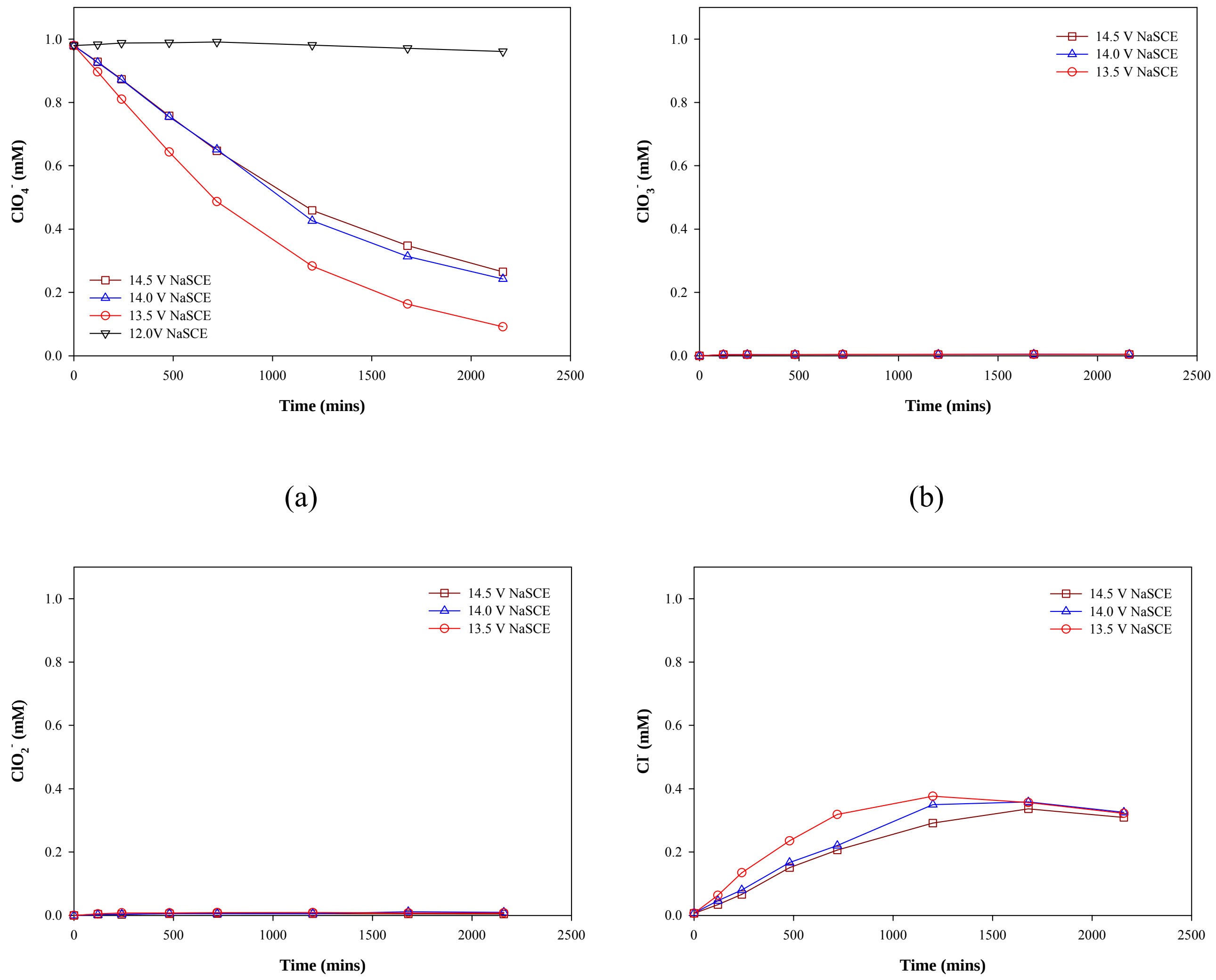
FIGURE 3.1. Pitting potentials as a function of the concentration of perchlorate.

3.3.2 Influence of Potential on Perchlorate Reduction

Based on results of experiments to determine the pitting potential of Ti(0) in perchlorate solutions, experiments were conducted to evaluate perchlorate reduction during pitting corrosion. Current and the concentrations of perchlorate and its reduction products were monitored over time. Vigorous formation of gas bubbles was observed at both the working electrode (Ti(0)) and counter electrode (Pt mesh) as soon as potential was applied. Oxygen was expected at the Ti(0) electrode due to oxidation of water and hydrogen was expected at the Pt electrode due to water reduction. Gas bubbles slowly diminished over time and only small gas bubbles were observed from the Ti(0) electrode after pitting corrosion began. However, gas evolution from the Pt mesh counter electrode persisted over the course of the experiment. Figure 3.2a illustrates how imposed potential affected changes in perchlorate concentration in solutions with 1 mM initial concentration of perchlorate. When the potential was imposed at 12.0 V_{NaSCE}, which is less than the pitting potential (13.4 V_{NaSCE}, Figure 3.1), the perchlorate concentration does not change over time. However when the applied potential is higher than the pitting potential, the perchlorate concentration decreases over time. In order to examine the possibility that perchlorate was being reduced at the Pt counter electrode, the Ti(0) electrode was replaced with a graphite carbon electrode and a potential of 14.5 V_{NaSCE} was imposed. The concentration of perchlorate did not change over time. Other potentials (14.0, 13.5, and 12.0 V_{NaSCE}) were also examined and showed no changes in perchlorate concentration. These results are presented in Appendix A. This indicates that the reduction of perchlorate did not occur at the Pt counter electrode but at the Ti(0) electrode.

Generally, it is expected that higher potentials would produce higher current and thereby more pitting corrosion. However, perchlorate reduction rate decreased with increasing applied potential (Figure 3.2a). Furthermore, the average current decreased (16.3, 11.5, 9.4 mA) as potential increased (13.5, 14.0, and 14.5 V_{NaSCE}, respectively). This unusual behavior is caused by the formation of surface oxide films of different thicknesses. The increases of the thickness of the film during the pitting corrosion are apparently contradictory behavior because the pitting corrosion causes breakdown of surface oxide film. However, since the pitting corrosion is localized breakdown of oxide film, the imposing anodic potential above pitting potential on metal can cause both the growth of surface oxide film on metal where pitting is not developed (reference) and the breakdown of surface oxide film on metal where pitting is developed. It is known that the thickness of the oxide film formed is directly proportional to the applied potential and this thickness can be estimated from the color of the surface oxide film on titanium (*93, 94*). A thin titanium oxide film is transparent. However, as the oxide film grows in thickness, the oxide film reflects different wavelengths of light and produces different colors (*93-96*). During the course of the experiments in this study, the color of titanium surface changed from a metallic gray to yellow/brass after the potential was applied and slowly turned to purple, purple blue, gray blue and finally dark gray, which are representative of thicker oxide films. Repeated observations confirmed that higher imposed potentials rapidly formed colors that represent thicker surface oxide films. The thicker films could hinder formation of stable pit developments and produce a lower number of pits (*62*), and thereby result in lower currents. The correlation of decreased perchlorate reduction rates and decreased current indicate that the rate of reduction is mainly governed by the current rather than potential, as long as the potential exceeds the pitting potential.

Figures 3.2b c and d illustrate how concentrations of products of perchlorate reduction change. As perchlorate concentration decreased, chloride concentration increased. However, the increase in chloride concentration was less than the decrease in perchlorate concentration and the chloride concentration began to decrease after a time that depended on experimental conditions. Small amounts of chlorate (ClO_3^-) (< 4.7 μM) and chlorite (ClO_2^-) (<11.7 μM) were detected, but their concentrations remained almost constant and did not vary with changes in concentrations of perchlorate and chloride. It has been suggested that the reduction of perchlorate occurs via the sequential formation of chlorate, chlorite and chloride (*91*). However, relatively small amounts of chlorate and chlorite accumulated compared to chloride, which indicates that they are rapidly converted to chloride. Final mass recoveries of Cl based on measurements of ClO_4^-, ClO_3^-, ClO_2^-, and Cl^- were 43.5, 59.4, and 59.5 % for experiments at 13.5, 14.0, and 14.5 V_{NaSCE} respectively. These low recoveries of Cl could be caused by oxidation of chloride to chlorine (Cl_2). The pitting potential of Ti(0) is greater than the standard oxidation potential for converting chloride to chlorine, so it is possible that this conversion occurs on the surface of Ti(0).



(a) (b) (c) (d)

FIGURE 3.2. Influence of imposed potential on removal of perchlorate and production of products. (a) perchlorate (b) chlorate (c) chlorite (d) chloride**.**

3.3.3 Electrochemical Chloride Oxidation

Oxidation of chloride to chlorine, chlorite, chlorate, and perchlorate were examined in experiments conducted with a solution of 1 mM chloride with an imposed current of 1 mA. Figure 3.3 shows that the chloride concentration decreases over time, but that the rate of chloride removal is different after pitting corrosion begins. Small amount of chlorate (< 9.7 μM) and chlorite (<3.8 μM), but no perchlorate were detected. The first three data points represent chloride concentrations before pitting developed and the last six data points are chloride concentrations after pitting developed. Linear regressions on the first three points and the last six points showed slopes that differed by over 400 % before and after pitting corrosion developed. This indicates a correlation between chloride oxidation and pitting corrosion, but does not confirm the oxidation of chloride at the pitting site. However, a previous study observing bromide (Br^-) oxidation on Ti(0) surface supports the supposition that chloride is oxidized at the pitting site (*58*). Scanning electrochemical microscopy (SECM) showed that bromide is oxidized to bromine (Br_2) at localized sites on Ti(0) that correspond to pitting sites. Therefore, the results in Figure 3.2 and 3.3 indicate that both oxidation and reduction reactions take place simultaneously at pitting sites on Ti(0).

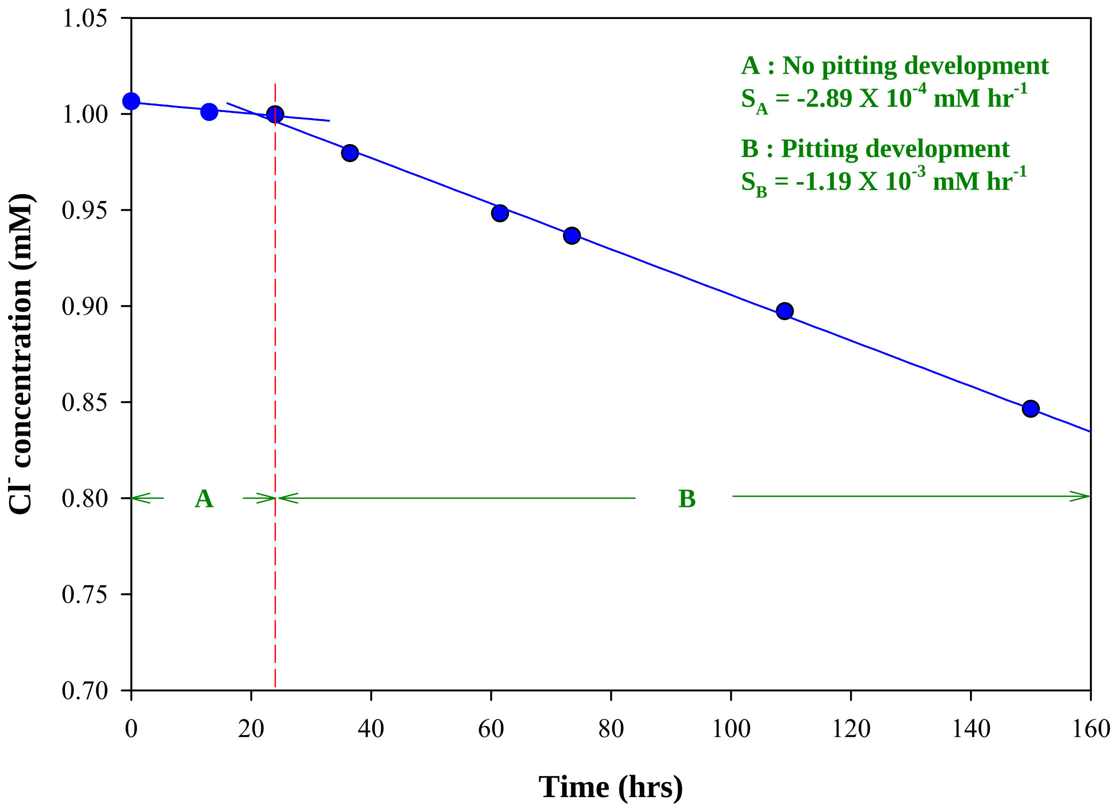


FIGURE 3.3. Chloride concentrations over time during electrochemical experiments at 1 mA current.

3.3.4 Effect of Current on Perchlorate Reduction

The influence of current on perchlorate reduction was examined by applying constant currents of different values and measuring concentrations of perchlorate over time. All experiments were conducted until the power supply could not sustain the current at the desired value. As shown in Figure 3.4a, the rate of perchlorate reduction is increased by raising the current. Figure 3.4a also shows that the experiments at high currents ended earlier, due to the earlier depletion of perchlorate and chloride concentrations that are required to sustain constant current. The amount of chloride oxidation is calculated using Cl based material balance and assumptions: 1) perchlorate is only reduced to chloride (no accumulation of chlorate and chlorite) and 2) the rate of chloride oxidation is the only important rate of chloride removal. The amount of chloride oxidized at a given time is as follows

$$[Cl^-]_{t,ox} = [ClO_4^-]_i - [ClO_4^-]_t + [Cl^-]_i - [Cl^-]_t \qquad (3.1)$$

where $[Cl^-]_{t,ox}$ represents total chloride concentration oxidized at a given time (t), $[ClO_4^-]_i$ and $[Cl^-]_i$ are initial perchlorate and chloride concentration, and $[ClO_4^-]_t$ and $[Cl^-]_t$ are perchlorate and chloride concentrations at a given time. Figure 3.4b presents the amount of chloride oxidized over time. The amount of chloride oxidized is increased by increasing current and solid lines in Figure 3.4b represent linear regression. Figure 3.4a shows that the perchlorate concentrations gradually decreased over time for all currents, but the chloride concentrations increased initially and decreased later. This behavior is caused by differences in the rates of production of chloride by reduction of perchlorate and the rates of loss of chloride caused by its oxidation to Cl_2. Initially, the rate of formation of chloride is higher than chloride oxidation and chloride accumulates. However, the rate of perchlorate reduction decreases as perchlorate is depleted and chloride accumulates, but the rate of chloride oxidation remains constant over time.

The effect of current on the rates of perchlorate reduction and chloride oxidation can be explained by Faraday's law. Faraday's laws states that the amount of material undergoing chemical change at an electrode is directly proportional to the amount of electrical charge passed through the electrode (*97*).

$$m = \frac{Q_t}{nF} \tag{3.2}$$

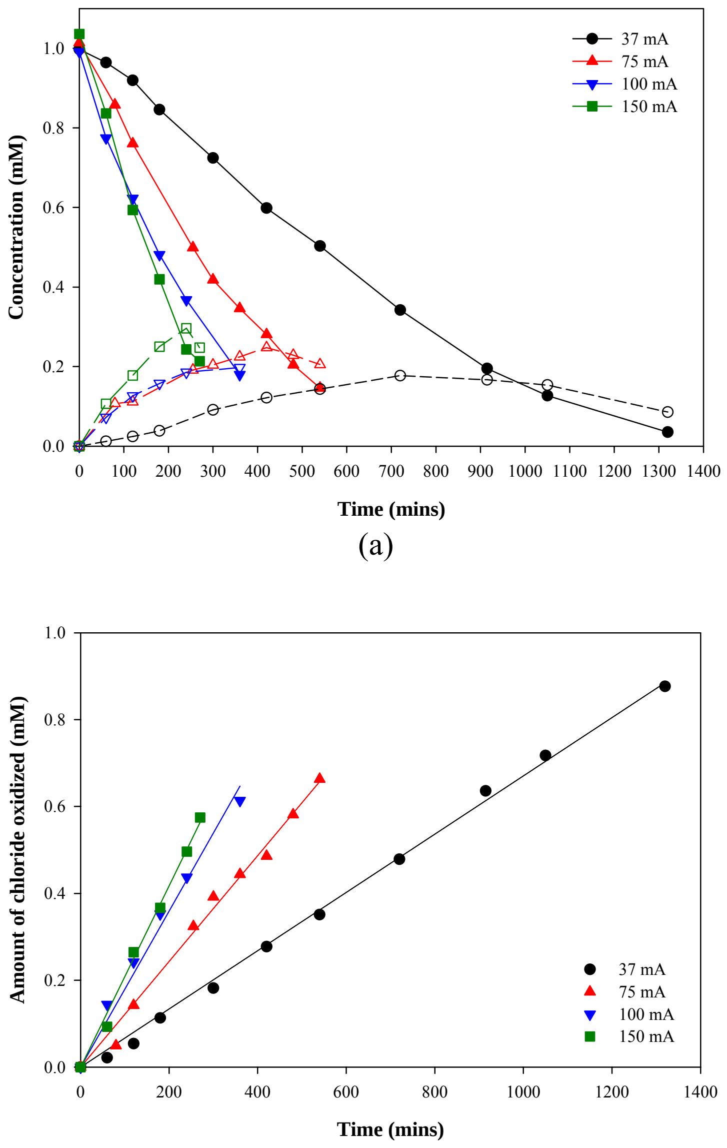
where m is the amount of material undergoing reaction (mol), n represents the number of electrons transferred per molecule that undergoes conversion, F is faraday's constant (96,485 C mol^{-1}), Q_t is total amount of electrical charge (C). If current remains constant over time, then the total amount of charge is equal to the product of the current and time.

$$m = \frac{It}{nF} \tag{3.3}$$

where I is current (A), and t is overall reaction time (s). Eq 3.3 indicates that higher current will cause electrochemical conversions to occur to a greater extent. Thus, it is inferred that higher currents increase the rate of pitting corrosion which results in higher rates of perchlorate reduction. Higher current could also be associated with faster rates of oxidation of chloride to Cl_2, if this oxidation occurs on the electrode surface made available by removal of the protective film within the pit. Additionally, a slight initial delay in removal of perchlorate is observed in the data obtained with current of 37 mA and this delay could be related to the induction time for development of pitting corrosion. The induction time is defined as the time required to develop the first pit on a metal surface and it is a function of aggressive anion concentration, thickness of surface oxide film, potential, and current density (*62*). Thinner films and higher anion concentration, potential, and current density result in shorter induction times. Since the current density is defined as a current divided by the surface area, shorter induction times are expected at higher currents when surface area is constant. Figure 3.4 shows a discernable lag at the lowest current, but no measurable lag at higher current, which indicates that pitting began with negligible induction time at the higher currents.

3.3.5 Influence of Surface Area of Ti(0) and Solution pH on Perchlorate Reduction

The surface area is an important parameter governing the rate of zero-valent metal reactions because it determines the number of surface sites available for reaction. However, the experimental results shown in Figure 3.5 indicate that the influence of surface area concentration of Ti(0) on the rate of perchlorate reduction is negligible, even when it varies by a factor of 8 (11.6 cm^2/L to 92.5 cm^2/L). The concentrations of perchlorate for the experiment conducted with a surface area concentration of 92.5 cm^2/L are higher than others, which might make it appear that the rate of removal is slower. However, the fact that the concentrations are higher is the result of a lag in beginning removal, rather than slower removal. The negligible influence of concentration of electrode surface area on perchlorate removal is explained by the mechanism of electrochemically induced pitting corrosion. Perchlorate reduction takes place at the pitting site and its rate is increased by imposing higher current.



(a)

(b)

FIGURE 3.4. Effect of current on perchlorate reduction and chloride production. (a) perchlorate (filled points) and chloride (emptied points) concentrations and (b) amount of chloride oxidized. Surface area concentration was 92.5 cm^2/L.

Increasing the surface area would probably increase the number of pitting sites, but the activity of each pitting site would be decreased unless current was increased proportionally, i.e. if current density (current/electrode surface area) were held constant. Therefore, increasing the concentration of electrode surface area has a negligible effect on the rate of perchlorate reduction.

Figure 3.6 shows the influence of solution pH on perchlorate reduction. The rate of perchlorate reduction is the same at pH 7.2 and 10.0 and is slightly increased at pH 2.0. It has been reported that rapid dissolution of metals produces strongly acidic conditions within a pit as the result of metal hydrolysis (*60*). Therefore, conditions within the pit where reduction occurs may not be strongly affected by pH in solution. However, since a lower solution pH would tend to produce more strongly acidic conditions inside pits, a lower solution pH may promote perchlorate reduction to some extent.

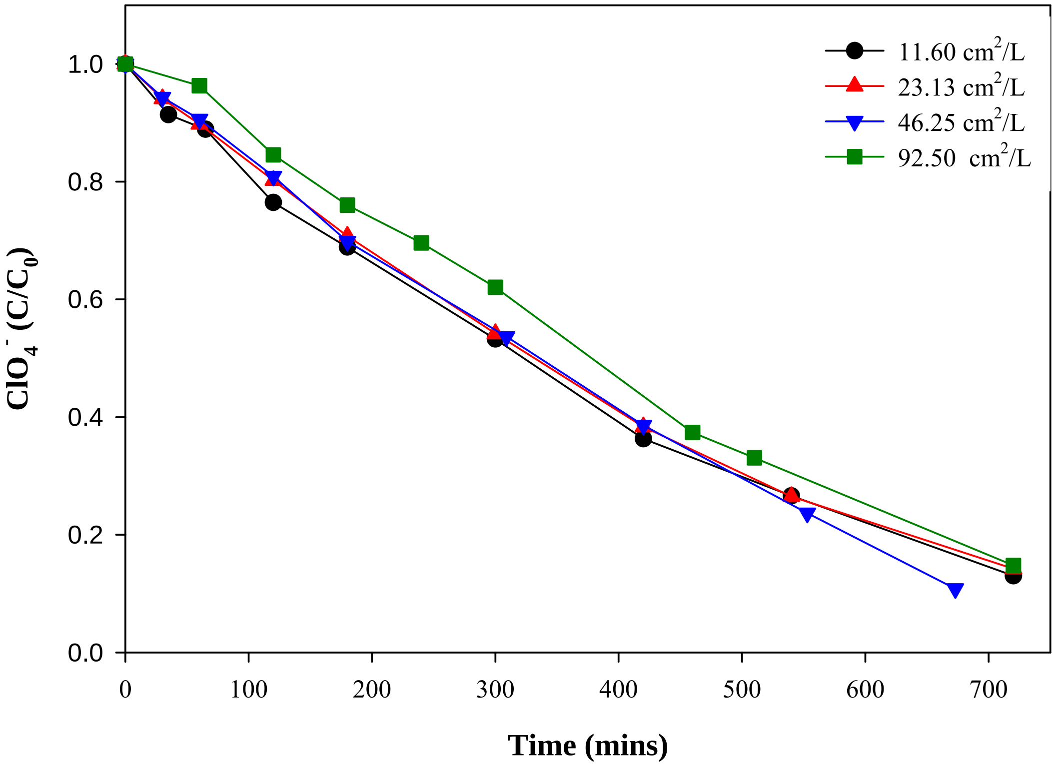


FIGURE 3.5. Influence of surface area concentration of titanium electrode on perchlorate reduction. Initial perchlorate concentration was 0.98 ± 0.017 mM and current was 50 mA.

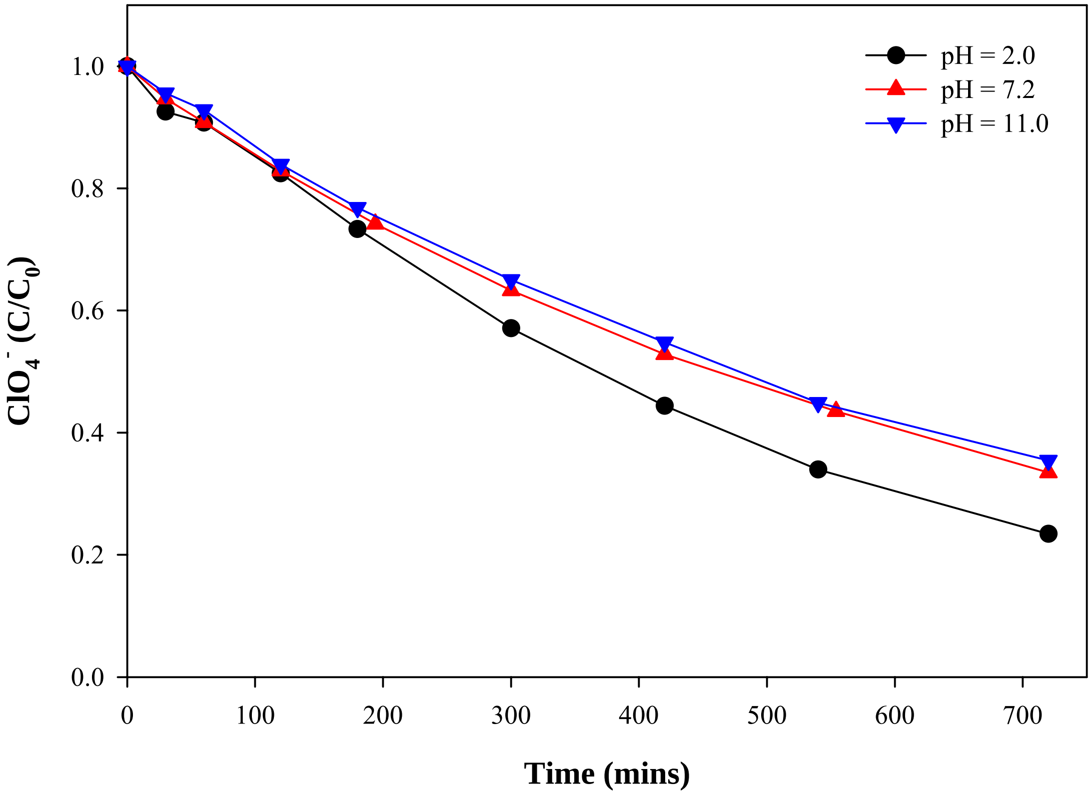


FIGURE 3.6. Influence of solution pH on perchlorate reduction. Initial perchlorate concentration was 10.15 ± 0.35 mM, current was 370 mA, and surface area concentration of titanium electrode was 92.5 cm^2/L.

3.3.6 *Trace Levels of Perchlorate Removal.*

Perchlorate concentrations have been detected in groundwater and drinking waters generally at trace levels, i.e. at concentrations less than 1,000 µg/L. The literature on other metals indicates that it would be possible to develop pitting corrosion with trace levels of perchlorate (*62*). However, pitting was not observed when solutions contained only trace levels of perchlorate and current was observed to rapidly drop due to growth of thicker surface oxide film on Ti(0). Most natural water contains chloride that is an aggressive anion that promotes development of pitting corrosion. It is a reasonable scenario that chloride would be present in water that contained trace levels of perchlorate. Thus, the behaviors of trace levels of perchlorate were examined in the presence of various concentrations of chloride, current, and surface area concentration of Ti(0).

Figure 3.7 shows removal of trace levels of perchlorate in the presence of various concentrations of chloride. These results show increased removal of perchlorate at lower chloride concentrations, but that the experiments at lower chloride ended earlier, due to inability to maintain the specified current. This is due to the earlier depletion of chloride that is needed to maintain pitting corrosion. Chloride concentrations at the final sampling points were 97, 82, 82, and 82 μM for 0.20, 0.45, 0.84, and 2.02 mM initial chloride concentrations, respectively. These results indicate that the presence of chloride has both beneficial and detrimental effects on perchlorate removal. Chloride can induce pitting corrosion that results in removal of trace levels of perchlorate, but it also inhibits the rate of perchlorate removal. A detailed inhibition mechanism will be presented in Chapter V.

Figure 3.8 shows the influence of current on the rate of perchlorate removal. The rate of removal of trace levels of perchlorate increased with increasing current, which is consistent with results shown in Figure 3.4. Effects of surface area concentrations were also investigated over the range from 11.6 cm^2/L to 92.5 cm^2/L as shown in Figure 3.9.

Results of these experiments showed that surface area concentration had negligible influence on the rates of removal of trace levels of perchlorate.

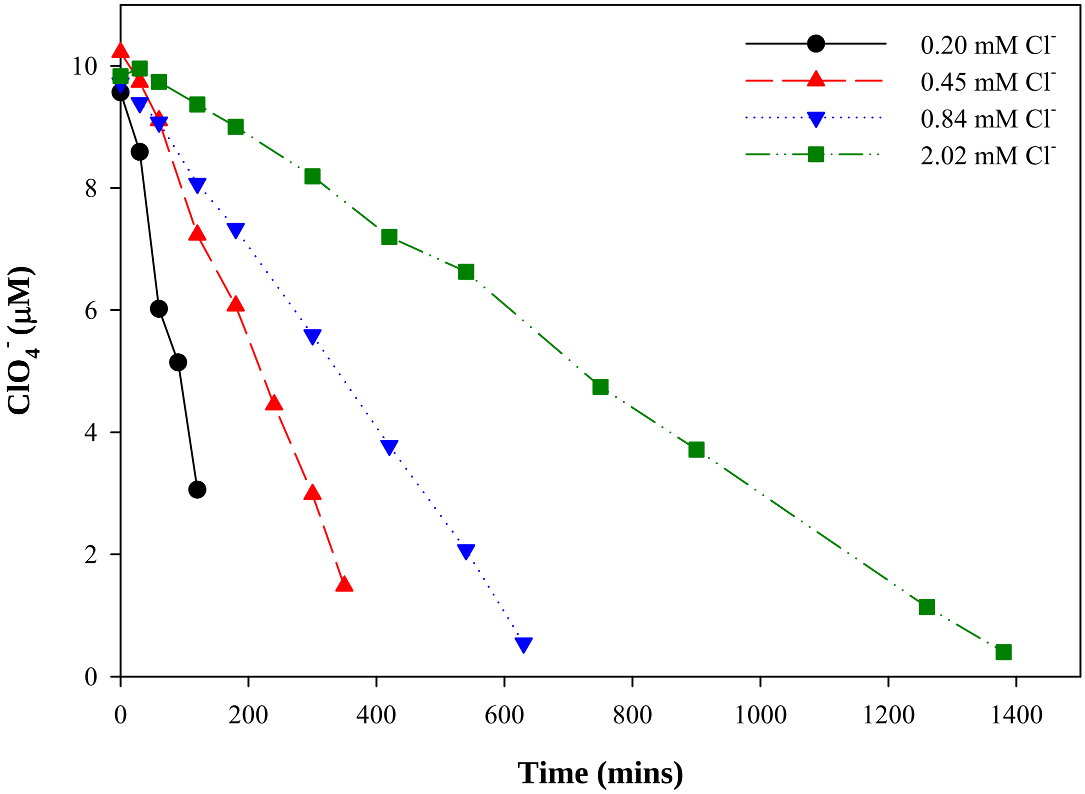


FIGURE 3.7. Influence of chloride concentrations on reduction of trace levels of perchlorate. Current intensity was 50 mA and surface area concentration of titanium was 46.25 cm^2/L.

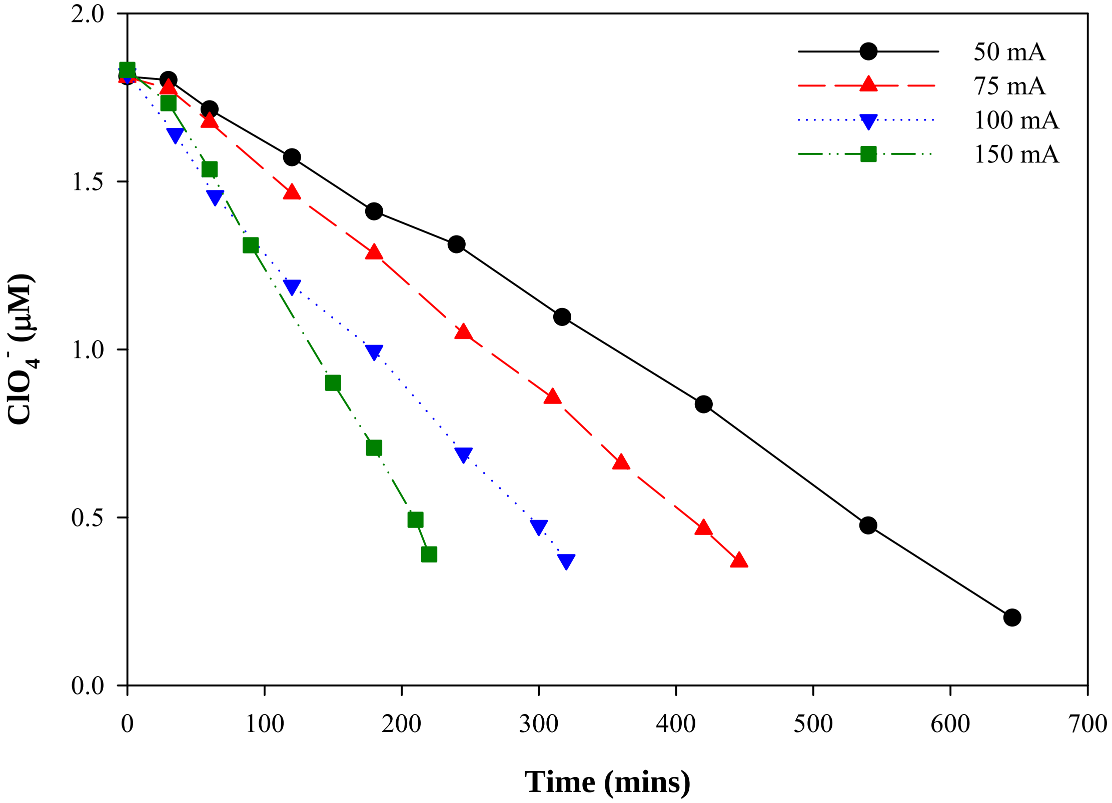


FIGURE 3.8. Influence of current on reduction of trace levels of perchlorate. Initial chloride concentration was 1.06 ± 0.02 mM and surface area concentration of titanium electrode was 46.25 cm^2/L.

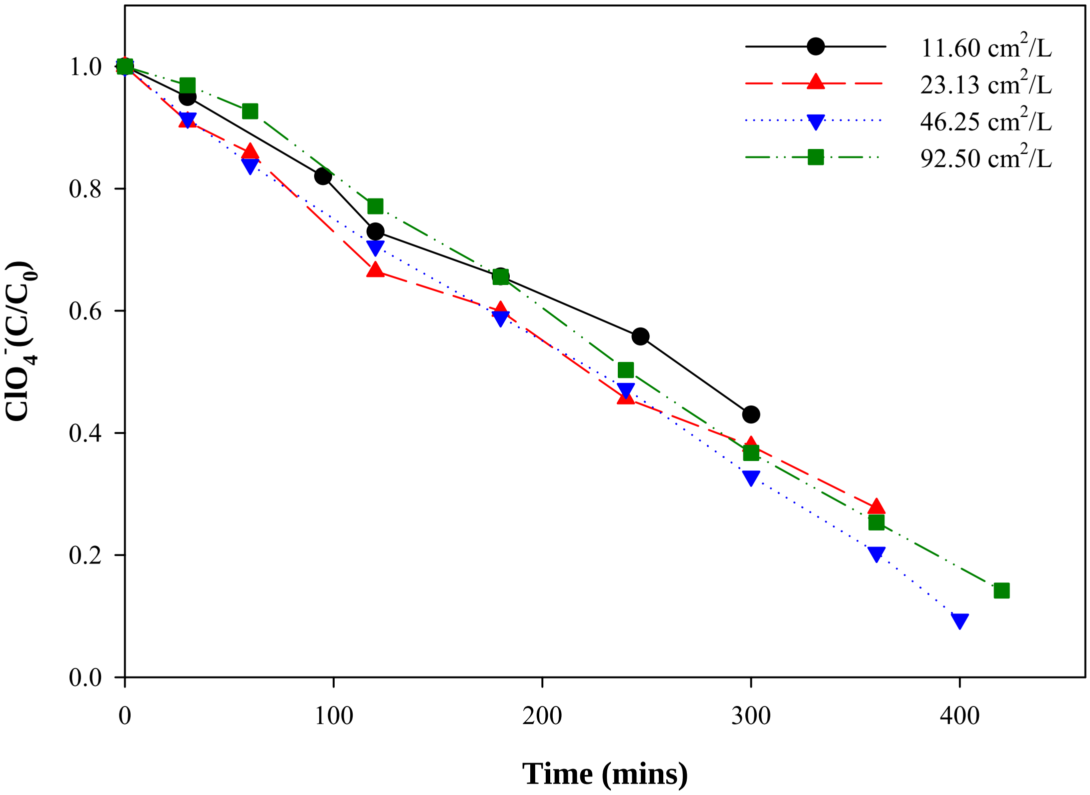


FIGURE 3.9. Influence of surface area concentration of titanium electrode on removal of trace levels of perchlorate. Initial perchlorate concentration was 4.82 ± 0.17 µM and current was 80 mA.

3.4 Conclusions

A new methodology to reduce perchlorate to chloride has been presented. It is based on using titanium metal to produce active reductants in solution via electrochemically induced pitting corrosion. Results of experiments have been presented to evaluate the effects of imposed potential, current, solution pH, and surface area concentration of Ti(0) electrode on rates of perchlorate reduction. Solution pH and surface area of Ti(0) electrodes showed negligible effects on perchlorate reduction. Reduction of perchlorate was not dependent on the imposed electrochemical potential as long as the potential was maintained above the pitting potential of Ti(0). However, the rate of perchlorate reduction did depend on the current. Reduction of trace levels of perchlorate in the presence of chloride showed that perchlorate reduction rates are easily controllable by changing current, and they are fast enough to be applied in a treatment system. Furthermore, this technology can achieve concentrations of perchlorate that are below the recommended Drinking Water Equivalent Level (DWEL) of 24.5 μg/L. However, the requirement of high potentials needed to produce active reductants and the inhibition of perchlorate removal by chloride restricts its immediate application in treatment systems. Therefore, methodologies are needed to lower the pitting potential of Ti(0) and to minimize the effects of chloride before the process can be applied to treatment systems.

CHAPTER IV

MECHANISM OF PERCHLORATE REDUCTION DURING THE PITTING CORROSION OF TI(0)

4.1 Introduction

Applications of zero-valent metals are familiar technologies for reducing organic and inorganic contaminants in natural water. Physicochemical sorption and chemical reduction are the mechanisms by which zero-valent metal technologies abate contaminants. In the chemical reduction mechanism, the contaminant is reduced by the dissolved metal ions and direct contact with metal surface that is generally promoted via pitting corrosion. Several studies have reported that the presence of chloride (Cl^-), pretreatment with acid, or ultrasound pretreatment of the metal improve the treatment efficiency by stimulating pitting corrosion (*89, 90, 98-100*). Moreover, studies have reported that pitting corrosion is involved in reduction of perchlorate by zero-valent metals. Prinz and Strehblow (*64*) reported perchlorate reduction by zero-valent iron at pitting sites during the measurement of iron's pitting potential. They measured the increase of the concentration of chloride over time at the pitting site using X-ray Photoelectron Spectroscopy (XPS). Aluminum was reported to reduce perchlorate by a mechanism involving an unstable aluminum ion (Al^+) that was formed during anodic dissolution of Al through the pitting corrosion (references in (*62*)). Reduction of perchlorate was also observed at the pitting site during electropolishing of titanium in acetic acid solution that contained perchlorate (*65, 66*). Chloride, which is the final reduction product of perchlorate, was found in the solution and in the oxide film. In the oxide film, the chloride concentration increased at locations closer to the interface between titanium metal and the oxide film. The presences of chloride in the oxide film and solution were explained by production during reduction of perchlorate at discreet sites on the metal surface formed through pitting corrosion.

Chapter III investigated the influence of electrochemical (potential, current, and surface area of Ti(0)) and environmental parameters (solution pH) on perchlorate reduction at the pitting site on Ti(0). Results showed that rates of perchlorate reduction were strongly dependent on the electrochemical parameters, especially current. In this Chapter, perchlorate reduction mechanisms are suggested based on hypothetical mechanisms from the literature and evaluated using observations made visually and with scanning electron microscopy and experimental results including reduction of perchlorate using Ti(0) as both anode and cathode of an electrochemical cell, reduction of perchlorate with transitory titanium ions, X-ray diffraction (XRD) analysis of Ti(0) oxidation products, dissolution valence of Ti(0), and molar ratio of consumed Ti(0) to reduced perchlorate. Furthermore, a hypothetical mechanism for perchlorate reduction at the pitting site on Ti(0) was proposed in an effort to understand perchlorate reduction at the pitting site.

4.2 Materials and Methods

4.2.1 Chemicals

Sodium perchlorate (98.0 +%, Aldrich) was used in this study as a source of perchlorate. Ti(0) sheets (99.97 %) were purchased from ESPI Corp Inc and cut to appropriate sizes for the experiments. The Ti(0) sheets were washed with acetone to remove organic impurities and rinsed several times with deionized water, then dried in room temperature and stored in a desiccator.

4.2.2 Perchlorate Reduction with Ti(II) and Ti(III) Containing Solutions.

Ti(III) solutions of 100 and 200 mM were prepared by dissolving $TiCl_3$ (99.9 %, Aldrich) in 1 N and 5 N HCl (Fisher). A Ti(II) solution was prepared by a modification of the method reported by Kölle and Kölle (*53*) and is based on the following reaction.

$$2Ti^{3+} + 6F^{-} \rightarrow [TiF_6]^{2-} + Ti^{2+} \qquad (4.1)$$

A solution containing KF (99.0 %, ACS grade, EM) (600 mM) and $TiCl_3$ (200 mM) in 1 N and 5 N HCl was prepared to generate a solution which would contain 100 mM Ti(II) if the reaction in equation 4.1 were to go to completion. Absorption spectrums of Ti(II) and Ti(III) were measured using a UV-VIS spectrophotometer (Hewlett Packard G1103A). All experiments with Ti(II) and Ti(III) were conducted using an anaerobic chamber filled with a mixed gas containing 5 % hydrogen and 95 % nitrogen. The deionized water was purged with 99.99 % argon gas for 2 hours and stored in an anaerobic chamber until use. All Ti(II) and Ti(III) solutions were prepared fresh and discarded after 12 hrs.

4.2.3 Determinations of Dissolution Valence and Molar Ratio of $\Delta Ti(0)/\Delta ClO_4^-$.

Experiments to determine the dissolution valence of Ti(0) and the molar ratio of ΔTi(0)/ΔClO_4^- were conducted with an electrochemical cell having two electrodes (anode and cathode) and operated at constant current. The constant current was supplied by a DC power supply (Kenwood, Model PW18-1.8AQ). The anode and cathode sizes and materials, and reactor and effective reactor volume were the same as described in Chapter III for experiments to determine the pitting potential. The weight loss of Ti(0) was determined by measuring the weight of Ti(0) before and after experiments. After experiments, Ti(0) was washed with tap water, and carefully scrubbed with a plastic brush to remove precipitate on the Ti(0) surface. Washing and brushing were repeated several times. Ti(0) was rinsed several times with deionized water and dried in room temperature and measured weight.

4.2.4 Analytical Methods

Concentrations of ClO_4^-, ClO_3^-, ClO_2^-, and Cl^- were analyzed using a Dionex 500 ion chromatograph equipped with a 4-mm Dionex AS–16 analytical and guard column. The eluent concentration, gradient operation, and injection sample loop size were the same as in a previous study (*76*), except that NaOH was used instead of KOH. Concentrations of perchlorate less than 1 mg/L were analyzed isocratically with a 1.00 mL min^{-1} flow of 50 mM NaOH as eluent and a 1000-µL injection sample loop.

The compositions of the oxidation by-products of Ti(0) were analyzed using X-ray diffraction (XRD) with a Riga automated diffractometer using Cu Kα radiation. Samples were carefully collected after each experiment and washed several times with deionized water (shake for 5-minutes, separate by centrifugation, decant supernatant). After washing, the samples were placed in a vacuum drying oven held at 30 ˚C (Thelco Inc, Model 19) for one week and stored in caped bottles until analysis.

4.3 Results and Discussions

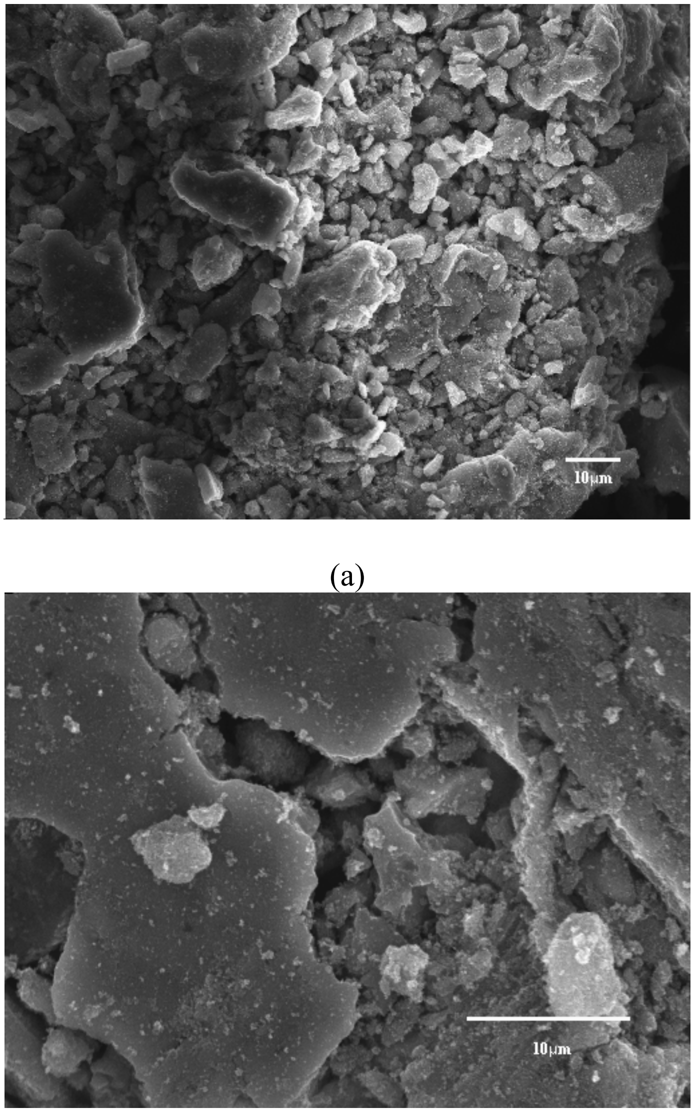
4.3.1 Possible Mechanisms for Perchlorate Reduction

In zero-valent metal systems, it has been shown that pitting corrosion enhances the rate of contaminant removal. The localized breakdown of the surface oxide film due to pitting corrosion promotes direct reduction by increasing the contact of contaminants to the exposed bare metal surface (*76, 89, 90, 101*). However, the direct reduction by the underlying Ti(0) is not an appropriate mechanism to explain perchlorate reduction in this study. The standard electrode reduction potential for ClO_4^-/Cl^- is 1.29 V (*26*) so substantial reduction of perchlorate to form chloride would not occur at the potentials needed to induce pitting corrosion of Ti(0) (> 12.5 V_{NaSCE}).

There are some studies that have reported similar anomalous behavior during dissolution of other metals. Systems containing Al(0), Be(0), Ti(0), and Zn(0) showed hydrogen evolution when these metals were anodically polarized by imposition of an external potential or by contacting them with more noble metals (references in (*102*), references in (*103*), (*85, 86*)). The potentials applied to the anode were above the H^+/H_2 equilibrium potential, so the behavior appeared to contradict thermodynamics. Several mechanisms have been suggested to explain these anomalous behaviors observed during electrochemical dissolution of metals. They include ejection of particles of bare metal during disintegration of the electrode surface, a high potential drop caused by increased resistance of films, and formation of transitory and unexpected partially oxidized metal ions (*85, 86, 102, 103*). The first and third mechanisms would result in hydrogen production away from the electrode surface and the second mechanism would result in hydrogen production at the surface of the film on the electrode.

4.3.2 Bare Titanium Metal Particle Ejection

Ejection of bare metal particles during metal corrosion by imposition of an external potential was observed in the experiments using Be(0), Mg(0), Zn(0), Cd(0), and Al(0). The ejected metal particles were either dispersed in solution as particles with diameters of the order of 10^{-1} μm or associated with metal precipitates (references in (*102, 103*)). In order to investigate possible Ti(0) particle ejections, optical microscopic observations were conducted to identify Ti(0) particles dispersed in solution and analysis by scanning electron microscopy (SEM) and X-ray diffraction (XRD) were conducted to identify particles associated with the precipitate. The optical microscopic observations found that no Ti(0) particles were dispersed in the solution. The precipitates were observed using scanning electron microscope (SEM) and no Ti(0) particles were found in the precipitate as shown in Figure 4.1. Instead, dark gray Ti(0) particles were observed by eye on the bottom of the reactor after long hours of operation. Some of these gray particles were over 1 mm. These particles were probably disintegrated debris from Ti(0) edges during pitting corrosion. It is believed that these particles are not responsible for the perchlorate reduction due to their larger size and color. Ti(0) is always covered by a thin titanium oxide film that is transparent, thus Ti(0) has a metallic gray color. However, as the oxide film on Ti(0) grows in thickness by imposition of electrochemical potential or exposing oxidizing chemicals, the oxide film reflects different wavelengths of light and produces different colors (*93-96*). In this study, long hours of imposing an electrochemical potential on Ti(0) change its color from a metallic gray to dark gray due to growth of the oxide film. This dark gray color was identical to that of larger Ti(0) particles found in the precipitate. If micro-scale Ti(0) particles without oxide film are ejected from the pitting site, they would be oxidized due to its unstable thermodynamic nature of bare Ti(0). However, if these micro-scale Ti(0) particles are not completely oxidized, then they would be passivated by the formation of surface oxide film and they could be embedded in oxide precipitates which would make them undetectable by microscopic observation. Previous studies reported that X-ray diffraction (XRD) can detect the presence of metallic Ti(0) even it was covered by surface oxide film that was generated by electrochemical anodization and thermal oxidation (*67, 104-106*). Thus, the precipitates produced in 1 mM of perchlorate solutions at different currents were collected and analyzed using XRD to investigate the possible presence of metallic Ti(0) particles associated with precipitates. Figure 4.2 shows that the dried precipitates contain mainly synthetic anatase and brookite. No metallic Ti(0) was observed in the XRD analysis. However, if ejected bare Ti(0) particles are completely oxidized or small amount of metallic Ti(0) remained in the precipitate, the XRD analysis could be inconclusive in providing evidence of the presence of Ti(0) particles associated with precipitates. Thus, results of XRD analysis cannot be used to completely rule out ejection of Ti(0) particles as a possible mechanism to describe perchlorate reduction at the pitting sites.



(a)

(b)

FIGURE 4.1. SEM images of the precipitate produced at 100 mA. (a) × 1000 (b) × 3000.

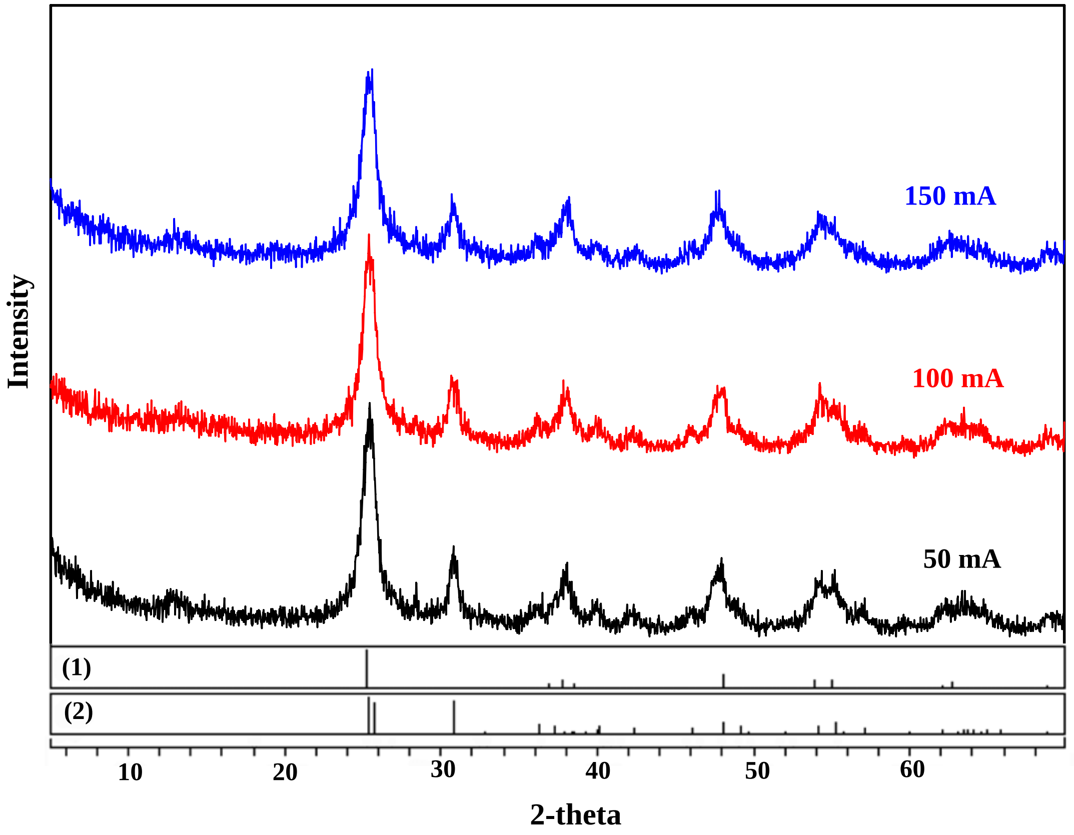


FIGURE 4.2. XRD analysis of precipitates produced under different current conditions. (1) synthetic anatase; (2) brookite.

4.3.3 High Ohmic Drop

During electropolishing of Ti(0) in a mixture of perchloric and acetic acids, it was observed that perchlorate was reduced to chloride in spite of imposed potentials that apparently would make that reaction thermodynamically infeasible (*66*). This was explained by development of lower potential than standard electrode reduction potential for ClO_4^-/Cl^- at the pitting site by the high ohmic resistance of the salt film. Several studies reported that during pitting corrosion the bottom of the pit is covered by a salt film consisting of metal salts or metal oxy-anion salts (*85, 86, 107-115*). This salt film is produced by massive dissolution of the metal at the pit, super-saturation of dissolved metal cations, and their precipitation at the bottom of the pit. For titanium in halide solutions, the composition of the salt film was titanium tetrahalide or oxy-halide (*85*). Beck (*86*) calculated potential drop by salt film in pit on Ti(0) in HBr solution. The result showed that salt film caused a potential drop that was 80 to 125 % of the applied potential. However, his calculation was based on an assumption. As hydrogen gas issued from the pit during experiments, the author assumed that the potential inside pit was negative compared to the H^+/H_2 equilibrium potential. This assumption was used to calculate the potential drop across the salt film by simply subtracting summations of open circuit potential, ohmic potential drop outside of the pit, and ohmic potential drop inside pit from the applied potential. Thus, the calculated potential drop might not represent the actual potential drop caused by the salt film. Moreover, there are other studies that contradict this result by reporting that the potential drop by the salt film is very small (*73, 116-118*). For example, the potential drop caused by the salt film near zirconium electrodes was only 0.03 V when the applied potential was 0.2 V (*73*) and potential drop for nickel was 0.5 V when the applied potential was 0.9 V (*116*). In this study, potentials over 12.5 V were imposed to develop pitting corrosion on Ti(0). Thus, it is questionable that the salt film could cause the potential drop below the ClO_4^-/Cl^- equilibrium potential at pitting site on Ti(0).

Other possible causes for a large potential drop in the pit are formation of solid corrosion products, accumulation of hydrogen gas, and existence of colloids (*73, 119*). Among them, solid corrosion product would more likely be developed a potential drop that results in potential below the ClO_4^-/Cl^- equilibrium potential and perchlorate reduction. During the metal dissolution, the pitting sites are covered with metal oxide or hydroxide precipitates. In the course of the experiments in this study, white oxide and hydroxide precipitates, believed to be mainly TiO_2, were formed and covered the Ti(0) surfaces. In order to investigate possible perchlorate reduction on the solid corrosion precipitate, experiments were conducted using Ti(0) electrodes that were covered with natural oxide film. Cathodic potentials (-1.5, -2.0 and -2.5 V) were imposed but no changes in perchlorate concentration were observed as shown in Figure 4.3. This is consistent with a study (*78*) using a titanium electrode coated with TiO_2 that showed less than 2 % reduction of perchlorate with initial perchlorate concentrations of 0.1 to 50 mM. Several other studies reported that direct cathodic reduction of perchlorate is a very sluggish reaction on other metal electrodes (references in (*120*)). Therefore, it is believed that perchlorate reduction by the high ohmic drop at the pitting sites of Ti(0) is not likely to be the mechanism of observed perchlorate reduction.

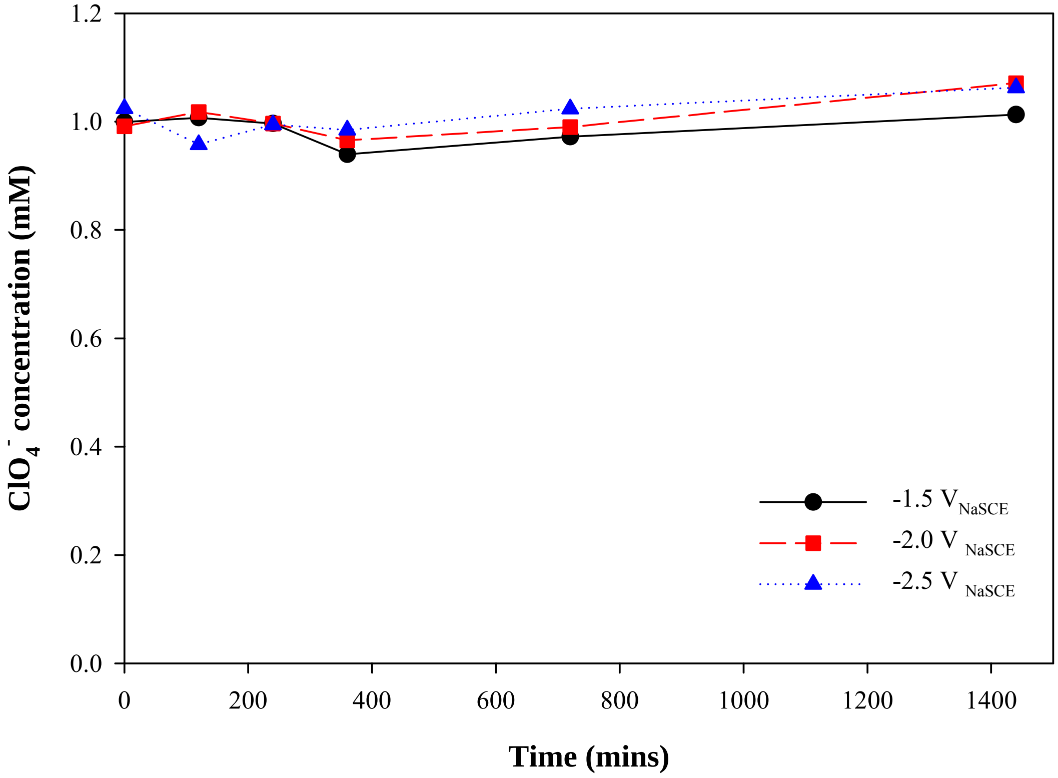


FIGURE 4.3. Direct electrode reduction of perchlorate on Ti(0).

4.3.4 Transitory Titanium Metal Ion Dissolutions

Formation of transitory or uncommon metal ions is the most widely accepted hypothesis to describe the anomalous behavior of compounds being reduced at metal electrodes during anodic polarization (*102, 103*). Ti(0) could produce two transitory ions (Ti^{2+} and Ti^{3+}) that would be intermediates before formation of the final product of Ti(IV). Ti(III) can exist as solids phases such as titanium halide ($Ti(X)_3$, where X = F, Cl, Br, or I) and titanium oxide (Ti_2O_3) or in the aqueous phase as Ti^{3+} (*25, 50*). Ti(II) is not common, but its existence has been shown by the presence of titanium halide ($Ti(X)_2$, where X = F, Cl, Br, or I), titanium hydride (TiH_2), and titanium oxide (TiO) in solid phases (*50*). However, the presence of Ti(II) in the aqueous phase is not well documented. Only a few studies have observed the formation of greenish-brown or greenish-yellow solutions believed to contain Ti(II) during dissolution of TiO with solutions of non-oxidizing acids or dissolution of Ti(0) with solutions of acids containing excess fluoride (F^-) (*52, 53*).

Visual observations were conducted to identify the presence of transitory titanium metal species in solutions during Ti(0) dissolution. However, there was no indication of Ti(II) or Ti(III) being present in the solution during experiments, because there were no greenish-yellow (Ti(II)) and violet (Ti(III)) colors observed. Microscopic observations also failed to show the existence of any solid compounds of Ti(II) and Ti(III) that are black and violet colors when they from either hydride or oxide (*50*). However, it is possible that Ti(0) could undergo dissolution to form Ti(II) and Ti(III) that exists only near the surface of Ti(0). An especially likely location would be inside the pitting sites.

In order to investigate whether perchlorate is reduced by transitory titanium ions, experiments were carried out with solutions of Ti(II) and Ti(III). Figure 4.4 shows absorption spectrums of Ti(II) and Ti(III) solutions. The Ti(II) solution showed the same green color and the same absorption spectrum with maximums at 430 and 660 nm as has been reported (*53*). The Ti(III) solution shows an absorption band at 505 nm, which is similar to that reported by previous studies (*81*). The concentration of H^+ had a negligible effect on the absorption spectrum of Ti(III), but the absorption peak at 430 nm for Ti(II) was slightly shifted to longer wavelength at higher concentrations of H^+. Figure 4.5 shows how concentrations of perchlorate were reduced in solutions of Ti(II) and Ti(III). There is a higher rate of perchlorate reduction with Ti(III) than with Ti(II) and higher rates with both were observed at higher concentrations of H^+.

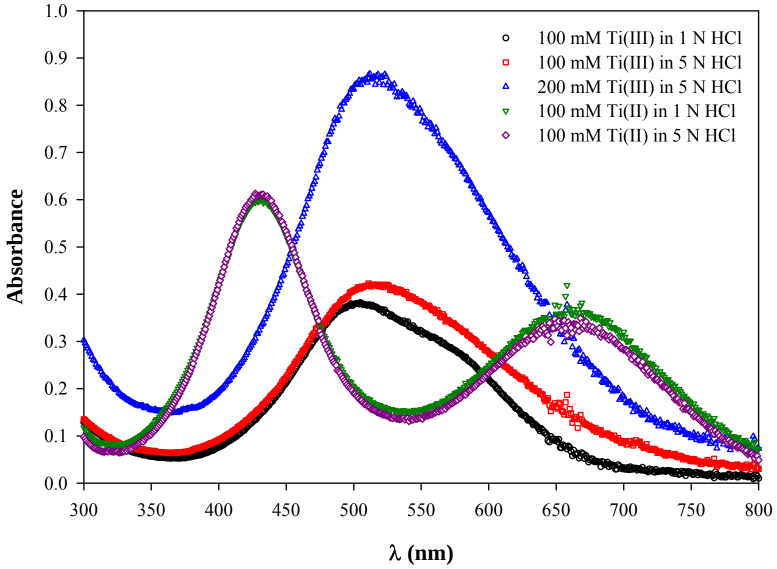


FIGURE 4.4. Adsorption spectrums of Ti(II) and Ti(III) solutions.

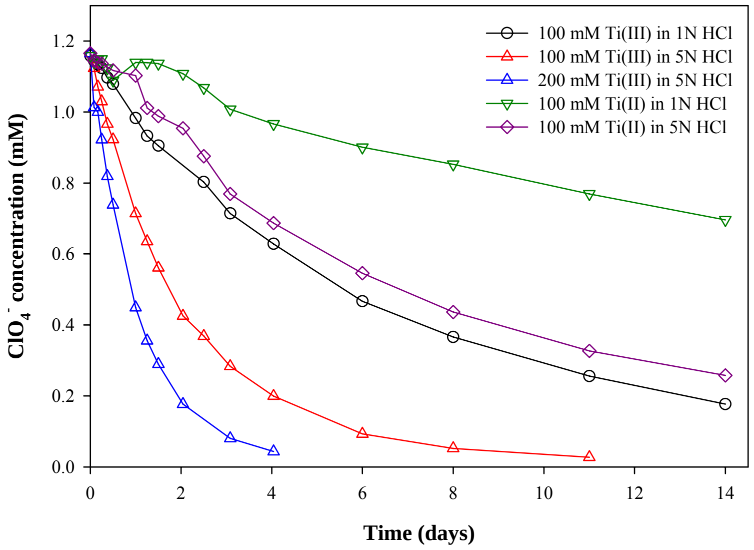


FIGURE 4.5. Perchlorate reduction with Ti(II) and Ti(III).

Initial pH of the experiments shown in Figure 3.2 in Chapter III was 6.0 and the final pH was 7.5. Within this pH range, it is expected that perchlorate reduction by Ti(II) and Ti(III) would be much slower than shown in Figure 4.5. However, pitting corrosion produces lower pH conditions inside the pit that could promote the reaction rate. Pitting corrosion occurs in a localized area in which substantial amounts of metal can dissolve. The dissolved metal ions undergo hydrolysis reactions that develop a high concentration of H^+ inside of the pit (*60, 62*). Dissolution of Ti(0) would produce Ti(IV) as the primary product, whether it is formed by oxidation of Ti(0) at the electrode or by oxidation of transitory species such as Ti(II) and Ti(III). The hydrolysis of Ti(IV) would produce H^+ ions as shown by the following.

$$Ti^{4+} + H_2O \rightarrow TiO^{2+} + 2H^+ \qquad (4.2)$$

$$TiO^{2+} + H_2O \rightarrow TiO_2 + 2H^+ \qquad (4.3)$$

These hydrolysis reactions would maintain the lower pH in the pit during the pitting corrosion of Ti(0). Furthermore, there is some evidence in the literature that suggests that concentrations of anions such as perchlorate are dramatically increased inside pits because of the need to maintain electro-neutrality during production of metal cations such as Ti^{4+} and TiO^{2+} (*60, 62*). Measurements of chloride concentrations in pits developed on a stainless austenitic steel showed that chloride concentrations accumulated in the pits at concentrations up to 20 times higher than in the external solution (*113*). Thus, pitting corrosion of Ti(0) could produce not only lower pH, but also higher perchlorate concentrations in the pits which could induce faster perchlorate reduction. However, it is hard to determine whether Ti(II) or Ti(III) is responsible for perchlorate reduction at the pitting site of Ti(0) based on results presented in Figure 4.5.

Two other measurements were made in order to further evaluate the role of Ti(II) and Ti(III) in perchlorate reduction. One measured the dissolution valence using Faraday's law and the other calculated the molar ratio of Ti(0) consumed to perchlorate reduced. Faraday's law defines that the amount of chemical change at the electrode is proportional to the total quantity of electric charge passed. Then, the titanium dissolution valence was calculated based on titanium weight loss.

$$n_{\mathrm{Ti}} = \frac{\mathrm{Mw}_{\mathrm{Ti}} Q_t}{\Delta \mathrm{M}_{\mathrm{Ti}} F} \tag{4.4}$$

where n_{Ti} represents the dissolution valence of titanium, $\Delta\mathrm{M}_{\mathrm{Ti}}$ is loss of mass of Ti(0) (g), $\mathrm{Mw}_{\mathrm{Ti}}$ is atomic weight of titanium, and F is Faraday's constant (= 96,485 C/mole). The total quantity of electric charge passed, Q_t (C), is defined as

$$Q_t = \int I dt \tag{4.5}$$

where I represents current (A), and t is time (s).However, three chemical reactions were assumed to be possible at the Ti(0) electrode: titanium dissolution, water oxidation, and chloride oxidation, but the charge consumptions by the water and chloride oxidations were assumed to be negligible as following reasons. As mentioned in Chapter III, vigorous formation of gas bubbles at the Ti(0) anode that were expected oxygen was only observed during the initial stage of an experiment. After pitting corrosion began, formation of gas bubbles on Ti(0) surface diminished and only small gas bubbles that have been identified by others as being hydrogen gas (*73, 85*), were observed on the Ti(0) electrode after the initial period. This indicates that charge consumption by water oxidation would be only concentrated before pitting developments and the charge consumption by water oxidation would be negligible after pitting development. Since the pitting corrosion was observed within minutes during the course of experiments for dissolution valence measurements, it was assumed that the charge consumed by the water oxidation is neglected. The amounts of electrical charge consumed by chloride oxidation were calculated using the amounts of Cl lost from solution.

$$Q_{\mathrm{Cl}} = \frac{\Delta \mathrm{M}_{\mathrm{Cl}}}{\mathrm{Mw}_{\mathrm{Cl}}} n_{\mathrm{Cl}} F \tag{4.6}$$

where Q_{Cl} represents electrical charge consumption by Chloride oxidation, $\Delta\mathrm{M}_{\mathrm{Cl}}$ loss of mass of Cl (g), $\mathrm{Mw}_{\mathrm{Cl}}$ is atomic weight of chlorine, and n_{Cl} is the number of electrons transferred per chlorine molecule that undergoes oxidation (= 1). The chlorine loss (mol) ($\Delta\mathrm{M}_{\mathrm{Cl}}$ / $\mathrm{Mw}_{\mathrm{Cl}}$) was calculated

$$\frac{\Delta \mathrm{M}_{\mathrm{Cl}}}{\mathrm{Mw}_{\mathrm{Cl}}} = ([\mathrm{ClO_4^-}]_{\mathrm{i}} + [\mathrm{Cl^-}]_{\mathrm{i}} - [\mathrm{ClO_4^-}]_{\mathrm{f}} - [\mathrm{Cl^-}]_{\mathrm{f}}) \times \mathrm{V_R} \tag{4.7}$$

where $[\mathrm{ClO_4^-}]_{\mathrm{i}}$ and $[\mathrm{Cl^-}]_{\mathrm{i}}$ represent the initial molar concentrations of perchlorate and chloride, $[\mathrm{ClO_4^-}]_{\mathrm{f}}$ and $[\mathrm{Cl^-}]_{\mathrm{f}}$ are the molar concentrations of perchlorate and chloride measured at the final sampling time, and $\mathrm{V_R}$ is effective solution volume. Table 4.1 shows relative electric charge consumption by chloride oxidation to total electric charge applied under various experimental conditions. The electric charge consumptions by chloride oxidation were less than 4 % of total electric charge applied, even in higher chloride concentration solutions. Thus, the electric charge consumption by chloride oxidation was assumed to be negligible compared to titanium dissolution, so the titanium dissolution valence was calculated only considering titanium weight loss.

TABLE 4.1. Electric charge consumptions by chloride oxidation under different concentrations of ClO_4^- and Cl^-.

$ClO_4^-{}_i$ (mM)	$ClO_4^-{}_f$ (mM)	$Cl^-{}_i$ (mM)	$Cl^-{}_f$ (mM)	Q_t (C)	$Q_{Cl,r}$ (%)*
0.98	0.09	6.6×10^{-3}	0.32	2112	1.3^{**}
0.98	0.27	6.6×10^{-3}	0.31	1218	1.6^{**}
0.48	0.04	0.29	0.12	2160	2.2^{***}
0.47	0.29	1.94	1.37	2160	2.7^{***}
9.8×10^{-3}	4.0×10^{-4}	2.02	0.08	4140	3.6^{***}
1.0×10^{-3}	5.0×10^{-5}	1.89	0.07	4200	3.3^{***}

$^*Q_{Cl,r} = Q_{Cl}/Q_t \times 100$; ** $V_R = 500$ mL; *** $V_R = 800$ mL

Table 4.2 shows the dissolution valence of titanium calculated in experiments at various concentrations of perchlorate and chloride. Experiments at each condition were replicated at least three times. As the concentration of perchlorate increases from 1 mM to 500 mM, the dissolution valence decreases from 3.77 ± 0.09 to 2.67 ± 0.01. However, when only chloride is present, the dissolution valence is maintained around +4, and is independent of the concentration of chloride. These results show that the valence of Ti(0) dissolution depends on whether the solution contains perchlorate or chloride, and concentration of perchlorate. Additionally, Table 4.2 strongly implies that ejection of bare Ti(0) particles does not occur at the pitting site. If bare Ti(0) particle were ejected at the pitting site, ΔM_{Ti} would be increased and dissolution valence should less than +4 in chloride solutions. However, the constant dissolution valence at different chloride concentrations and different amounts of charge passed indicate that no bare Ti(0) particles were ejected at the pitting site. Furthermore, previous results including optical microscopic observations, precipitates observation using scanning electron microscope (SEM) (Figure 4.1), and XRD analysis of precipitates (Figure 4.2) support no bare Ti(0) particle ejection from the pitting site. Therefore, perchlorate reduction is not caused by bare Ti(0) metal particles ejected from the Ti(0) electrode.

Figure 4.6 shows the molar ratio of Ti(0) consumed to perchlorate reduced ($\Delta Ti(0)/\Delta ClO_4^-$) as a function of the amount of charge passed through the electrode for two different initial concentration of perchlorate. Values of $\Delta Ti(0)/\Delta ClO_4^-$ for both initial concentrations gradually increase with increasing electric charge passed. In order to completely reduce one mole of perchlorate to chloride, four moles of Ti^{2+} and eight moles of Ti^{3+} are required and most of the data in Figure 4.6 lies the range between these two values. However, data early in the experiments show ratios below 4. This could be caused by the precipitates on electrodes, which primarily consist of TiO_2. Small amounts of these precipitates remained on the electrodes, because they were hard to remove completely, even with repeated cleanup with a plastic brush. The mass of these precipitates on the electrodes would be measured as mass of Ti(0) and cause the measured changes in Ti(0) to be too low, resulting in ratios that are too low. However, as more charge is passed, the weight loss by dissolution would increase to values much larger than the weight of the precipitate remaining on the electrodes after cleaning.

Therefore, errors caused by the remaining precipitate would decrease as increasing the charge passed.

TABLE 4.2. Observed dissolution valence for pitting corrosion of titanium under different concentrations of ClO_4^- and Cl^-.

Types of anion	Concentration (mM)	Total Charge (*C*)	Average Weight Loss (m*g*)	Valence
ClO_4^-	1	1000	131.6	3.77 ± 0.09
	10	1000	156.8	3.17 ± 0.01
	50	1000	167.3	2.97 ± 0.01
		2000	335.9	2.95 ± 0.01
	100	1000	173.1	2.87 ± 0.02
	250	1000	178.60	2.78 ±0.04
	500	1000	186.2	2.67 ± 0.01
Cl^-	10	1000	120.4	4.12 ± 0.03
	100	1000	121.3	4.09 ± 0.01
		2000	240.06	4.13 ± 0.09

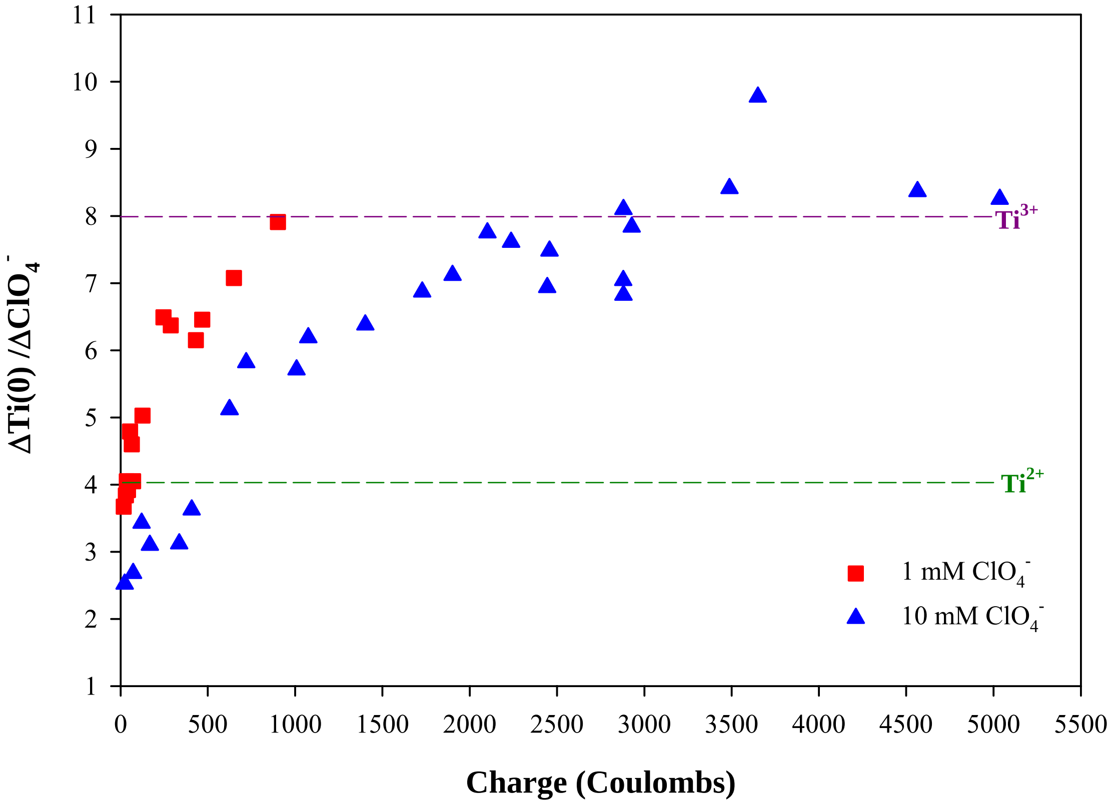


FIGURE 4.6. Molar ratio of titanium consumed to perchlorate removed.

Results in Table 4.1 and Figure 4.6 are inconclusive concerning whether Ti(II) or Ti(III) is the primary products of dissolution of Ti(0) and therefore the most likely reductant for perchlorate. However, there is a hypothesis in the literature that describes formation of uncommon metal ions during electrochemical dissolution of metals (*102, 103*). This hypothesis applied to the results in Figure 4.6 and Table 4.1 strongly suggests that Ti(II) is the primary product of the dissolution of Ti(0) that could be responsible for reduction of perchlorate. The hypothesis is that metals pass through stepwise oxidations during electrochemical metal dissolution. Suppose that metal has two oxidation states (+I and +II). The first step in electrochemically dissolving the metal would produce M(I). Further oxidation of M(I) to M(II) could be caused by two pathways. One is a chemical oxidation by an oxidizing agent that is present in solution. The other pathway is further electrochemical oxidation at the anode (metal surface) and depends on M(I) being strongly adsorbed to the anode metal surface (*103*). The relative importance of chemical or electrochemical oxidation of M(I) to M(II) is determined by the presence of oxidizing agents and their concentrations. If there are no oxidizing agents or they are present at low concentrations, electrochemical oxidation is predominant and the dissolution valence of the metal would be +2. However, if there are oxidizing agents present and they exist at high concentrations, chemical oxidation is predominant and the dissolution valence of the metal would be less than +2. Higher concentrations of the oxidizing agent would result in more chemical oxidation of M(I) and lower dissolution valences that would approach +1.

If this mechanism is applied to Ti(0) dissolution, the first step would produce Ti(II), because the lowest oxidation state of titanium metal ion is +2. Further oxidation of Ti(II) would be caused by reaction at the electrode surface or with dissolved oxidizing agents. The oxidizing agent used in this study is perchlorate, so the chemical oxidation of Ti(II) could be described as follows.

$$4Ti^{2+} + ClO_4^{-} \rightarrow 4TiO^{2+} + Cl^{-} \qquad (4.8)$$

However, it is also possible that electrochemically produced chlorine would oxidize the produced Ti(II).

$$Ti^{2+} + Cl_2 \rightarrow Ti^{4+} + 2Cl^{-} \qquad (4.9)$$

The electrochemical oxidation of Ti(II) to Ti(IV) on the surface of an anodically polarized Ti(0) electrode can be described as follows.

$$Ti^{2+} \rightarrow Ti^{3+} + e^{-} \qquad (4.10)$$

$$Ti^{3+} \rightarrow Ti^{4+} + e^{-} \qquad (4.11)$$

Table 4.2 shows that the dissolution valence of Ti(0) gradually decreases from 3.77 to 2.67 when perchlorate concentrations increase from 1 mM to 500 mM. Increasing perchlorate concentrations would increase the extent of the reaction described by reaction 4.8 and would result in lowering the dissolution valence. However, when chloride is the only anion present, the reactions shown in reactions 4.10 and 4.11 would be predominant and dissolved Ti(II) would tend to be electrochemically oxidized to Ti(III) and Ti(IV), if dissolved Ti(II) is strongly adsorbed on the Ti(0) surface. This would result in a dissolution valence of +4 in chloride solution. The other explanation is also possible based on chlorine formation. If one mole of Ti(0) is oxidized to Ti(II), it will transfer 2 modes of electrons to the electrode. If the Ti(II) is oxidized by chlorine to Ti(IV), then there needs to be one mole of chlorine which would be produced by oxidation of 2 moles of chloride by transferring two moles of electrons to the electrode. The net electron transfer for loss of one mole of Ti(0) is 4 moles (2 moles form production of Ti(II) and 2 moles from production of chlorine) and dissolution valence results in +4. This would also result in a dissolution valence of +4 in chloride solution. Figure 4.6 shows that values of $\Delta Ti(0)/\Delta ClO_4^-$ gradually increase with increasing electric charge passed. This is related to perchlorate and chloride concentrations. Decreasing concentrations of perchlorate and increasing concentrations of chloride occur by increasing the amounts of electric charge passed, because there has been more time for the reduction reaction to occur. The lowering concentration of perchlorate would cause the extent of the reaction shown by reaction 4.8 to decrease, while the increasing concentration of chloride would cause the extent of reactions shown by reaction 4.9 or reactions 4.10 and 4.11 to increase. Therefore, as the amount of charge passed increases, more amount of dissolved Ti(II) are electrochemically or chemically oxidized by increasing chloride concentration and this results in values of $\Delta Ti(0)/\Delta ClO_4^-$ increase. These results indicate that mechanism for perchlorate reduction that is based on formation of transient metal ions fairly well describes experimental results for dissolution of Ti(0). However, there is a critical problem. The standard electrode potential of TiO^{2+}/Ti^{2+} is -0.14 V (*26*). Thus, it is possible that Ti(II) could be chemically oxidized by reaction with water. This chemical oxidation of Ti(II) would also result in a dissolution valence less than +4. However, the dissolution valences of Ti(0) in chloride solutions were about +4, which suggests that there was no substantial reaction of Ti(II) with water.

There is some evidence observed during experiments that suggests that there was no substantial Ti(II) oxidation by water during pitting corrosion. Two video clips were made during experiments and they are presented in the Appendix D. Video Clip 1 shows gas bubble evolutions from electrodes during experiments with solutions of 25 mM perchlorate and Video Clip 2 shows it for solutions of 25 mM chloride. Similar gas bubbles have been identified by others as being hydrogen gas (*73, 85, 86*). Gas evolution is vigorous during the stage of pit nucleation in both chloride and perchlorate solutions. After the stage of pit nucleation, pitting sites are covered by the precipitates and the gas bubble evolution is weakened. Suppose that a small patch of bare Ti(0) is generated by electrochemically induced pitting corrosion on the surface of Ti(0). Two of the reactions that could occur include anodic dissolution of Ti(II) and subsequent oxidation of Ti(II) by water.

$$\mathrm{Ti(0)} \rightarrow \mathrm{Ti}^{2+} + 2\mathrm{e}^{-} \tag{4.12}$$

$$\mathrm{Ti}^{2+} + \mathrm{H_2O} \rightarrow \mathrm{TiO}^{2+} + \mathrm{H_2} \tag{4.13}$$

Additionally, perchlorate could be reduced by Ti(II) (reaction 4.8). Vigorous gas bubbles during pit nucleation indicate the importance of reaction that forms hydrogen gas (reaction 4.13). The reduction in the rate of gas formation results from formation of precipitate on the pitting site (reactions 4.2 and 4.3). For solutions that contain perchlorate, the lower rate of gas bubble evolution after pit nucleation that is shown in Video Clip 1 can be explained as being due to perchlorate consuming Ti(II) (reaction

4.8) rather than water (reaction 4.13) . When chloride is present rather than perchlorate, the lower rate of gas bubble evolution after pit nucleation shown in Video Clip 2 can be explained as being due to chlorine (reaction 4.9) or electrochemical oxidation (reactions 4.10 and 4.11) consuming Ti(II). Thus, the decrease in gas evolution after pit nucleation indicates that there is less chemical oxidation of Ti(II) by water.

4.3.5 Proposal of Ti(II) Dissolution Mechanism

Pitting corrosion on metal surface develops unique environments inside the pitting such as higher concentrations of aggressive anions and metal ions than those of external solution. These unique environments inside of the pitting sites might be responsible for uncommon Ti(II) dissolution and perchlorate reduction during the pitting corrosion of Ti(0). In general, metal dissolution is described by a hydroxo−ligand mechanism (*121*).

$$M + H_2O \rightarrow MOH_{ads} + H^+ + e^- \qquad (4.14)$$

$$MOH_{ads} \rightarrow MOH^+_{aq} + e^- \qquad (4.15)$$

$$MOH^+ + H^+ \rightarrow M^{2+} + H_2O \qquad (4.16)$$

However, several studies reported that aggressive anions are involved in metal dissolution during the pitting corrosion and electrochemical metal dissolution (*122-134*). These studies proposed that aggressive anions are adsorbed on the bare metal surface during pitting corrosion and stimulate metal dissolution. Two types of models were proposed to describe how anions are involved in metal dissolution: 1) indirect and 2) direct participation models. For the indirect participation model, the aggressive anions stimulate metal dissolution after localized breakdown of the surface oxide film, but the metal is dissolved as a hydroxo-metal complex (*122-126*). If Ti(0) is dissolved with indirect participation of anions in the dissolution process during the pitting corrosion, Ti(0) would be dissolved based on previous work (*122*).

$$\mathrm{Ti} + \mathrm{X}^{-} \leftrightarrow \mathrm{TiX}^{-}_{\mathrm{ads}} \tag{4.16}$$

$$\mathrm{TiX}^{-}_{\mathrm{ads}} + \mathrm{H_2O} \rightarrow \mathrm{TiOH}^{-}_{\mathrm{ads}} + \mathrm{H}^{+} + \mathrm{X}^{-} \tag{4.17}$$

$$\mathrm{TiOH}^{-}_{\mathrm{ads}} \leftrightarrow \mathrm{Ti}^{2+} + \mathrm{OH}^{-} + 2\mathrm{e}^{-} \tag{4.18}$$

where X^{-} is an aggressive anion that induces pitting corrosion. The direct participation model proposed that the anions not only prompt metal dissolution, but also leave the metal surface by forming complexes with dissolved metal ions (*127-133*). If Ti(0) would be dissolved with direct participation of anions in the dissolution process during the pitting corrosion, Ti(0) is dissolved through three possible Ti(0) dissolution pathways and they are presented below based on previous work (*131*).

OH^{-} stimulated dissolution

$$\mathrm{Ti} + \mathrm{H_2O} \leftrightarrow \mathrm{TiOH}_{\mathrm{ads}} + \mathrm{H}^{+} + \mathrm{e}^{-} \tag{4.19}$$

$$\mathrm{TiOH}_{\mathrm{ads}} \rightarrow \mathrm{TiOH}^{+} + \mathrm{e}^{-} \tag{4.20}$$

$$\mathrm{TiOH}^{+} + \mathrm{H}^{+} \leftrightarrow \mathrm{Ti}^{2+} + \mathrm{H_2O} \tag{4.21}$$

X^{-} stimulated dissolution

$$\mathrm{Ti} + \mathrm{H_2O} + \mathrm{X}^{-} \leftrightarrow \mathrm{TiXOH}^{-}_{\mathrm{ads}} + \mathrm{H}^{+} + \mathrm{e}^{-} \tag{4.22}$$

$$\mathrm{TiXOH}^{-}_{\mathrm{ads}} \rightarrow \mathrm{TiXOH} + \mathrm{e}^{-} \tag{4.23}$$

$$\mathrm{TiXOH} + \mathrm{H}^{+} \leftrightarrow \mathrm{Ti}^{2+} + \mathrm{H_2O} + \mathrm{X}^{-} \tag{4.24}$$

$H^{+}{-}X^{-}$ stimulated dissolution

$$\mathrm{Ti} + \mathrm{H_2O} + \mathrm{X}^{-} \leftrightarrow \mathrm{TiX}_{\mathrm{ads}} + \mathrm{H_2O} + \mathrm{e}^{-} \tag{4.25}$$

$$\mathrm{TiX_{ads} + H^+ \rightarrow TiXH^+_{ads}} \tag{4.26}$$

$$\mathrm{TiXH^+_{ads} + X^- \leftrightarrow TiX_2 + H^+ + e^-} \tag{4.27}$$

$$\mathrm{TiX_2 \leftrightarrow Ti^{2+} + 2X^-} \tag{4.28}$$

The relative importance of OH^-, X^- and $H^+{-}X^-$ stimulated dissolutions is determined by the presence of aggressive anions and solution pH. In general, reactions 4.19 to 4.21 might be predominant if Ti(0) undergoes dissolution. However, when solution contains higher concentrations of aggressive anions, the Ti(0) undergoes dissolution by reactions 4.22 to 4.24. However, if the solution contains higher concentrations of aggressive anions at lower solution pH, Ti(0) dissolution occurs by reactions 4.25 to 4.28.

During pitting corrosion of Ti(0), considerable enrichments of dissolved metal ions and anions in the pit cause a salt film to be developed at the bottom of the pit. The salt film works as a barrier and limits transportation of anions and dissolved metal ions to solution by separating bare metal surface to solution.(*85, 86, 111, 113*). It has been reported that the titanium salt film forms within 10^{-5} to 10^{-3} s following pit nucleation and its thickness ranges from 2 to 10 nm during pitting corrosion (*107*). However, the salt film has a very short life that lasts several seconds after interruption of current (*116*). Thus, it is hard to detect physical properties of a salt film. Beck (*85, 86*) assumed that salt film in pits of corroding Ti(0) is a compact film. However, for other metals, several studies postulated that the salt film is either porous (*110, 116, 118, 135*) or mixed that has both porous and compact film layers(*111, 136*). In this study, the physical property of salt film is assumed based on the experimental observations. Video Clips 1 and 2 showed gas issuing from the pitting site. The hydrogen gas evolution might disturb the formation of a compact salt film which has been suggested by others (*85, 86*) and might result in a more porous layer. The salt film interfaces with the bare Ti(0) and the pit solution. On the solution side, the dissolution of the salt film occurs and following hydrolysis reactions produce high concentrations of solid corrosion products such as TiO_2 and $TiO(OH)_2$, H^+ by the hydrolysis reactions of Ti(IV) (reactions 4.2 and 4.3), and anions. However, several studies presumed that the pH at the interface between the bare metal surface and the salt film is more basic than the external solution due to electrolytic migration of H^+ away from the bare metal surface (*116, 135*).

When Ti(0) undergoes dissolution to Ti(II), aggressive anion is transported from solution to the bare Ti(0) surface through salt film in order to balance the positive charge and concentrated at the at the interface between the bare Ti(0) and salt film (*114*). The dissolution of Ti(0) would be accelerated by the adsorption of the aggressive anion on bare Ti(0). If Ti(0) is dissolved with indirect participation of anions in the dissolution process by reactions 4.16 to 4.18, dissolved Ti^{2+} would reduce perchlorate at the interface between the bare Ti(0) and salt film. However, if Ti(0) is dissolved with direct participation of anions, Ti(0) would be dissolved by forming Ti(II) and anion complexes. Since the pH is higher than solution pH due to electrolytic migration of H^+ away from the bare metal surface (*116, 135*), the formation of titanium anion complex might be developed by reactions 4.22 to 4.24, rather than by reactions 4.25 to 4.28. Then, bare Ti(0) would be dissolved as $Ti(ClO_4)OH$ for solutions that contain perchlorate. This dissolved complex of Ti(II) and perchlorate provides the opportunity for an oxidation/reduction reaction to occur that would reduce perchlorate and oxidize Ti^{2+} to

TiO^{2+}. However, for solutions that contain chloride without perchlorate, TiClOH would be formed and would dissociate to Ti^{2+} and Cl^{-} without a redox reaction occurring. As the salt film works as a barrier that limits transport of dissolved metal ions to the solution, a high concentration of Ti^{2+} produced by dissociation of TiClOH (direct participation model) or dissolution of Ti(0) to Ti^{2+} (indirect participation model) would accumulate at the interface between the salt film and bare Ti(0). The majority of Ti^{2+} would be either electrochemically or chemically oxidized to Ti(IV). The electrochemical oxidation of Ti^{2+} could occur on the bare Ti(0) surface or on surface of the salt film, which is plausible because of a low potential drop across the salt film. The chemical oxidation of Ti^{2+} could be developed by oxidizing agent present in solution such as water or chlorine that is produced by electrochemical oxidation of chloride. The Ti(IV) produced by this oxidation would be regenerate the salt film and keep the bare Ti(0) separate from the bulk solution in the pit.

4.4 Conclusions

This chapter has investigated how perchlorate is reduced at Ti(0) that is polarized at high anodic potential. Three possible mechanisms (ejection of bare Ti(0) particles, high ohmic potential drop, and transitory titanium metal ions) were examined and a mechanism involving Ti(II) as a transitory ion is proposed as the one that best describes experimental observations. Pitting corrosion develops a unique condition in the pit in which high concentrations of dissolved metal ions, anions and H^{+} exist This condition develops a salt film at the bottom of pit where anions stimulate metal dissolution. The aggressive anions are adsorbed on the metal surface, form surface complexes with the metal, and then dissolve to partially oxidized metal ion or form soluble complexes with aggressive anions. Thus, it is proposed that during pitting corrosion of Ti(0), the aggressive anion is adsorbed on the bare Ti(0) surface and Ti(0) dissolves two possible pathways: 1) Ti(0) dissolves to Ti(II) by indirect participation of aggressive anions, and 2) the aggressive anion forms a surface complex with partially oxidized Ti and dissolves to form a soluble complex with Ti(II), such as $Ti(ClO_4)OH$ and TiClOH by direct participation of aggressive anions. Furthermore, the salt film limits the transport of Ti(II) to the bulk solution. This promotes either electrochemical oxidation of Ti(II) on the Ti(0) surface or possibly in the salt film, or chemical oxidation of Ti(II) by electrochemically produced chlorine.

CHAPTER V

INTERFERENCE OF ANIONS ON PERCHLORATE REDUCTION DURING THE PITTING CORROSION OF TI(0)

5.1 Introduction

Several anions including nitrate (NO_3^-), sulfate (SO_4^{2-}), and phosphate (PO_4^{3-}) are present in groundwater and surface water. Even though the concentrations of these anions vary depending on the geological and environmental characteristics of the water, they are present in relatively higher concentrations than perchlorate. In general, nitrate, sulfate, and phosphate have been classified as non-aggressive anions because they are not very effective in promoting corrosion. In fact, they often act as corrosion inhibitors by tending to prevent the initiation of corrosion and depressing its progression by competitive adsorption (*59, 60, 62*). These anions have a higher or similar affinity for the surface oxide film on Ti(0) than perchlorate (*62, 67, 137, 138*). Thus, the presence of these anions in a water contaminated with perchlorate would affect the perchlorate reduction by inhibiting the development of pitting corrosion on Ti(0). Moreover, as nitrate is an oxidizing agent, nitrate could consume Ti(II) or other reductants produced at the pitting site of Ti(0).

This chapter describes results of experiments that determined the influence of nitrate, sulfate, and phosphate on the rate of perchlorate reduction during pitting corrosion of Ti(0). Also, chemical conversions of these anions were investigated with an emphasis on conversion of nitrate. Additionally, possible mechanisms for inhibition of perchlorate reduction were explored by comparing the effects of these anions to the effects of more aggressive anions, such as fluoride (F^-), chloride (Cl^-), bromide (Br^-) and iodide (I^-), which induce and promote metal corrosion.

5.2 Material and Methods

5.2.1 Chemicals

Sodium perchlorate (98.0 +%, Aldrich) was used in this study as a source of perchlorate. Anion sources are sodium phosphate (ACS certified, Fisher), sodium nitrate (ACS certified, Fisher), sodium sulfate (99.0 %, EM), potassium fluoride (99.0 %, EM), sodium chloride (99.0 %, EM), potassium bromide (ACS certified, Fisher) and potassium iodide (99.0 %, EM). Ti(0) sheets (99.97 %, ESPI) were purchased from ESPI Corp Inc and cut to appropriate sizes for the experiments. The Ti(0) sheets were washed with acetone to remove organic impurities and rinsed several times with deionized water, then dried in room temperature and stored in an air tight desiccator until the experiment.

5.2.2 Batch Experiments

Electrochemical experiments were carried out in a lab-scale, two-electrode (anode and cathode) electrochemical cell, whose effective volume was 800 mL. Both the anode and cathode were Ti(0) sheets (99.97 %) and a constant current was supplied by a DC power supply (Kenwood, Model PW18-1.8AQ). The cell was gently mixed at 60 RPM with a stirring bar (2.5 cm length, 8 cm diameter) in order to reduce the accumulation of precipitates of titanium oxide or hydroxide on the anode surface. The dimensions of the anode were 0.05 cm × 2.5 cm × 7.25 cm and the dimensions of the cathode were 0.05 cm × 5.0 cm × 7.25 cm for all experiments except those that measured pitting potential. An 8-mL sample was taken at each time interval and filtered by a 0.22-µm nylon membrane filter (Magna). The filtered sample was kept in a refrigerator without any further treatment until analysis, which usually occurred within two days.

The pitting potential measurements were conducted in a 1-L corrosion reactor (Princeton Applied Research, TN) that had an effective solution volume of 500 mL. This reactor incorporates a three-electrode configuration with a saturated calomel reference electrode that was guided in a bridge tube. The working Ti(0) electrode had an effective surface area of 5.0 cm^2 and the counter electrode was Pt mesh with dimensions of 2 cm× 2 cm. Electrochemical potential was controlled using a potentiostat (Solartron Analytical, Model 1287A) and the potentiodynamic polarization method was used in which the open-circuit potential (OCP) was swept to 14.5 V (NaSCE) at a 1 mV/s rate.

5.2.3 Analytical Methods

Concentrations of ClO_4^-, ClO_3^-, ClO_2^- and Cl^- were analyzed using a Dionex 500 ion chromatograph equipped with a 4-mm Dionex AS–16 analytical and guard column. Other anions (NO_3^-, NO_2^-, SO_4^{2-}, and PO_4^{3-}) were analyzed using a Dionex DX-80 ion chromatograph equipped with a 4-mm Dionex AS-14 analytical and guard column, and DS-5 detection stabilizer. Concentrations of other anions (F^-, Br^-, and I^-) were not measured in this study, but were calculated based on known additions. Concentration of NH_4^+ was determined by the Phenate method using UV-VIS spectrophotometer (Hewlett Packard G1103A) at 640 nm with a light path of 1 cm (*139*).

Precipitates of Ti(0) were analyzed using X-ray diffraction (XRD) with a Riga automated diffractometer using Cu Kα radiation and X-ray photoelectron spectrometer (XPS) equipped with Mg Kα/Al Kα anode. The precipitate was carefully collected and washed several times with deionized water by repeated centrifugation, decanting supernatant, washing with deionized water and shaking for 5 minutes. After washing, the precipitate was placed in a 30 ˚C vacuum oven (Thelco Inc, Model 19) for one week and stored in caped bottles until analysis. Analyses of the XRD results were conducted using MDI Jade 6.5 software (Materials Data Inc., USA).

5.3 Results and Discussion

5.3.1 Influence of Nitrate on Perchlorate Reduction

The influence of nitrate (0.4 to 2.2 mM) on perchlorate reduction during pitting of Ti(0) was investigated using a 1.0 mM solution of perchlorate and applying a 80 mA current to the electrodes. As nitrate is also an oxidant, its concentration and its reduction by-products (nitrite and ammonium ions) were measured. Figure 5.1 shows that perchlorate removal seems to be only slightly affected by concentrations of nitrate as high as 1.1 mM. When the nitrate concentration is increased to 2.2 mM, the rate of perchlorate reduction is much slower during early stages of the reaction. However, one thing that is particularly noticeable about the results with 2.2 mM nitrate is that there is an initial delay in perchlorate reduction. This initial delay is caused by the induction time of pitting corrosion (*62*), which is the time required to develop stable pitting corrosion. As nitrate is a corrosion inhibitor, increasing its concentration would delay development of stable pitting. Thus, a slower rate of perchlorate reduction was observed until full development of pitting corrosion occurred. This was well supported by visual observations of the pitting development during experiments. Without nitrate, visible pitting sites and precipitates were identified within minutes. However, as the nitrate concentration increased, it took more time before visible pitting sites and precipitates were observed. Thus, if the effect of the induction time is considered, nitrate only slightly inhibits the rate of perchlorate reduction. Figure 5.2 shows this by plotting the concentrations of nitrate shifted in time by the estimated induction time (60 min. for 1.1 mM, 360 min. for 2.2 mM). Data points that were taken at times below the estimated induction times are not plotted.

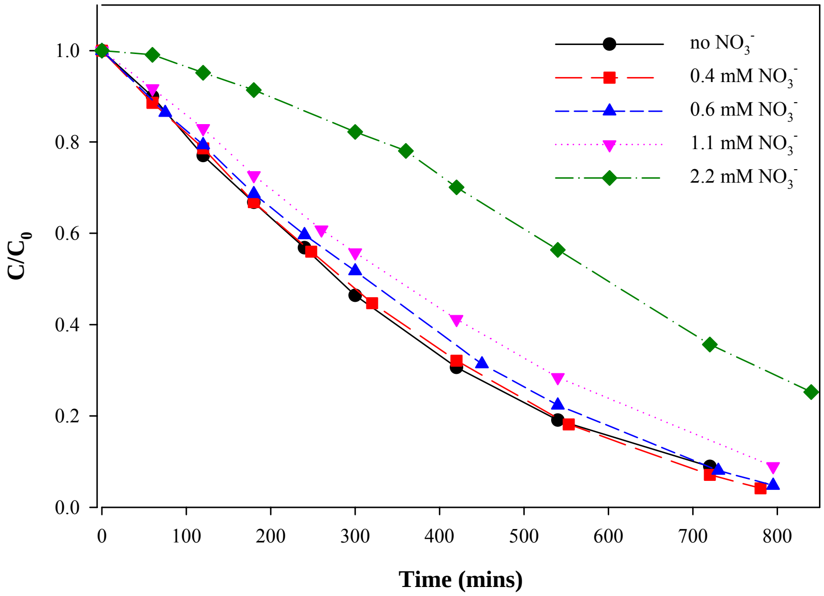


FIGURE 5.1 Influence of nitrate concentrations on perchlorate reduction. Perchlorate concentration was 1.03 ± 0.01 mM and current intensity was 80 mA.

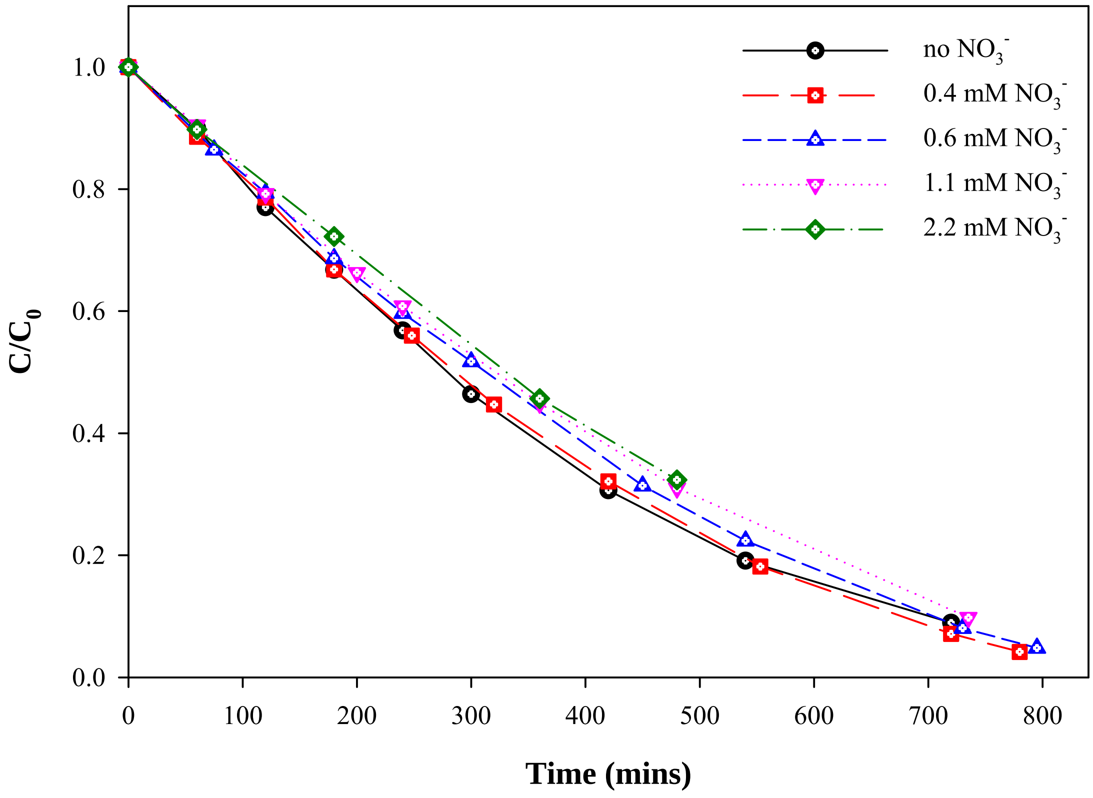
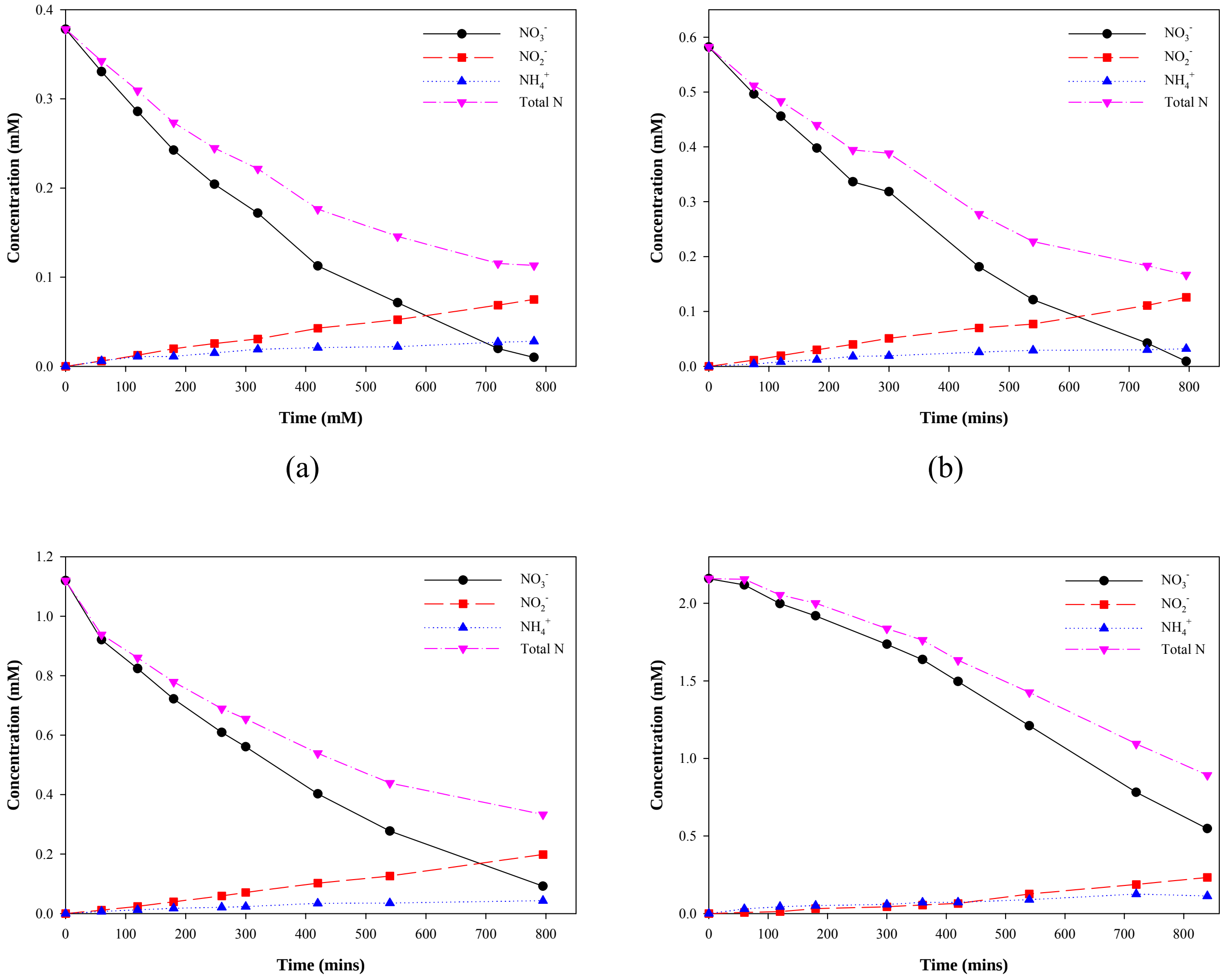


FIGURE 5.2 Effect of nitrate on perchlorate reduction with some data shifted in time. Perchlorate concentration was 1.03 ± 0.01 mM and current intensity was 80 mA. Data for 1.1 mM nitrate were shifted 60 min and data at lower times were eliminated. Data for 2.2 mM nitrate were shifted 360 min and data at lower times were eliminated.

Figure 5.3 presents the concentrations of nitrate, nitrite, ammonium and total nitrogen (N) measured in the same experiments presented in Figure 5.1. The concentrations of nitrate decrease and the products of its reduction (nitrite and ammonium) gradually increase over time. As perchlorate is reduced at the pitting site, nitrate is probably being reduced by the same reductant, which is believed to be dissolved Ti(II).



(a) (b)

(c) (d)

FIGURE 5.3. Conversion of nitrogen species during electrochemical reduction of 1.03 ± 0.01 mM perchlorate at various initial concentrations of NO_3^-. (a) 0.4 mM NO_3^-, (b) 0.6 mM NO_3^-, (c) 1.1 mM NO_3^-, (d) 2.2 mM NO_3^-. Current was 80 mA.

However, alternative explanations are possible. Nitrate could be reduced by dissolved Ti(III), which has been reported as an effective reductant for nitrate. (*140-147*). Nitrate could also be reduced by direct reduction at the Ti(0) cathode, which has been reported (*148*). The possibility of direct reduction at the Ti(0) cathode was evaluated in an experiment conducted by replacing the Ti(0) anode with a graphite anode and using a 2-mM nitrate solution and 80-mA current. The nitrate concentration did not change over a 12 hr. period. Thus, it can be concluded that nitrate is only reduced at pitting sites on the Ti(0) anode.

The total concentration of nitrogen (nitrate + nitrite + ammonium) decreased over time and showed total nitrogen losses of 70, 71, 70, and 59 % from solutions of 0.4, 0.6, 1.0, and 2.2 mM nitrate, respectively at the final sampling point. There are two possible hypotheses that support nitrogen loss during the pitting corrosion of Ti(0): 1) dissociation of ammonium to ammonia and following release of ammonia to ammonia gas, and 2) formation of N-containing titanium compounds. The initial pH values of the solutions were between 7.2 and 7.6, and gradually increased over time, reaching values over 10.0 for all four experiments. The acid dissociation constant for ammonium is $10^{-9.26}$ at 25 ˚C (*149*), which indicates that ammonia becomes the predominant species at pH greater than 9.26. In general, gas compounds dissolved in solution follow the principle that the solubility of a gas in the solution is directly proportional to the partial pressure of the gas above the solution at the equilibrium. Typical partial pressures of ammonia gas in the atmosphere range from 0.1×10^{-9} to 5×10^{-9} atm and its Henry's law constant is $10^{1.76}$ $\mathrm{M \cdot atm^{-1}}$ (*149*). Concentration of dissolved ammonia possibly present in the solution is from 5.7×10^{-6} to 2.9×10^{-4} mM. Moreover, the electrochemical reaction produces hydrogen gas (H_2) at the cathode through water reduction. Therefore, since the final pH values were over 10.0 for all four experiments shown in Figure 5.3, it is possible that the losses of N could be caused by the dissociation of ammonium to ammonia and release of ammonia to the atmosphere as ammonia gas. Several studies using Ti(III) to reduce nitrate support this mechanism of nitrogen loss (*140, 143, 147*). In a strongly alkaline solution, nitrate is reduced to ammonia within minutes by Ti(III) and 100 ± 1 % of nitrate was converted to ammonia and released as ammonia gas (*140*). However, under strongly acidic conditions, nitrate is reduced by Ti(III) to either nitric oxide (NO) or nitrous oxide (N_2O) (*142, 144, 146*).

In order to investigate the loss of nitrogen by release to a gas, experiments were conducted at three different initial pH conditions, 2.2, 7.3 and 11.2 and show in Figure 5.4. The acidic pH condition was achieved by using a mixture of 1.0 mM HCl and 2.0 mM HNO_3. The pH values were increased by adding NaOH to a mixture of 1.0 mM HCl and 2.0 mM HNO_3. Figure 5.4 shows that the total nitrogen losses at 360 min are 41, 37, and 39 % for initial conditions of pH 2.2, pH 7.3, and pH 11.2, respectively. The rates of nitrate reduction are similar for initial pH values of 2.2 and 7.3, but the rate for initial pH of 11.2 is higher. Initial/final values of pH were 2.2/2.6, 7.3/10.0, and 11.2/10.5. Higher nitrite concentrations are observed at initial pH of 11.2. Ammonium concentrations are not much different at the different pH conditions. Even though there is a difference in the rate of nitrate reduction, total nitrogen losses are similar regardless of pH conditions.

Since the total nitrogen losses are not affected by the solution pH, stripping of ammonia to the atmosphere would not be the reason for the loss of nitrogen.

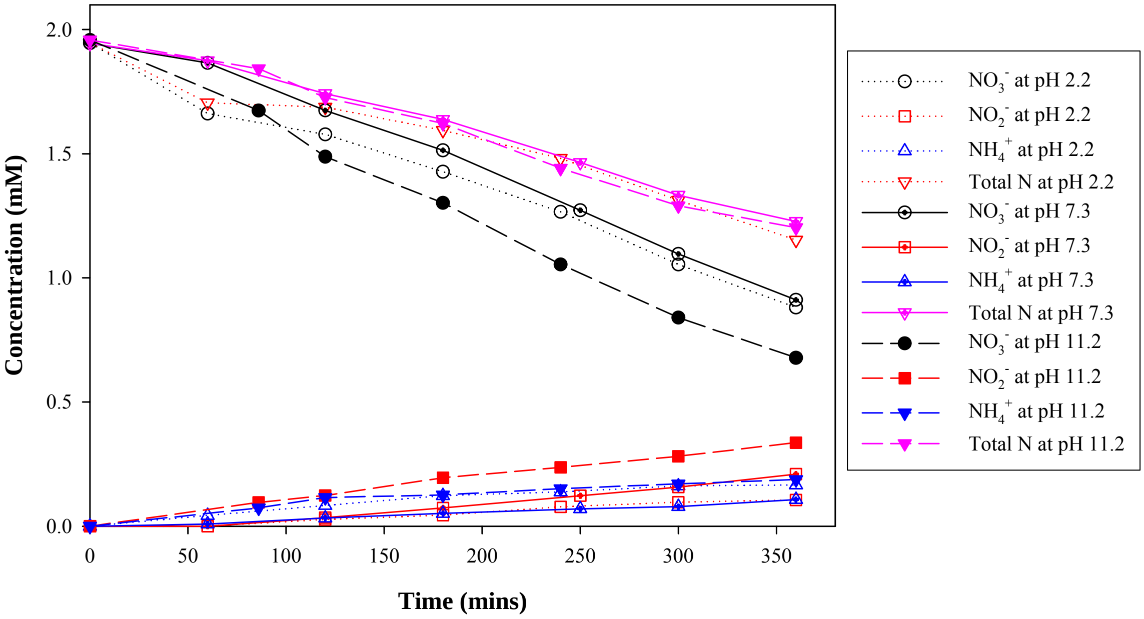


FIGURE 5.4 Influence of solution pH on N balance. Current was 125 mA, and initial/final pH values were 2.2/2.6, 7.3/10.0, and 11.2/10.5. Nitrate concentration was 1.95 ± 0.01 mM.

It has been reported that titanium has high affinities for oxygen and nitrogen. It forms titanium dioxide (TiO_2) and titanium nitride (TiN) when it burns with oxygen and nitrogen gases (*25, 50*). Thus, formation of N-containing titanium compounds during nitrate reduction is a possible explanation for the loss of nitrogen from solution. Chemical and electrochemical dissolution studies on titanium in nitrate solutions have reported that nitrate and nitrite were detected inside the oxide film (*150, 151*). Moreover, it was observed in this study that light yellow or beige particles formed along with white precipitates on the titanium electrode. These particles are similar in color to the yellow or brown colored particles of titanium nitride (*25, 50*). In order to examine the possible presence of N-containing titanium compounds in these precipitates, the precipitate formed with 250 mA of current in a mixture of 10 mM perchlorate and 5 mM nitrate was collected and analyzed using X-ray diffraction. The results are shown in Figure 5.5. An analysis of the diffractogram using MDI Jade 6.5 software shows that the precipitate primarily contains titanium dioxide solids such as anatase and brookite and titanium oxide nitride. However, peaks for titanium oxide nitride ($TiO_{0.34}N_{0.74}$) are indistinguishable from those for titanium oxide peaks, so it is possible that both solids are present. In order to confirm the presence of titanium oxide nitride, another precipitate was produced using a mixture with more nitrate (10 mM) and less perchlorate (1 mM) than the mixture used to produce the precipitates used to produce the results shown in Figure 5.5. Figure 5.6 shows the result of XRD analysis for the high-nitrate sample. Analysis of the results with MDI Jade 6.5 software indicates the possible presence of the same compounds (anatase, brookite, and $TiO_{0.34}N_{0.74}$), but the peak spectrum is different than shown in Figure 5.5. One broad peak is observed around 2θ values between 18˚ and 40˚. Several peaks between 40˚ and 70˚ are identical to those of anatase and brookite. The broad peak formed between 18˚ and 40˚ is similar to that of a poorly crystalline TiO_xN_y (*152, 153*). However, it is also possible that poor crystalline development of anatase could cause the broad peak formed between 18˚ and 40˚ (*154*). In order to further evaluate the possible presence of N-containing titanium compounds, the precipitate was analyzed with XPS. Figure 5.7 shows that the precipitate consists of Ti and O and no nitrogen atoms were detected. Therefore, even though XRD diffractogram analyses indicated the possible presence of a N-containing titanium compound, XPS analysis confirms that there is no N-containing titanium compound produced during pitting corrosion of Ti(0) in solutions of nitrate within detection limit of XPS. However, it is not clear why the light yellow or beige particles are formed at the pitting site of Ti(0). It has been shown that loss of N-balance is not caused by the release of ammonia to the atmosphere and it is not caused by the formation of N-containing titanium oxide compounds. Therefore, loss of N-balance is probably caused by the formation of gaseous compounds such as NO, N_2O, or N_2.

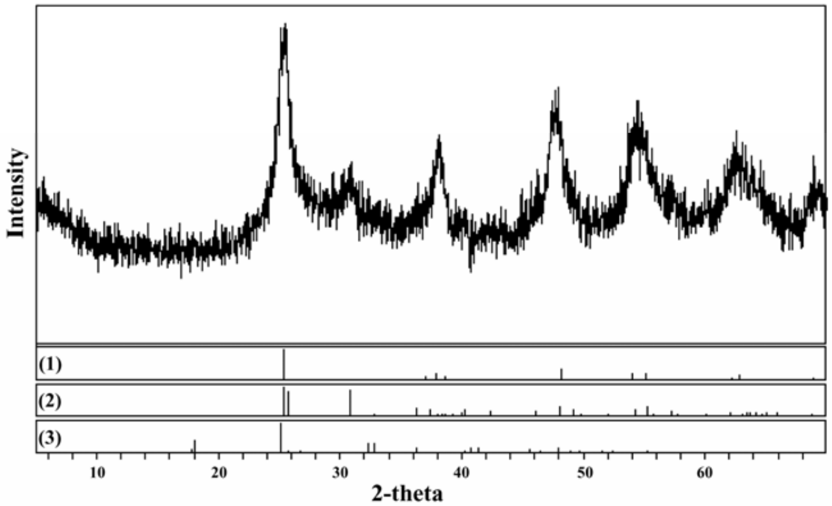


FIGURE 5.5 XRD analysis result of the precipitate produced from a mixture of 10 mM perchlorate and 5 mM nitrate with current of 250 mA. (1) Synthetic anatase, (2) brookite, and (3) Titanium oxide nitride ($TiO_{0.34}N_{0.74}$).

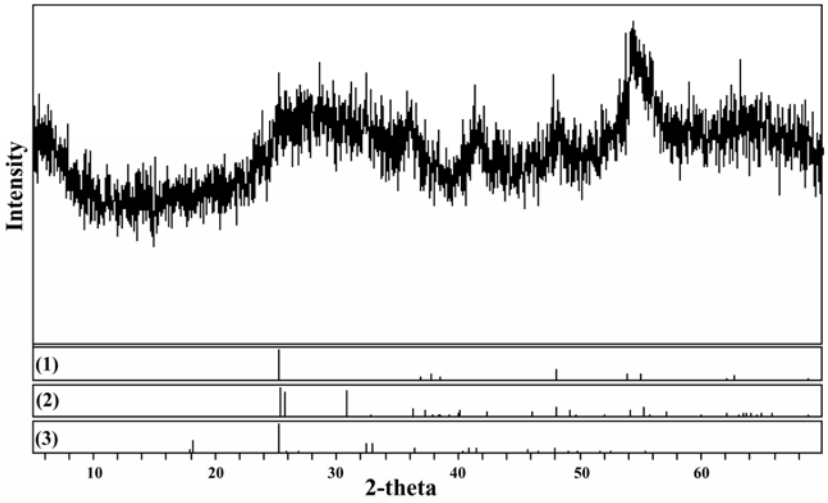


FIGURE 5.6 XRD analysis result of the precipitate produced from the mixture of 1 mM perchlorate and 10 mM nitrate with current of 250 mA. (1) Synthetic anatase, (2) brookite, and (3) Titanium oxide nitride ($TiO_{0.34}N_{0.74}$).

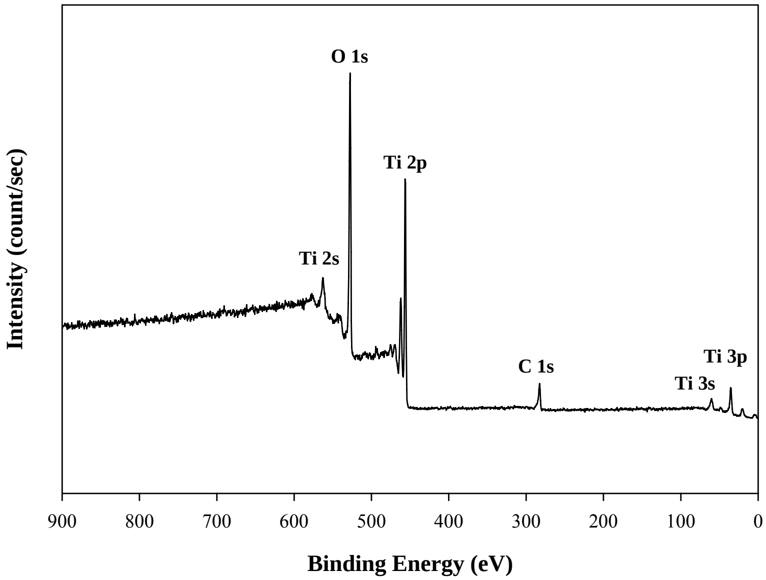
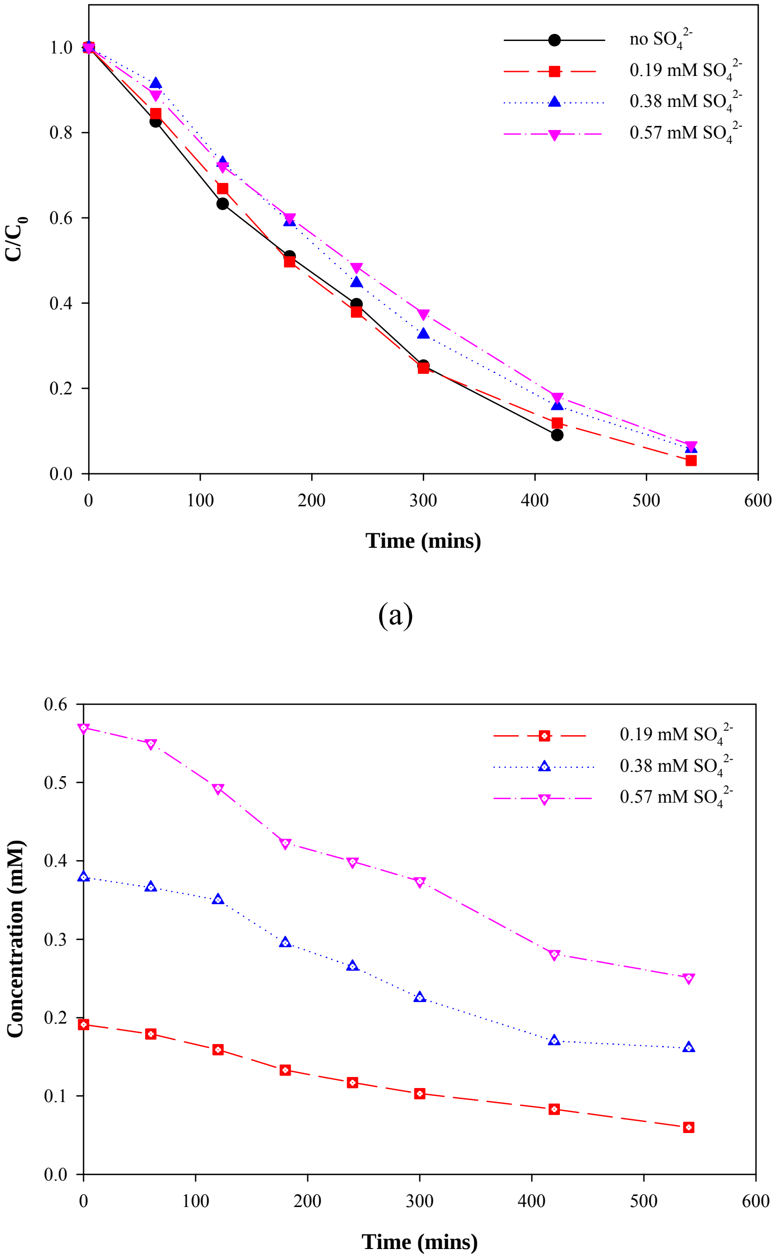


FIGURE 5.7. XPS analysis of the precipitate produced from the mixture of 1 mM perchlorate and 10 mM nitrate with current of 250 mA.

5.3.2 Influence of Sulfate and Phosphate on Perchlorate Reduction

The influences of sulfate and phosphate (0.2 to 0.6 mM) on perchlorate reduction during pitting corrosion of Ti(0) were examined. Experiments were conducted with a 1-mM solution of perchlorate and imposed currents of 100 mA and 60 mA. Experiments were carried out with concentrations of sulfate and phosphate greater than 1 mM, but Ti(0) was rapidly passivated and no pitting was observed. Furthermore, a constant current could not be maintained but dropped rapidly. One noticeable difference in these experiments was that solutions that contained sulfate and phosphate showed different pitting behaviors than those with only perchlorate. In the solutions with only perchlorate, solid precipitates were released from the pitting site and deposited at the bottom of the reactor. However, in the solutions with sulfate, a white plume was released from the pitting site and dissipated in the solution causing it to turn into a milky color after several hours. In the phosphate solution, amorphous precipitates were released from the pitting site. These precipitates aggregated and formed shapes like fluffy cotton balls. These aggregates of precipitates covered the Ti(0) surface, especially at the pitting site, and they grew in size over time. As presented in Figure 5.8a, the removal of perchlorate is only slightly affected by increasing sulfate concentrations. There is a slightly greater lag time in perchlorate removal at higher sulfate concentrations, which indicates that the induction time for stable pitting development is slightly increased at higher sulfate concentrations. Figure 5.8b shows that the sulfate concentrations also decrease over time. However, if data only from the period after the induction time (about 60 min for 0.38 and 0.57 mM SO_4^{2-}) is considered, sulfate does not inhibit the rate of perchlorate removal and this figure is presented in Appendix A. For phosphate, the rates of perchlorate removal are not affected by increasing phosphate concentration and the phosphate concentrations decrease over time, as shown in Figure 5.9.

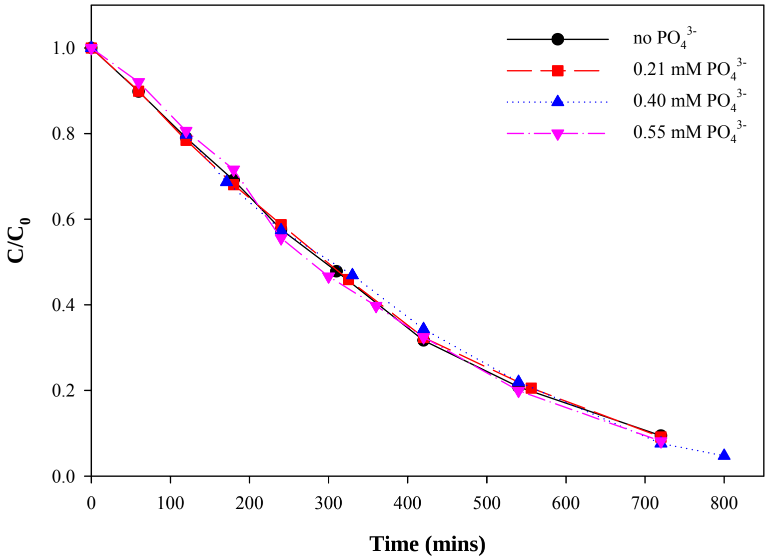
The decrease of the sulfate and phosphate concentrations could not be caused by chemical reduction of sulfate and phosphate. Theoretically, it is thermodynamically possible for sulfate and phosphate to be chemically reduced to compounds with lower oxidation states. However, in practice, it is hard to chemically reduce sulfate and phosphate in aqueous solutions under ambient conditions (*52*). It has been reported that sulfate and phosphate are incorporated into surface oxide films and that they can penetrate inside of them (*93, 155, 156*) in a way that is like nitrate. In order to examine the behavior of sulfate and phosphate with titanium compounds, precipitates were generated in experiments conducted by imposing 250 mA current onto solutions of 10 mM perchlorate and 5 mM sulfate or phosphate. The dried precipitates showed different colors. The precipitate produced in solutions that contained phosphate were white, but the precipitate produced in solutions that contained sulfate were gray. However, XRD analysis of both precipitates detected only titanium dioxide (anatase and brookite) and not any S- and P-containing titanium compounds, as presented in Figure 5.10. However, if S- and P-containing titanium compounds are present in amorphous or poorly crystalline structures, it would be hard to detect them using XRD analysis. Thus, further analyses using XPS were conducted to identify the presence of S and P-containing titanium compounds in the precipitate. Figure 5.11 shows that 1.3 % of atomic concentration of sulfur and 2.3 % of phosphorous are found in the precipitate. Therefore, concentration decreases of sulfate and phosphate during the pitting corrosion of Ti(0) would be caused by the S and P-containing titanium compounds in the precipitate or adsorption of these anions on the precipitate.



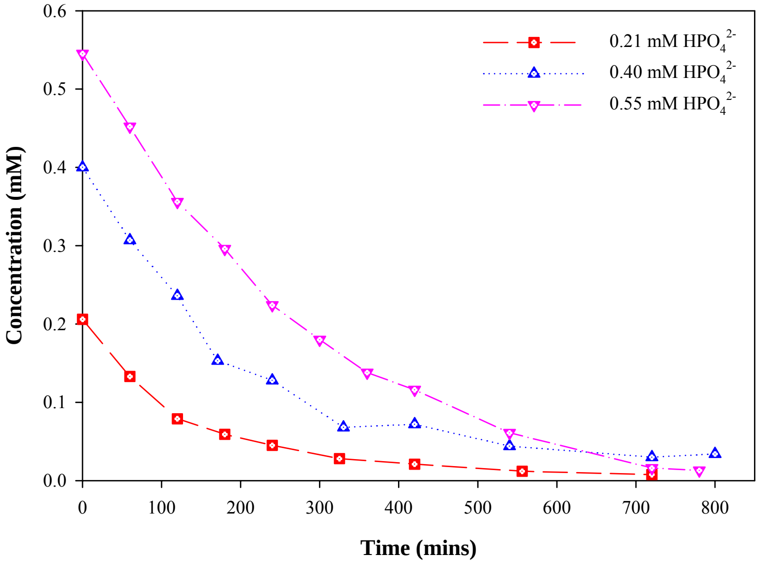
(a)

(b)

FIGURE 5.8 (a) Influence of sulfate ion on perchlorate reduction and (b) sulfate concentration changes. Current was 100 mA. Perchlorate concentration was 1.02 ± 0.01 mM.

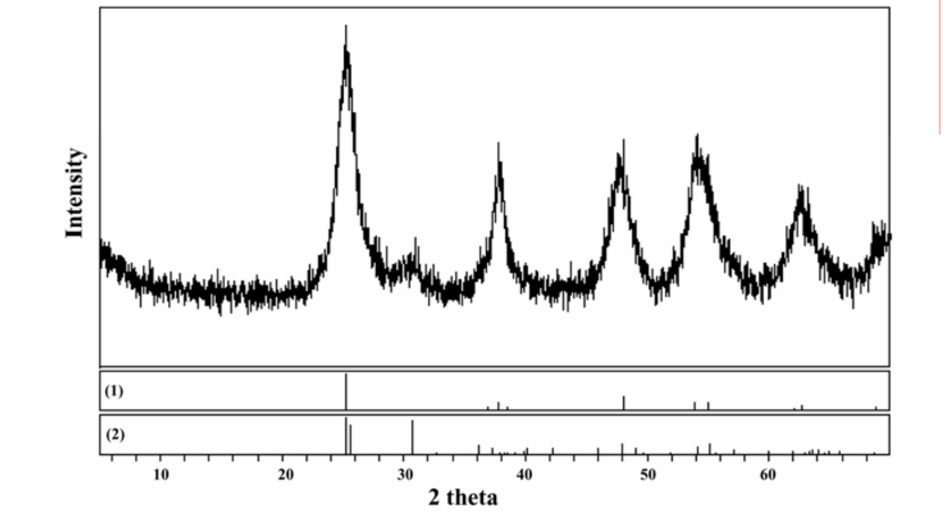


(a)

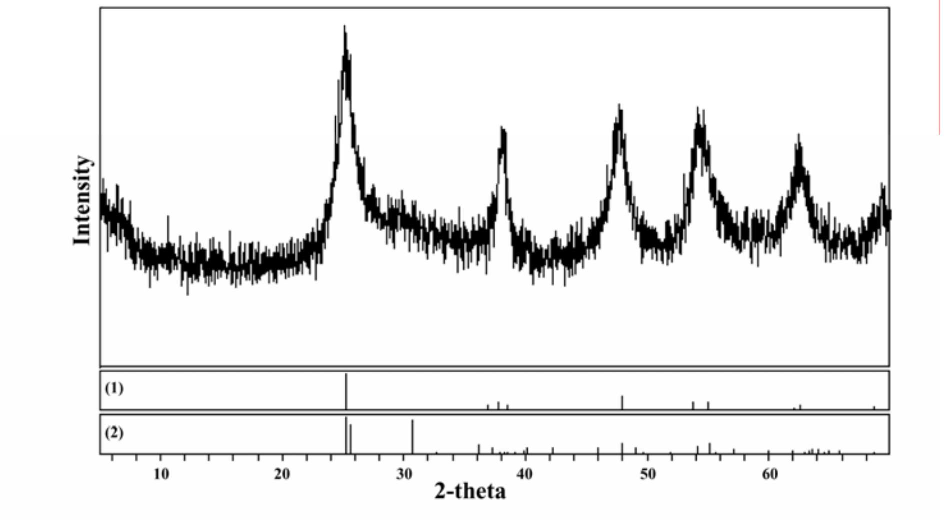


(b)

FIGURE 5.9 (a) Influence of phosphate ion on perchlorate reduction and (b) phosphate concentration changes. Current was 60 mA. Perchlorate concentration was 1.02 ± 0.00 mM.

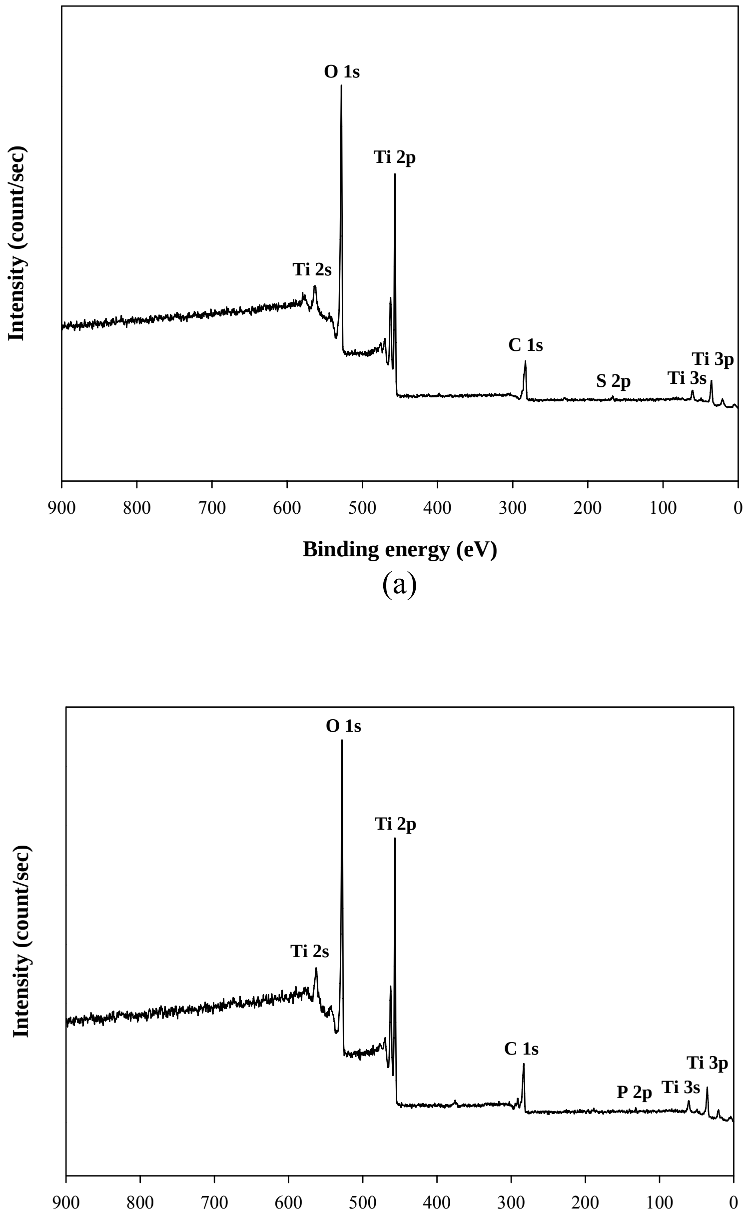


(a)



(b)

FIGURE 5.10. XRD results of the precipitate produced from the mixture of 10 mM of perchlorate and 5 mM sulfate or 5 mM phosphate solution with current of 250 mA: (a) sulfate, (b) phosphate ((1) synthetic anatase, (2) brookite)).



(a)

(b)

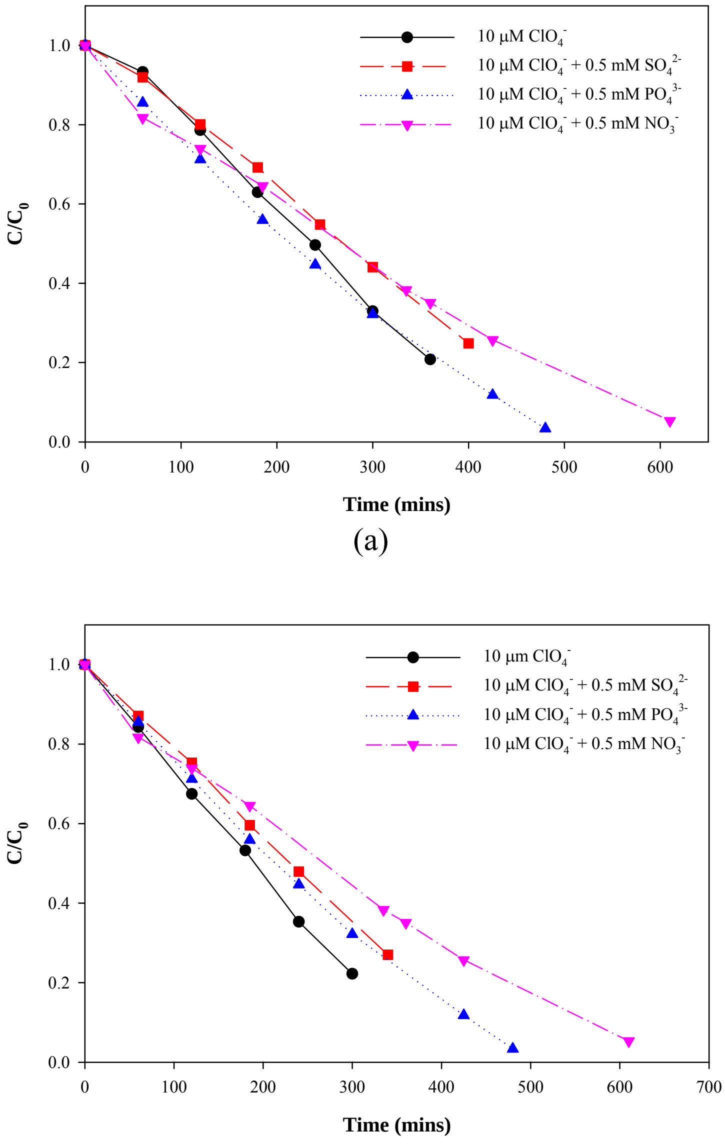
FIGURE 5.11. XPS results of the precipitate produced from the mixture of 10 mM of perchlorate and 5 mM sulfate or 5 mM phosphate solution with current of 250 mA: (a) sulfate, (b) phosphate.

5.3.3 Influence of Anions on the Trace Levels of Perchlorate Reduction

Figure 5.12a presents the influence of nitrate, sulfate and phosphate on the removal of trace levels of perchlorate. Initial concentrations of perchlorate were 10 μM; chloride concentration was 1 mM; and anion concentrations were 0.5 mM. Perchlorate removal shows similar behavior to that observed at higher concentrations. However, if only data taken after the induction time (60 min for ClO_4^- only and with SO_4^{2-}) is considered, sulfate and phosphate only slightly inhibit the rate of perchlorate reduction. This effect is less than that of nitrate as shown in Figure 5.12b.

5.3.4 Mechanism of Perchlorate Reduction Inhibition

The presence of nitrate, sulfate or phosphate slightly inhibits or does not inhibit the rate of perchlorate reduction. However, the presence of chloride slowed the rate of perchlorate reduction as shown in Figure 3.7 in Chapter III. In general, nitrate, sulfate and phosphate inhibit metal corrosion, which is the reason they have been used as corrosion inhibitors (*59, 60, 62*). However, chloride is an aggressive anion that promotes corrosion of metals. Thus, it is possible that the ability of nitrate, sulfate and phosphate to inhibit corrosion could explain their weak effects on the rate of perchlorate reduction. In order to investigate this possibility, the influences of halide ions, including fluoride, chloride, bromide, and iodide on perchlorate reduction of were examined. However, there is one thing needed to be mentioned. Generally, the aggressive anion is halide anions such as fluoride, chloride, bromide, and iodide and halid containing anions such as perchlorate, which promote metal corrosion (*62*). However, Ti(0) shows a different behavior with other metals.



(a)

(b)

FIGURE 5.12 (a) Influence of non-aggressive anions on reduction of trace levels of perchlorate and (b) some data shifted in time (Data for perchlorate only and with sulfate shifted 60 min and data at lower times eliminated). Initial chloride concentration was 1.00 ± 0.02 mM, initial perchlorate concentration was 10 ± 0.01 µM, and current was 90 mA.

For Ti(0), fluoride is not an aggressive anion that promotes pitting corrosion. Pitting potentials or surface oxide film breakdown potentials that have been measured previously or in this study are presented in Table 5.1. The pitting or oxide film breakdown potentials of sulfate, phosphate, and fluoride are much higher and nitrate is slight higher than perchlorate, and in the order: $SO_4^{2-} > F^- > PO_4^{3-} > NO_3^- \geq ClO_4^-$. However, chloride, bromide, and iodide have lower or similar pitting potentials than does perchlorate and in the order: $ClO_4^- > Cl^- > I^- > Br^-$. Based on these potential values, sulfate, phosphate, fluoride, and nitrate inhibit pitting corrosion, and chloride, bromide, and iodide promote pitting corrosion, if pitting corrosion is induced by perchlorate on Ti(0). Figure 5.13 shows that iodide and fluoride have negligible effects on the rate of perchlorate reduction, but chloride and bromide greatly inhibit it. One consistent behavior is found that anions (sulfate, phosphate, nitrate and fluoride) that possibly inhibit the pitting corrosion of Ti(0) do not inhibit perchlorate reduction. Therefore, it is possible that inhibition of perchlorate reduction is caused by whether the anion inhibits or promotes pitting corrosion of Ti(0) induced by perchlorate. However, it is needed to explain a reason why iodide that promotes pitting corrosion of Ti(0) less inhibit perchlorate reduction than those of chloride and bromide.

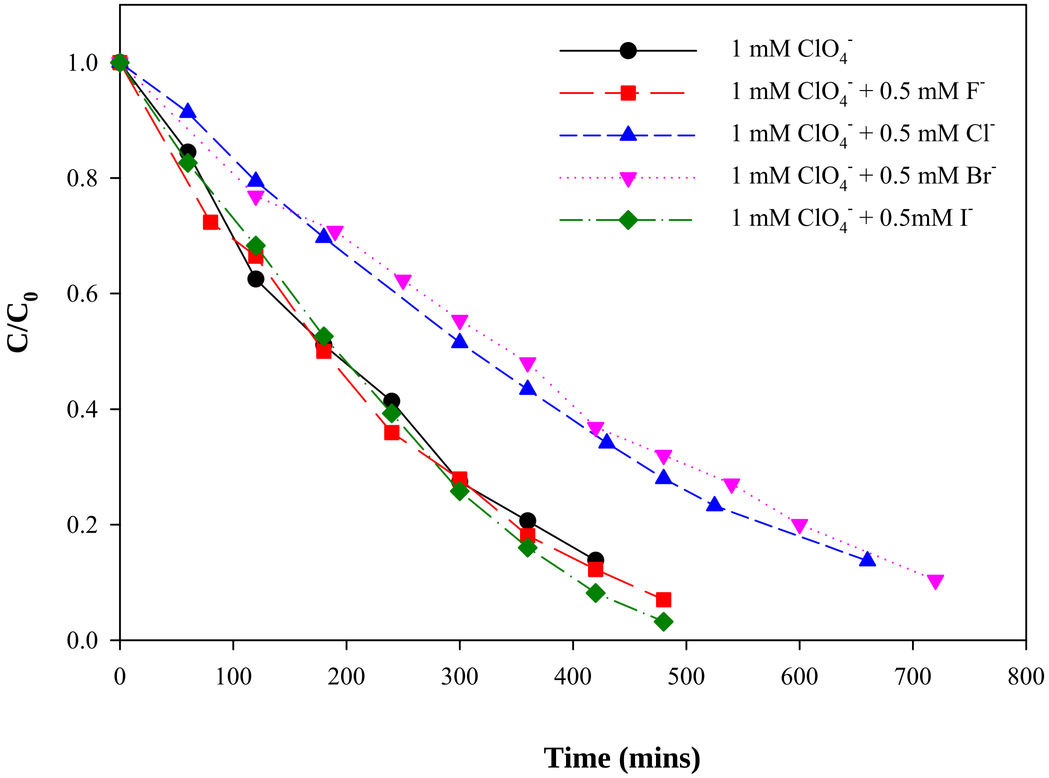


FIGURE 5.13 Influence of halide ions on perchlorate reduction. Initial perchlorate concentration was 1.00 ± 0.01 mM and current was 90 mA.

TABLE 5.1 Pitting or oxide film breakdown potentials for titanium in different solutions.

	Concentration (M)	Potential (V (NaSCE))	Reference
F^-	1	$90.9^{(1)}$	(*70*)
SO_4^{2-}	1	$92.8^{(1)}$	(*70*)
PO_4^{3-}	unknown	$55.0^{(1)(2)}$	(*155*)
NO_3^-	0.1	13.55	This study
ClO_4^-	0.1	12.53	This study
Cl^-	1	12.89	(*70*)
	1	9.35	(*67*)
	0.1	11.79	(*70*)
	0.1	9.44	(*67*)
Br^-	1	1.01	(*70*)
	0.1	1.44	(*67*)
I^-	1	2.52	(*70*)
	0.1	7.54	(*67*)

(1) represents surface oxide film breakdown potential
(2) is voltage across the anode and cathode, and others are the potential of the anode with respect to NaSCE.

Perchlorate is believed to be reduced by dissolved Ti(II) near the pitting site on the Ti(0) surface. In Chapter IV, it was proposed that dissolved Ti(II) is produced by stimulation of adsorption of aggressive anions on bare Ti(0) and Ti(0) is dissolved to

Ti(II) by two possible pathways: 1) Ti(0) is dissolved to Ti(II) by indirect participation of aggressive anions without forming complex with aggressive anion and 2) Ti(0) is dissolved to Ti(II) by direct participation of aggressive anions forming Ti(II) and anion complex such as such as $Ti(ClO_4)OH$ and TiClOH. Based on these proposed dissolution mechanisms of Ti(0) to Ti(II), two possible inhibition mechanisms of perchlorate reduction can be developed with either the consumption of Ti(II) or inhibition of the production of Ti(II). The inhibition of perchlorate reduction by consumption of dissolved Ti(II) is developed based on Ti(0) dissolution to Ti(II) model without formation of anion complexes. Chloride and bromide greatly inhibit the rate of perchlorate reduction. In Chapter III, experiments were described that showed that chloride was oxidized to chlorine during pitting corrosion. Also, oxidation of bromide to bromine during pitting site has been reported (*58*). It is thermodynamically possible for chlorine and bromine to oxidize Ti(II) to Ti(IV). In Chapter IV, it was reported that the dissolution valence of Ti(0) in chloride solution was observed to be +4. It was hypothesized that Ti(0) undergoes dissolution to Ti(II) and subsequent electrochemical oxidation of Ti(II) to Ti(IV) on Ti(0) surface or possibly on salt film, and these oxidations result in dissolution valence +4 in chloride solution. However, the other explanation was also proposed based on possible chlorine formation. If one mole of Ti(0) is oxidized to Ti(II) it will transfer 2 modes of electrons to the electrode. If the Ti(II) is oxidized by chlorine to Ti(IV), then there needs to be one mole of chlorine which would be produced by oxidation of 2 moles of chloride by transferring two moles of electrons to the electrode. The net electron transfer for loss of one mole of Ti(0) is 4 moles (2 moles form production of Ti(II) and 2 moles from production of chlorine) and dissolution valence results in +4. This supports possible oxidation of Ti(II) by chlorine or bromine. However, there is also a study that reported electrochemical oxidation of iodide to iodine (I_2) on Ti(0) during the pitting corrosion (*85, 86*). Thus, it is possible for iodine produced by electrochemical oxidation to oxidize Ti(II) to Ti(IV). However, Figure 5.13 shows that iodide did not inhibit perchlorate reduction, which indicates that consumption of Ti(II) by oxidized halide products (chlorine and bromide) might not be a right explanation for describing inhibition of perchlorate reduction by chloride and bromide. However, thermodynamically, iodide is less reactive than chlorine and bromine. Therefore, it is possible that higher reactivity of chlorine and bromine oxidize Ti(II) and cause inhibition of perchlorate reduction, but less reactive iodide oxidizes less Ti(II) and produces less inhibition of perchlorate reduction than those of chlorine and bromine.

The other possible inhibition mechanism is inhibition of the production of Ti(II) and perchlorate complex. This is developed based on Ti(0) dissolution to Ti(II) model by direct participation of aggressive anion forming complex Ti(II) with anion. It was proposed that Ti(0) dissolution is stimulated by adsorption of aggressive anions on bare Ti(0) surface after pitting initiation and Ti(0) is dissolved to Ti(II) by forming a complex with adsorbed aggressive anions. For example, the adsorption of perchlorate on bare Ti(0) accelerates Ti(0) dissolution to Ti(II) and the adsorbed perchlorate on Ti(0) is desorbed by forming complex with Ti(II) during dissolution of Ti(0) to Ti(II). Furthermore, perchlorate that stimulates Ti(0) dissolution to Ti(II) and forming complex is believed to be only involved reaction with Ti(II) and reduced to chloride. Other aggressive anions such as chloride and bromide, also promote Ti(0) dissolution to Ti(II) by forming complex as TiClOH and TiBrOH. However, these Ti(II) would not involve in perchlorate reduction and would be electrochemically oxidized to Ti(IV). Therefore, it is possible that inhibition of perchlorate reduction might be caused by competitive adsorption of the aggressive anions that stimulates Ti(0) dissolution to Ti(II) and desorbed by forming complex with Ti(II) on bare Ti(0) with the aggressive anions.

The affinities of anions to adsorb on bare Ti(0) were investigated using data in the literature. No studies of anion adsorptions to bare Ti(0) have been reported; however, there are reports in the literature on adsorption of anions to the surface oxide film covered Ti(0). Radiotracer studies of anion adsorption to the surface oxide film of Ti(0) showed that adsorption binding strength increased in the order $PO_4^{3-} > SO_4^{2-} > Cl^- > ClO_4^-$ (*138*). Basame and White (*67*) investigated the influence of anion concentration on pitting potential of titanium and estimated the adsorption binding strength on the surface oxide film in the order $Br^- > Cl^- >> I^-$. Another study showed that adsorption tendency increased in the order: $F^- >> Cl^- > I^-$ (*62*). No study compared the tendencies of nitrate and perchlorate to adsorb onto the oxide film covering the surface of Ti(0). However, one study reported that the adsorption binding strengths for nitrate on rutile are in the order: $Cl^- \approx ClO_4^- \approx NO_3^- > I^-$ (*137*). Adsorption tendencies compared to perchlorate are compared and summaries are presented in Table 5.2. Table 5,2 shows that chloride and bromide have higher adsorption tendency. However, iodide that promotes pitting corrosion of Ti(0) has lower adsorption tendency or possibly much less (*67*) than those of chloride and bromide. Therefore, it would be possible that inhibition of perchlorate reduction is caused by both whether anion inhibit or promote pitting corrosion of Ti(0) and adsorption tendencies of aggressive anions that promotes pitting corrosion of Ti(0).

TABLE 5.2 Summaries adsorption tendencies of anions compared to those of perchlorate.

Higher adsorption than perchlorate or similar to perchlorate	Lower adsorption than perchlorate
SO_4^{2-}, F^-, PO_4^{3-}, NO_3^-, Br^-, Cl^-	I^-

5.4 Conclusions

This Chapter examines the effects of non-aggressive anions (nitrate, sulfate, and phosphate) and aggressive anions (chloride, bromide, iodide, fluoride) on the rate of perchlorate reduction during pitting corrosion of Ti(0). These anions are commonly found in groundwater and surface water. It has been shown that the rate of perchlorate reduction was not substantially affected by the presence of nitrate, sulfate, and phosphate. These anions interacted with pitting corrosion and their concentrations decreased over time. Nitrate was chemically reduced to nitrite and ammonium and possibly to gaseous compounds such as nitrogen, nitric oxide and nitrous oxide. Both sulfate and phosphate concentrations decreased during pitting. However, their concentration decreases were not related to chemical reduction nor to formation of titanium compounds that contained sulfur or phosphorous, but they were caused by adsorption onto precipitates formed during the reaction. The mechanism by which some anions inhibit perchlorate reduction was investigated based on the proposed dissolution mechanisms of Ti(0) to Ti(II). The dissolution mechanism of Ti(0) to Ti(II) without forming complex with aggressive anion suggested that inhibition mechanism of perchlorate reduction would be caused by oxidation of dissolved Ti(II) by electrochemically generated chlorine and bromine. However, the dissolution mechanism of Ti(0) to Ti(II) with forming complex with aggressive anions proposed that inhibition of perchlorate reduction would be caused by both whether anion inhibit or promote pitting corrosion of Ti(0) developed by perchlorate and adsorption tendencies of aggressive anions that promotes pitting corrosion of Ti(0).

CHAPTER VI

KINETIC MODELS DESCRIBING RATE OF PERCHLORATE REDUCTION DURING PITTING CORROSION OF TI(0)

6.1 Introduction

Perchlorate (ClO_4^-) is a thermodynamically strong oxidizing agent (*26*)

$$ClO_4^- + 8H^+ + 8e^- = Cl^- + 4H_2O \qquad E_h^0 = 1.278 \text{ V (SHE)} \qquad (6.1)$$

Thus, its salts have been widely used in rocket propellants, pyrotechnics and munitions (*2*). However, once perchlorate is dissolved in the aqueous phase, it is kinetically inert. Kinetic studies using transition metal ions and other chemical reductants have reported that several to over thousands of days are required to complete one-half of the reactions at 1 mM of reductant concentrations (*27*). Perchlorate is also poorly reduced by direct electrochemical reduction at noble electrodes (*78-80*). These poor reactivities of perchlorate in chemical and electrochemical reactions are caused by its high activation energy and by competition with other anions for active sites on the electrode surface. However, there have been a few studies that have reported reduction of perchlorate at reasonable rates. Perchlorate reduction with Methylrhenium dioxide (CH_3ReO_2) showed that one mole of Methylrhenium dioxide reduces one mole of perchlorate to chlorate with a second-order rate constant of 7.3 L mol^{-1} s^{-1} at pH 0 and 25 ˚C (*28*). This rate constant corresponds to a half-life of only 2.3 min at a 1 mM initial concentration of Methylrhenium dioxide. The Methylrhenium dioxide showed the capability to abstract an oxygen atom from perchlorate and stabilize the transferred oxygen atom by transforming itself into Methylrhenium trioxide (CH_3ReO_3). This agrees with the requirements suggested by Taube for chemical reductants to effectively reduce perchlorate (*82*).

Other successful studies on perchlorate reduction used an iron salt or zero-valent iron under extreme conditions. Perchlorate in mixtures of ferric chloride and hydrochloric acid produced by regeneration of selective ion exchange resins loaded with perchlorate was reduced with ferrous ion under high temperature and pressure (*30*). The rate of perchlorate reduction by ferrous ion was dependent on temperature, with the half-live being approximately 8.0 min at 195 ˚C, However, when the temperature dropped to 110 ˚C, the half-live was extended to 139 hrs. Perchlorate reduction using zero-valent iron was very slow (*29, 76*) under ambient temperature (*29*). The half-life of perchlorate with acid-washed zero-valent iron was 325 days using a surface area concentration of 50 m^2/L at room temperature, but it increased to 15 hrs at 200 ˚C.

Previous chapters demonstrated the effects of several environmental and electrochemical factors on perchlorate reduction during pitting corrosion of Ti(0). Factors considered included solution pH, chloride presence, surface area of Ti(0), potential and current. Also, based on these experimental observations, mechanisms were proposed to describe perchlorate reduction during pitting corrosion of Ti(0) that could explain the influences of other anions on the process. In Chapter V, two possible inhibition mechanisms were suggested: 1) competitive adsorption of aggressive anions on bare Ti(0) surface and 2) Ti(II) consumption by produced chlorine. Thus, two different kinetic models are proposed to predict the rate of perchlorate reduction and how it is affected by environmental and electrochemical factors.

6.2 Materials and Methods

6.2.1 Chemicals

Sodium perchlorate (98.0 +%, Aldrich) and sodium chloride (99.0 %, EM) were used in this study as a source of perchlorate and chloride. Ti(0) sheets (99.97 %, ESPI) were purchased from ESPI Corp Inc and cut to appropriate sizes for the experiments. The Ti(0) sheets were washed with acetone to remove organic impurities and rinsed several times with deionized water, then dried at room temperature and stored in an air-tight desiccator until the experiment.

6.2.2 Batch Experiments

Electrochemical experiments were carried out in a lab-scale electrochemical cell that had an effective volume of 800 mL and contained two electrodes (anode and cathode). Both the anode and cathode were prepared from Ti(0) sheets (99.97 %) and constant current was supplied by a DC power supply (Kenwood, Model PW18-1.8AQ). The electrochemical potential was not monitored during the experiments, but preliminary experiments were conducted to ensure that it would be above the pitting potential under all experimental conditions. The dimensions of the anode were 0.05 cm × 2.5 cm × 7.25 cm and the dimensions of the cathode were 0.05 cm × 5.0 cm × 7.25 cm. The cell was gently mixed (60 rpm) by a magnetic stir bar (2.5 cm long x 8 cm diameter, VWR) to reduce the accumulation of solid titanium oxide or hydroxide on the anode surface. A 6-mL sample was taken at each time interval and filtered by 0.22-µm nylon membrane filters (Magna). The samples were kept in a 0 ˚C refrigerator without any treatment until analysis and most samples were analyzed within two weeks.

6.2.3 Analytical Methods

Concentration of perchlorate was analyzed using a Dionex 500 ion chromatograph equipped with a 4-mm Dionex AS–16 analytical and guard column. Chloride was analyzed using a Dionex DX-80 ion chromatograph equipped with a 4-mm Dionex AS-14 analytical and guard column, and DS-5 detection stabilizer.

6.2.3 Computational Methods

All computations, including linear and nonlinear regressions and solving ordinary differential equations, were conducted with Matlab 7.0 (Math Works Inc.). Linear and nonlinear regression results with Matlab 7.0 were compared to the results from SigmaPlot 8.0 (SPSS Inc) using regression tools to check their validity. Matlab coded computer programs are listed in Appendix B.

6.3 Results and Discussion

6.3.1 General Descriptions

Figure 6.1 shows a schematic diagram of perchlorate reduction at the site of pitting corrosion of Ti(0). The Ti(0) surface usually is coved by an oxide film (mainly TiO_2) that protects the underlying bare Ti(0) from being oxidized. However, pitting corrosion induces a localized breakdown of the surface oxide film and promotes oxidative dissolution of Ti(0). The location where this occurs will be called the pit. Perchlorate is transported from solution to the pit where it is believed to be reduced by dissolved Ti(II) that was produced electrochemically. Thus, kinetics of perchlorate reduction during pitting corrosion of Ti(0) in a batch system is described by the interactions between two domains (pit and solution). The following assumptions are made regarding those interactions: 1) there is no generation of perchlorate anywhere in the system, 2) perchlorate reduction occurs only in the pit, and 3) pit volume is much less than solution volume and remains constant over time.

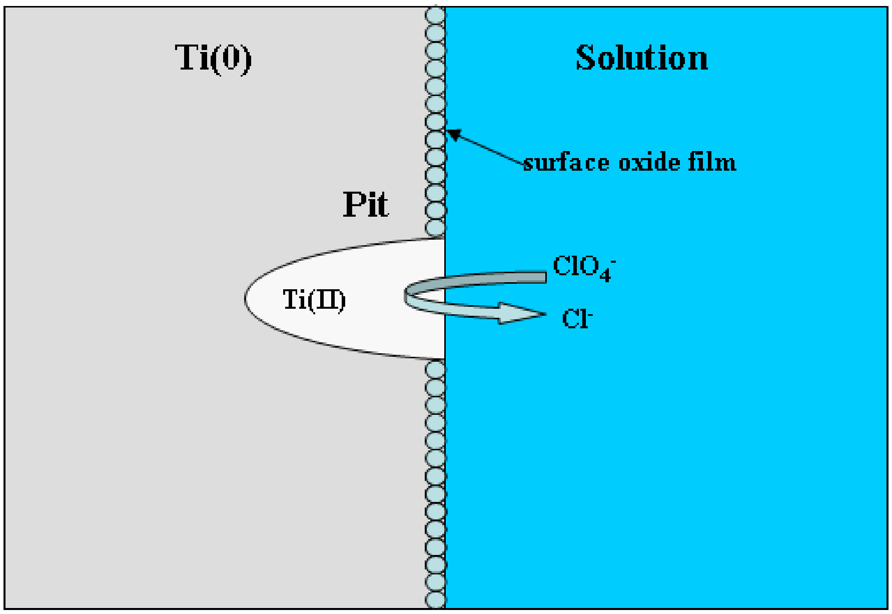


FIGURE 6.1 Schematic diagram of perchlorate reduction during pitting corrosion of Ti(0).

6.3.2 Ti(II) Consumption Kinetic Model

A kinetic model is developed based on the assumption that inhibition of perchlorate reduction is caused by the consumption of dissolved Ti(II) by electrochemically produced chlorine. Figure 6.2 describes reactions that would be developed in the pit when Ti(II) is consumed by electrochemically produced chlorine.

Perchlorate reduction is believed to be caused by dissolved Ti(II) in the pit. However, electrochemical oxidation of chloride to chlorine would also occur in the pit as presented in Chapter III. Chlorine produced in the pit would consume dissolved Ti(II) and be reduced to chloride, which can continue to cycle through the same reactions.

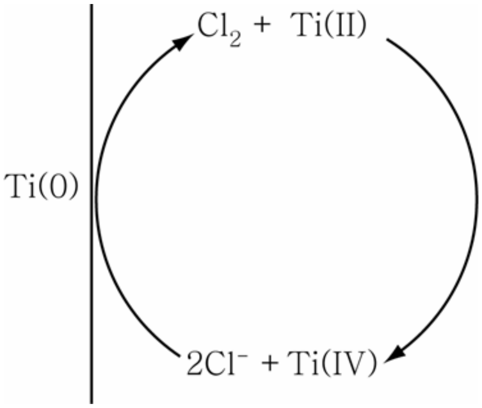


FIGURE 6.2. Mechanisms of Ti(II) consumption by chlorine in the pit.

Several studies reported that Ti(II) reduces oxidized compound obeying a second-order rate law (*54, 57, 157*). In this study, perchlorate is believed to be reduced by dissolved Ti(II), which is produced by pitting corrosion of Ti(0). Thus, the rate of perchlorate reduction within the pit is described with second-order kinetics as:

$$\gamma_{\mathrm{p,\,loss}} = k[\mathrm{Ti(II)}]_{\mathrm{p}}[\mathrm{ClO_4^-}]_{\mathrm{p}} \tag{6.2}$$

where k represents the second-order rate constant and $[\mathrm{Ti(II)}]_{\mathrm{p}}$ is Ti(II) concentration within the pit. A material balance on perchlorate in the pit is:

$$\mathrm{V_p}\frac{d[\mathrm{ClO_4^-}]_\mathrm{p}}{d\mathrm{t}} = \mathrm{M_{s\rightarrow p,ClO4}} - \mathrm{M_{p\rightarrow s,ClO4}} + \mathrm{V_p}\gamma_{\mathrm{p,\,prod}} - \mathrm{V_p}\gamma_{\mathrm{p,\,loss}} \qquad (6.3)$$

where $\mathrm{M_{s\rightarrow p,ClO4}}$ is the perchlorate mass flux from solution to the pit, $\mathrm{M_{p\rightarrow s,ClO4}}$ is the perchlorate mass flux from the pit to solution, $\mathrm{V_p}$ is volume of the pit, and $\gamma_{\mathrm{p,prod}}$ and $\gamma_{\mathrm{p,loss}}$ are rates of perchlorate production and loss. Since perchlorate is not produced in the pit ($\gamma_{\mathrm{p,prod}} = 0$), and eq 6.3 is rewritten to

$$\mathrm{V_p}\frac{d[\mathrm{ClO_4^-}]_\mathrm{p}}{d\mathrm{t}} = \mathrm{M_{s\rightarrow p,ClO4}} - \mathrm{M_{p\rightarrow s,ClO4}} - \mathrm{V_p}\gamma_{\mathrm{p,\,loss}} \qquad (6.4)$$

Perchlorate concentration changes in the pit can be described by substituting eq 6.2 into eq 6.4.

$$\mathrm{V_p}\frac{d[\mathrm{ClO_4^-}]_\mathrm{p}}{d\mathrm{t}} = \mathrm{M_{s\rightarrow p,ClO4}} - \mathrm{M_{p\rightarrow s,ClO4}} - \mathrm{V_p}k[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} \qquad (6.5)$$

The material balance on perchlorate in the solution is:

$$\mathrm{V_s}\frac{d[\mathrm{ClO_4^-}]_\mathrm{s}}{d\mathrm{t}} = \mathrm{M_{p\rightarrow s,ClO4}} - \mathrm{M_{s\rightarrow p,ClO4}} + \mathrm{V_s}\gamma_{\mathrm{s,\,prod}} - \mathrm{V_s}\gamma_{\mathrm{s,\,loss}} \qquad (6.6)$$

where $\mathrm{V_s}$ is solution volume (0.8 L), and $\gamma_{\mathrm{s,\,prod}}$ and $\gamma_{\mathrm{s,\,loss}}$ are rates of perchlorate production and loss. Since there is no perchlorate production ($\gamma_{\mathrm{s,\,prod}} = 0$) or loss ($\gamma_{\mathrm{s,\,loss}} = 0$) in the solution, eq 6.6 is simplified to:

$$\mathrm{V_s}\frac{d[\mathrm{ClO_4^-}]_\mathrm{s}}{d\mathrm{t}} = \mathrm{M_{p\rightarrow s,ClO4}} - \mathrm{M_{s\rightarrow p,ClO4}} \qquad (6.7)$$

Summation of eqs 6.4 and 6.7 yields a material balance of perchlorate for overall system.

$$\mathrm{V_s}\frac{d[\mathrm{ClO_4^-}]_\mathrm{s}}{d\mathrm{t}} + \mathrm{V_p}\frac{d[\mathrm{ClO_4^-}]_\mathrm{p}}{d\mathrm{t}} = -\mathrm{V_p}\gamma_{\mathrm{p,\,loss}} \qquad (6.8)$$

Eq 6.8 is further simplified by applying the assumption that solution volume is much larger than pore volume (Vs >> Vp).

$$\frac{d[\mathrm{ClO_4^-}]_\mathrm{s}}{d\mathrm{t}} = -\frac{\mathrm{V_p}}{\mathrm{V_s}}\gamma_{\mathrm{p,\,loss}} \tag{6.9}$$

Perchlorate concentration changes in the solution can be described by substituting eq 6.2 into eq 6.9.

$$\frac{d[\mathrm{ClO_4^-}]_\mathrm{s}}{d\mathrm{t}} = -\frac{\mathrm{V_p}}{\mathrm{V_s}}k[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} \tag{6.10}$$

How Ti(II) concentration changes with time in the pit is given by the material balance on Ti(II).

$$\frac{d[\mathrm{Ti(II)}]_\mathrm{p}}{d\mathrm{t}} = \gamma_{\mathrm{p,\,prod,\,Ti(II)}} - \gamma_{\mathrm{p,\,loss,\,Ti(II)}} \tag{6.11}$$

where $\gamma_{\mathrm{p,prod,Ti(II)}}$ represents the rate of Ti(II) production in the pit and $\gamma_{\mathrm{p,loss,Ti(II)}}$ is the rate of Ti(II) loss in the pit. Ti(II) is produced by electrochemical dissolution of Ti(0) and the rate of Ti(II) production under conditions of constant current is defined as follows.

$$\gamma_{\mathrm{p,\,prod,\,Ti(II)}} = k_{\mathrm{prod,\,Ti(II)}} \tag{6.12}$$

Ti(II) loss can occur by either chemical or electrochemical oxidations, as discussed in previous chapters. Thus, the rate of Ti(II) loss is given by

$$\gamma_{\mathrm{p,\,loss,\,Ti(II)}} = \sum\nolimits_{\mathrm{Ox}} k_{\mathrm{Ox}}\,[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{Ox}]_\mathrm{p} + k_{\mathrm{elec,p}} \tag{6.13}$$

where k_{Ox} represents the rate constant of Ti(II) oxidation by an oxidizing agent, $[\mathrm{Ox}]_\mathrm{p}$ is individual oxidizing agent concentration, $\sum_{\mathrm{Ox}}k_{\mathrm{Ox}}[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{Ox}]_\mathrm{p}$ is sum of the rate of Ti(II) oxidation by individual oxidizing agents, and $k_{\mathrm{elec,p}}$ is the rate of electrochemical oxidation of Ti(II) in the pit. For simplification, it is assumed that Ti(II) is only consumed by perchlorate and chlorine.

$$\frac{d[\mathrm{Ti(II)}]_\mathrm{p}}{d\mathrm{t}} = k_{\mathrm{prod,Ti(II)}} - 4k[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{ClO}_4^-]_\mathrm{p} - k_{\mathrm{Cl2}}[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{Cl}_2]_\mathrm{p} \tag{6.14}$$

where k_{Cl2} is the second-order rate constant for Ti(II) oxidation by Cl_2 in the pit.

A material balance on chloride is developed with the same procedure used for perchlorate.

$$\frac{d[\mathrm{Cl}^-]_\mathrm{s}}{d\mathrm{t}} = -\frac{\mathrm{V_p}}{\mathrm{V_s}}(\gamma_{\mathrm{p,\,loss,Cl}} + \gamma_{\mathrm{p,prod,Cl}}) \tag{6.15}$$

where $\gamma_{\mathrm{p,loss,Cl}}$ is the rate of Cl^- loss and $\gamma_{\mathrm{p,prod,Cl}}$ represents the rate of Cl^- production in the pit. The Cl^- is electrochemically oxidized in the pit and it is assumed that the rate of chloride oxidation follows a first-order rate equation.

$$\gamma_{\mathrm{p,loss,Cl}} = k_{\mathrm{Cl}}[\mathrm{Cl}^-]_\mathrm{p} \tag{6.16}$$

where k_{Cl} is the first-order rate constant for chloride oxidation. The net rate of chloride production depends on reactions of Ti(II) with chlorine and perchlorate. Molar units are assumed and stoichiometry of 2 moles Cl/mole Ti(II) is applied to relate the rate of chloride production to the rate of Ti(II) reaction with perchlorate.

$$\gamma_{\mathrm{p,prod,Cl}} = k[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{ClO}_4^-]_\mathrm{p} + 2k_{\mathrm{Cl2}}[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{Cl}_2]_\mathrm{p} \tag{6.17}$$

Then, the material balance for chloride in the pit and solution become:

$$\frac{d[\mathrm{Cl}^-]_\mathrm{p}}{d\mathrm{t}} = \mathrm{M}_{\mathrm{s}\to\mathrm{p,Cl}} - \mathrm{M}_{\mathrm{p}\to\mathrm{s,Cl}} + 2k_{\mathrm{Cl2}}[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{Cl}_2]_\mathrm{p} + k[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{ClO}_4^-]_\mathrm{p} - k_{\mathrm{Cl}}[\mathrm{Cl}^-]_\mathrm{p} \tag{6.18}$$

$$\frac{d[\mathrm{Cl}^-]_\mathrm{s}}{d\mathrm{t}} = -\frac{\mathrm{V_p}}{\mathrm{V_s}}(2k_{\mathrm{Cl2}}[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{Cl}_2]_\mathrm{p} + k[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{ClO}_4^-]_\mathrm{p} - k_{\mathrm{Cl}}[\mathrm{Cl}^-]_\mathrm{p}) \tag{6.19}$$

where $M_{s\rightarrow p,Cl}$ is the chloride mass flux from solution to the pit, $M_{p\rightarrow s,Cl}$ is the chloride mass flux from the pit to solution. The material balance equation for chlorine in the pit becomes:

$$\frac{d[\mathrm{Cl_2}]_\mathrm{p}}{d\mathrm{t}} = k_\mathrm{Cl}[\mathrm{Cl^-}] - k_\mathrm{Cl2}[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{Cl_2}]_\mathrm{p} - k_\mathrm{trans,Cl2}[\mathrm{Cl_2}]_\mathrm{p} \tag{6.20}$$

where $k_{\mathrm{trans,Cl2}}$ is the mass transfer coefficient for Cl_2 from the pit to solution, and it is assumed that the concentration of chlorine in solution is zero ($[Cl_2]_s = 0$).

The set of equations (eqs 6.5, 6.10, 6.14, 6.18, 6.19 and 6.20) contain several unknown parameters. Thus, the following assumptions were made to simplify the equations: 1) mass transport of chloride and perchlorate between pit and solution was caused by concentration gradients and the transport coefficients were the same for both compounds.

$$M_{s\rightarrow p,ClO4} - M_{p\rightarrow s,ClO4} = k_{\mathrm{trans}}\,([\mathrm{ClO_4^-}]_s - [\mathrm{ClO_4^-}]_p) \tag{6.21}$$

$$M_{s\rightarrow p,Cl} - M_{p\rightarrow s,Cl} = k_{\mathrm{trans}}\,([\mathrm{Cl^-}]_s - [\mathrm{Cl^-}]_p) \tag{6.22}$$

Thus, eqs 6.5 and 6.18 are rewritten to

$$\frac{d[\mathrm{ClO_4^-}]_\mathrm{p}}{d\mathrm{t}} = k_\mathrm{trans}([\mathrm{ClO_4^-}]_\mathrm{s} - [\mathrm{ClO_4^-}]_\mathrm{p}) - k[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} \tag{6.23}$$

$$\frac{d[\mathrm{Cl^-}]_\mathrm{p}}{d\mathrm{t}} = k_\mathrm{trans}([\mathrm{Cl^-}]_\mathrm{s} - [\mathrm{Cl^-}]_\mathrm{p}) + 2k_\mathrm{Cl2}[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{Cl_2}]_\mathrm{p} + k[\mathrm{Ti(II)}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} - k_\mathrm{Cl}[\mathrm{Cl^-}] \tag{6.24}$$

2) single pit is assumed and the pit has a hemispherical shape and with a volume of 10^{-4} L that remains constant; and 3) chlorine exists only in the pit ($[Cl_2]_s = 0$) and its diffusion coefficient is 8.64×10^{-5} cm^2 min^{-1}. Thus, chlorine mass transport coefficient ($k_{\mathrm{trans,Cl2}}$) is 4.24×10^{-4} min^{-1} and estimated from

$$k_{\mathrm{trans,Cl2}} = \frac{\mathrm{D_{Cl2}}}{\mathrm{r_p}} \frac{\mathrm{A_p}}{\mathrm{V_p}} \tag{6.25}$$

where D_{Cl2} is diffusion coefficient of chlorine, A_p is surface area of pit, r_p is pit radius, and V_p is pit volume.

Parameters were estimated by nonlinear regression on perchlorate concentration using the Matlab function 'nlinfit' combined with the Matlab function 'ode23s'. It is believed that concentrations in the pit change much faster than those in solution, which results in slow execution when using 'ode45'. Therefore, the set of equations (eqs 6.10, 6.14, 6.19, 6.20, 6.23 and 6.24) was solved using the Matlab function 'ode23s', which is designed to be more efficient with stiff sets of differential equations such as found here. Since pitting is developed electrochemically, experimental data sets obtained with different constant currents at 1.0 mM of perchlorate were used. These data sets were the same ones used to calibrate the competitive adsorption model. Table 6.1 shows nonlinear regression results that were obtained by assuming different values of the mass transfer coefficient. Rate of Ti(II) production ($k_{\mathrm{prod,Ti(II)}}$) is not affected by changing the mass transfer coefficient. However, the rate constants for perchlorate reduction (k) and chloride oxidation (k_{Cl}) increased and rate constant for Ti(II) oxidation by chloride (k_{Cl2}) decreased with decreasing values of the mass transfer coefficient. More importantly, decreasing the value of the mass transfer coefficient increased uncertainties in calculated values of rate constants. Thus, nonlinear regressions and later model simulations were conducted at high mass transfer coefficient ($k_{\mathrm{trans}} = 5 \times 10^{4}\ \mathrm{min}^{-1}$). High mass transfer coefficient of chloride and perchlorate might be attributed by electroneutrality that maintains an electrically neutral charge and electromigration that causes ionic migration. Moreover, the electroneutrality was reported as an extremely powerful force that can adjust solution concentration instantaneously. Therefore, higher mass transfer of chloride and perchlorate would be a reasonable assumption. However, transport of chlorine is not affected by electroneutrality because chlorine is neutrally charged specie. Thus, chlorine mass transport coefficient ($k_{\mathrm{trans,Cl2}}$) is not changed to higher mass transfer coefficient.

Figure 6.3 shows influence of current at unit volume on the rate constants for chloride oxidation and Ti(II) production. Chloride is electrochemically oxidized to chloride and Ti(II) is produced by electrochemical dissolution of Ti(0). Thus, their rates are expected to increase with increasing current. The rate constant for Ti(II) production increases with increasing current per unit volume (I_v). The rate constant for chloride oxidation seems to increase with current, but high uncertainties occur when I_v is above 150 mA L^{-1}, which prevents making conclusion with confidence. However, chloride is electrochemically oxidized to chlorine and Faraday's law defines that rates of electrochemical reactions are directly proportional to the current they produce. If the current produced by any reactions remains a constant fraction of the total current, then measured rates would be proportional to current. Thus, linear regressions were conducted to determine relationships between rate constants and current per unit volume. Other rate constants were not affected by current and their values are summarized in Table 6.2. Generally, chlorine was reported as a strong oxidizing compound and perchlorate was a inert compound in aqueous phase toward chemical reudctant. However, rate constant of perchlorate reduction is 1.0 ± 0.5 × 10^5 $\text{mM}^{-1}\cdot\text{min}^{-1}$. Rate constant of Ti(II) oxidation by chlorine is 3000 times less than that of perchlorate reduction by Ti(II).

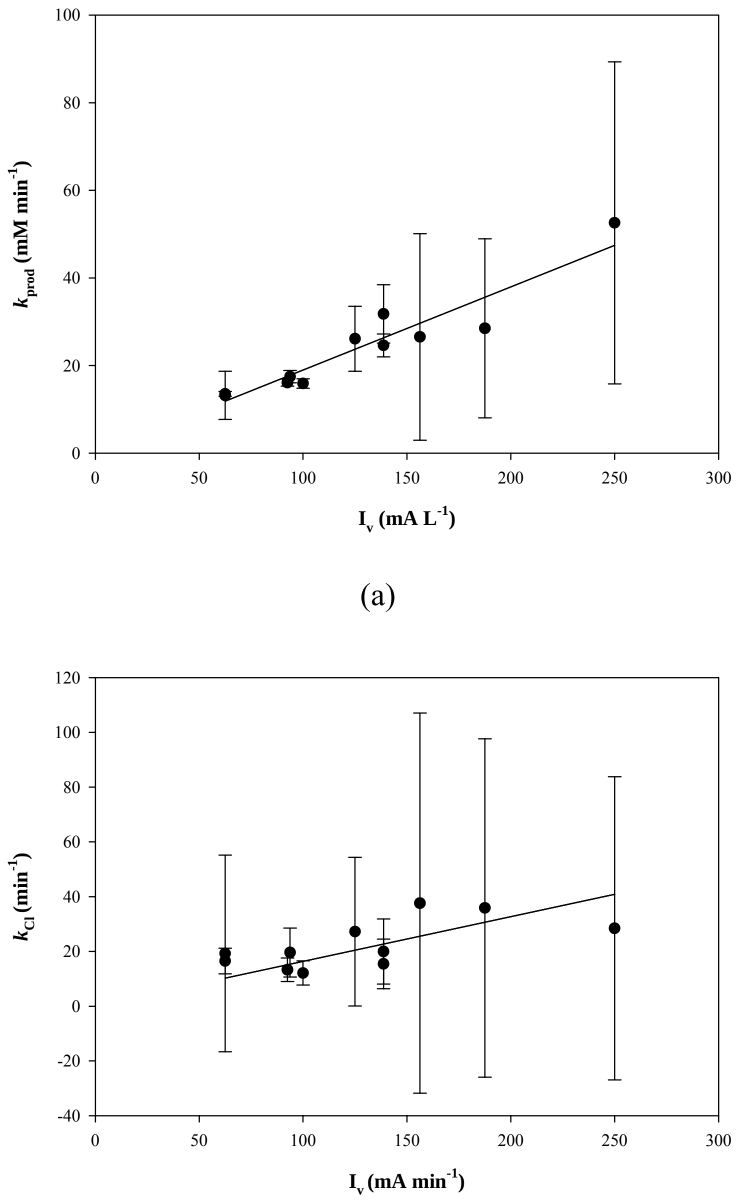
TABLE 6.1. Influence of mass transfer rate on uncertainties of estimated rate constants at current =75 mA.

k_{trans} (min^{-1})	k_{Cl} (min^{-1})	k_{Cl2} (mM^{-1} min^{-1})	k (mM^{-1} min^{-1})	$k_{\text{prod,Ti(II)}}$ (mM min^{-1})
1×10^5	18.5 (± 64.2 %)	20.4 (± 91.6 %)	8.0×10^4 (± 29.6 %)	17.4 (± 10.2 %)
1×10^4	19.4 (± 98.7 %)	21.5 (± 83.1 %)	8.5×10^4 (± 76.6%)	17.5 (± 5.4%)
1×10^3	21.17 (± 79.9 %)	18.6 (± 93.2 %)	8.8×10^4 (± 66.3 %)	17.44 (± 9.8 %)
1×10^2	25.0 (± 3819.5 %)	16.3 (± 9899.4 %)	1.5×10^5 (± 7267.9%)	17.6 (± 14.9 %)
5 × 10	13.3 (± 556.9 %)	12.2 (± 5750.8%)	1.5×10^5 (± 5687.5 %)	17.5 (± 14.5 %)

TABLE 6.2. Estimated rate constants for Ti(II) consumption kinetic model.

$k'_{\text{Cl}}{}^{*}$ (min^{-1} L mA^{-1})	$k'_{\text{prod,Ti(II)}}{}^{**}$ (mM L mA^{-1} min^{-1})	k ($\text{mM}^{-1}\cdot\text{min}^{-1}$)	k_{Cl2} (mM^{-1} min^{-1})
0.16·± 0.04	0.19 ± 0.02	1.0 ± 0.5 × 10^5	33.3 ± 14.4

* k_{Cl} (min^{-1}) = $k'_{\text{Cl}} \times I_v$; ** $k_{\text{prod,Ti(II)}}$ (mM min^{-1}) = $k'_{\text{prod,Ti(II)}} \times I_v$



(a)

(b)

FIGURE 6.3. Estimated rate constants for Ti(II) production (k_{prod}) and rate constants for electrochemical chloride oxidation (k_{cl}). $k_{trans} = 5\times 10^4$ min^{-1}.

6.3.3 Competitive Adsorption Kinetic Model

Another kinetic model is developed based on competitive adsorption of perchlorate and chloride to describe kinetics of perchlorate removal during oxidative dissolution of Ti(0). In Chapter IV, it was suggested that Ti(0) dissolution is predominately caused by the adsorption of aggressive anions such as chloride and perchlorate on the surface of bare Ti(0). Adsorption of perchlorate on bare Ti(0) accelerates the oxidative dissolution of Ti(0) to form a dissolved complex of perchlorate and Ti(II). The perchlorate that stimulates Ti(0) dissolution to Ti(II) and formation of a dissolved complex is believed to be involved in reactions only with Ti(II) and these reaction steps are presented in Figure 6.4. Other aggressive anions, especially chloride and bromide, are believed also to adsorb on bare Ti(0) sites and to compete with perchlorate for those sites.

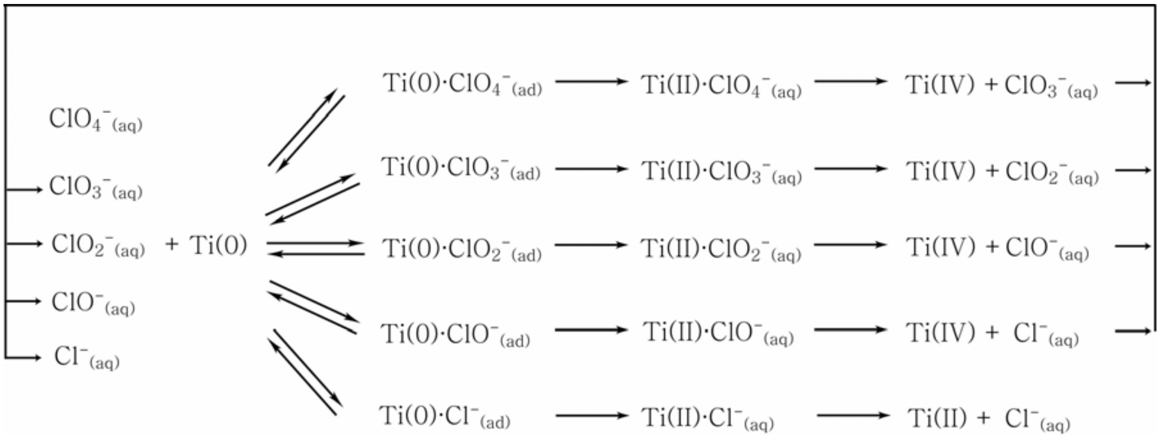


FIGURE 6.4 Perchlorate reduction pathways in the pit.

In order to describe perchlorate reduction by competitive adsorption, it is assumed that 1) the rate limiting step of perchlorate reduction is the oxidative dissolution of Ti(0) that forms the complex between Ti(II) and perchlorate ($\text{Ti(II)}\cdot\text{ClO}_4^-{}_{\text{(aq)}}$); 2) oxidative dissolution of Ti(0) ($\equiv\text{Ti(0)}^{\text{dis}}$) and chloride oxidation ($\equiv\text{Ti(0)}^{\text{ox}}$) sites are different; 3) $[\equiv\text{Ti(0)}]_\text{p}$ (= $[\equiv\text{Ti(0)}^{\text{dis}}]_\text{p}$ +$[\equiv\text{Ti(0)}^{\text{ox}}]_\text{p}$) is much less than $[\text{ClO}_4^-]_\text{p}$ and $[\text{Cl}^-]_\text{p}$ and sites are fully occupied by ClO_4^- and Cl^-; 4) the rates of adsorption and desorption reactions of perchlorate and chloride on ≡Ti(0) are rapid enough to reach equilibrium; and 5) the reduction products of perchlorate (i.e. chlorate (ClO_3^-), chlorite (ClO_2^-) and hypochlorite (ClO^-)) are also adsorobed and stimulate oxidative dissolution that form complexes with Ti(II) and their rate of reduction are much faster than that of perchlorate. These assumptions lead to the simplified sequential step reaction models for perchlorate reduction and chloride oxidation in the pit as shown in Figure 6.5.

Net material balance on perchlorate in the pit is defined as a

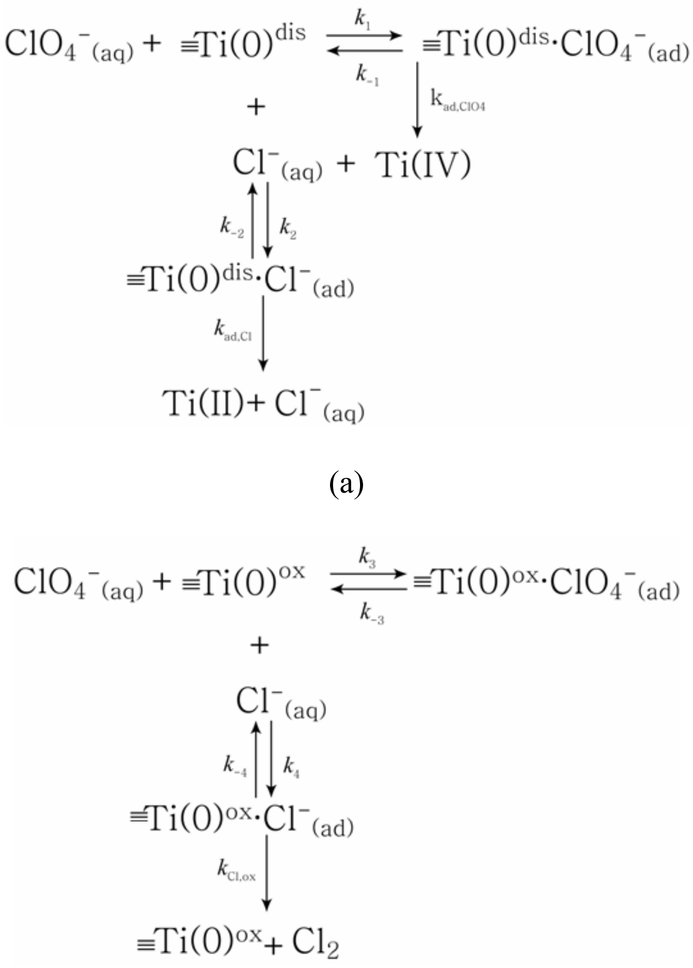
$$\frac{d[\text{ClO}_4^-]_{\text{p,net}}}{d\text{t}} = \frac{d[\text{ClO}_4^-]_{\text{p,}\equiv\text{Ti(0)}}}{d\text{t}} + \frac{d[\text{ClO}_4^-]_\text{p}}{d\text{t}} \tag{6.26}$$

where $d[\text{ClO}_4^-]_{\text{p,}\equiv\text{Ti(0)}}/d\text{t}$ is material balance on perchlorate on ≡Ti(0) and $d[\text{ClO}_4^-]_\text{p}/d\text{t}$ is material balance on perchlorate in pit solution. A material balance of perchlorate on ≡Ti(0) is:

$$\frac{d[\text{ClO}_4^-]_{\text{p,}\equiv\text{Ti(0)}}}{d\text{t}} = \gamma_{\text{prod,}\equiv\text{Ti(0)}\cdot\text{ClO4,dis}} + \gamma_{\text{prod,}\equiv\text{Ti(0)}\cdot\text{ClO4,ox}} - \gamma_{\text{loss,}\equiv\text{Ti(0)}\cdot\text{ClO4,dis}} - \gamma_{\text{loss,}\equiv\text{Ti(0)}\cdot\text{ClO4,ox}} \tag{6.27}$$

where $\gamma_{\text{prod,}\equiv\text{Ti(0)}\cdot\text{ClO4,dis}}$ and $\gamma_{\text{prod,}\equiv\text{Ti(0)}\cdot\text{ClO4,ox}}$ represent rates of $\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{ClO}_4^-$ and $\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{ClO}_4^-$ production, and $\gamma_{\text{loss,}\equiv\text{Ti(0)}\cdot\text{ClO4,dis}}$ and $\gamma_{\text{loss,}\equiv\text{Ti(0)}\cdot\text{ClO4,ox}}$ are rates of

$\equiv Ti(0)^{dis} \cdot ClO_4^-$ and $\equiv Ti(0)^{ox} \cdot ClO_4^-$ loss. The $\gamma_{prod,\equiv Ti(0) \cdot ClO4,dis}$ and $\gamma_{prod,\equiv Ti(0) \cdot ClO4,ox}$ are occurred by adsorption of perchlorate on $\equiv Ti(0)^{dis}$ and $\equiv Ti(0)^{ox}$.



(a)

(b)

FIGURE 6.5 a) Simplified perchlorate reduction pathways in the pit and b) Chloride oxidation pathways in the pit.

$$\gamma_{\mathrm{prod,\equiv Ti(0)\cdot ClO4,dis}} = k_1[\equiv \mathrm{Ti(0)^{dis}}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} \tag{6.28}$$

$$\gamma_{\mathrm{prod,\equiv Ti(0)\cdot ClO4,ox}} = k_3[\equiv \mathrm{Ti(0)^{ox}}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} \tag{6.29}$$

The $\gamma_{\mathrm{loss,\equiv Ti(0)\cdot ClO4,dis}}$ is occurred by desorption and oxidative dissolution from $\equiv\mathrm{Ti(0)^{dis}\cdot ClO_4^-}$ and $\gamma_{\mathrm{loss,\equiv Ti(0)\cdot ClO4,ox}}$ is from desorption of $\equiv\mathrm{Ti(0)^{ox}\cdot ClO_4^-}$.

$$\gamma_{\mathrm{loss,\equiv Ti(0)\cdot ClO4,dis}} = k_{-1}[\equiv \mathrm{Ti(0)^{dis}\cdot ClO_4^-}]_\mathrm{p} + k_{\mathrm{ad,ClO4}}[\equiv \mathrm{Ti(0)^{dis}\cdot ClO_4^-}]_\mathrm{p} \tag{6.30}$$

$$\gamma_{\mathrm{loss,\equiv Ti(0)\cdot ClO4,ox}} = k_{-3}[\equiv \mathrm{Ti(0)^{ox}\cdot ClO_4^-}]_\mathrm{p} \tag{6.31}$$

Substitutions of eqs 6.28, 6.29, 6.30 and 6.31 to 6.27 gives

$$\begin{aligned}\frac{d[\mathrm{ClO_4^-}]_{\mathrm{p,\equiv Ti(0)}}}{d\mathrm{t}} = {} & k_1[\equiv \mathrm{Ti(0)^{dis}}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} + k_3[\equiv \mathrm{Ti(0)^{ox}}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} - \\ & k_{-1}[\equiv \mathrm{Ti(0)^{dis}\cdot ClO_4^-}]_\mathrm{p} - k_{-3}[\equiv \mathrm{Ti(0)^{ox}\cdot ClO_4^-}]_\mathrm{p} - \\ & k_{\mathrm{ad,ClO4}}[\equiv \mathrm{Ti(0)^{dis}\cdot ClO_4^-}]_\mathrm{p}\end{aligned} \tag{6.32}$$

A material balance on perchlorate in the pit solution is

$$\frac{d[\mathrm{ClO_4^-}]_\mathrm{p}}{d\mathrm{t}} = \gamma_{\mathrm{prod,ClO4,p}} - \gamma_{\mathrm{loss,ClO4,p}} \tag{6.33}$$

where $\gamma_{\mathrm{prod,ClO4,p}}$ represents the rate of perchlorate production and $\gamma_{\mathrm{loss,ClO4,p}}$ is the rate of perchlorate loss in the pit solution. Since there is no generation of perchlorate anywhere in the system, the $\gamma_{\mathrm{prod,ClO4,p}}$ is only caused by desoprtion of perchlorate from $\equiv\mathrm{Ti(0)^{dis}\cdot ClO_4^-}$ and $\equiv\mathrm{Ti(0)^{ox}\cdot ClO_4^-}$.

$$\gamma_{\mathrm{prod,ClO4,p}} = k_{-1}[\equiv \mathrm{Ti(0)^{dis}\cdot ClO_4^-}]_\mathrm{p} + k_{-3}[\equiv \mathrm{Ti(0)^{ox}\cdot ClO_4^-}]_\mathrm{p} \tag{6.34}$$

The $\gamma_{\mathrm{loss,ClO4,p}}$ is occurred by adsorption of perchlorate on $\equiv\mathrm{Ti(0)^{dis}}$ and $\equiv\mathrm{Ti(0)^{ox}}$.

$$\gamma_{\mathrm{loss,ClO4,p}} = k_1[\equiv \mathrm{Ti(0)^{dis}}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} + k_3[\equiv \mathrm{Ti(0)^{ox}}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} \tag{6.35}$$

Then, material balance of perchlorate in the pit solution is rewritten by substitution of eqs 6.34 and 6.35 to eq 6.33

$$\frac{d[\mathrm{ClO_4^-}]_\mathrm{p}}{d\mathrm{t}} = k_{-1}[\equiv \mathrm{Ti(0)}^{\mathrm{dis}} \cdot \mathrm{ClO_4^-}]_\mathrm{p} + k_{-3}[\equiv \mathrm{Ti(0)}^{\mathrm{ox}} \cdot \mathrm{ClO_4^-}]_\mathrm{p} - k_1[\equiv \mathrm{Ti(0)}^{\mathrm{dis}}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} - k_3[\equiv \mathrm{Ti(0)}^{\mathrm{ox}}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} \tag{6.36}$$

From assumption, $[\equiv\mathrm{Ti(0)}]_\mathrm{p}$ is much less than $[\mathrm{ClO_4^-}]_\mathrm{p}$. Thus, $d[\mathrm{ClO_4^-}]_{\mathrm{p},\equiv\mathrm{Ti(0)}}/d\mathrm{t}$ is much less than $d[\mathrm{ClO_4^-}]_\mathrm{p}/d\mathrm{t}$. Then, $d[\mathrm{ClO_4^-}]_{\mathrm{p,net}}/d\mathrm{t} \approx d[\mathrm{ClO_4^-}]_\mathrm{p}/d\mathrm{t}$ and summation of eqs 6.32 and 6.36 produces

$$\frac{d[\mathrm{ClO_4^-}]_\mathrm{p}}{d\mathrm{t}} = -\gamma_{\mathrm{ClO4,p}} \tag{6.37}$$

where $\gamma_{\mathrm{ClO4,p}} = k_{\mathrm{ad,ClO4}}[\equiv\mathrm{Ti(0)}\cdot\mathrm{ClO_4^-}]_\mathrm{p}$. By introducing surface coverage (θ_t^{dis}), the $\gamma_{\mathrm{ClO4,p}}$ becomes

$$\gamma_{\mathrm{ClO4,p}} = k_{\mathrm{ad,ClO4}}[\equiv \mathrm{Ti(0)}^{\mathrm{dis}}]_\mathrm{p}\,\theta_{\mathrm{ClO4}}^{\mathrm{dis}} \tag{6.38}$$

where θ_t^{dis} represents total surface coverage of $\equiv\mathrm{Ti(0)}^{\mathrm{dis}}$ and this is defined as a

$$\theta_\mathrm{t}^{\mathrm{dis}} = \theta_{\mathrm{ClO4}}^{\mathrm{dis}} + \theta_{\mathrm{Cl}}^{\mathrm{dis}} = 1 \tag{6.39}$$

Since $\equiv\mathrm{Ti(0)}$ reaches rapid equilibrium with $\mathrm{ClO_4^-}$ and $\mathrm{Cl^-}$, surface coverage of perchlorate and chloride can be described with adsorption and desorption rate constant and their concentrations in the pit as

$$k_1[\equiv \mathrm{Ti(0)}^{\mathrm{dis}}]_\mathrm{p}[\mathrm{ClO_4^-}]_\mathrm{p} = k_{-1}[\equiv \mathrm{Ti(0)}^{\mathrm{dis}}]_\mathrm{p}\,\theta_{\mathrm{ClO4}}^{\mathrm{dis}} \tag{6.40}$$

$$k_2[\equiv \mathrm{Ti(0)}^{\mathrm{dis}}]_\mathrm{p}[\mathrm{Cl^-}]_\mathrm{p} = k_{-2}[\equiv \mathrm{Ti(0)}^{\mathrm{dis}}]_\mathrm{p}\,\theta_{\mathrm{Cl}}^{\mathrm{dis}} \tag{6.41}$$

Calculating the ratio of eq 6.40 to 6.41 and manipulating the result gives:

$$\theta_{\mathrm{Cl}}^{\mathrm{dis}} = \theta_{\mathrm{ClO4}}^{\mathrm{dis}} \frac{K_{\mathrm{Cl}}[\mathrm{Cl}^-]_{\mathrm{p}}}{K_{\mathrm{ClO4}}[\mathrm{ClO}_4^-]_{\mathrm{p}}} \tag{6.42}$$

where $K_{\mathrm{ClO4}} = k_1/k_{-1}$ and $K_{\mathrm{Cl}} = k_2/k_{-2}$. Substitution of eq 6.42 back to eq 6.39 gives:

$$\theta_{\mathrm{ClO4}}^{\mathrm{dis}} = \frac{[\mathrm{ClO}_4^-]_{\mathrm{p}}}{[\mathrm{ClO}_4^-]_{\mathrm{p}} + K_{\mathrm{I}}[\mathrm{Cl}^-]_{\mathrm{p}}} \tag{6.43}$$

where $K_{\mathrm{I}} = K_{\mathrm{Cl}}/K_{\mathrm{ClO4}}$. Substitution of eq 6.43 to eq 6.38 gives:

$$\gamma_{\mathrm{ClO4,p}} = \frac{k_{\mathrm{ad,ClO4}}[\equiv \mathrm{Ti(0)}^{\mathrm{dis}}]_{\mathrm{p}}[\mathrm{ClO}_4^-]_{\mathrm{p}}}{[\mathrm{ClO}_4^-]_{\mathrm{p}} + K_{\mathrm{I}}[\mathrm{Cl}^-]_{\mathrm{p}}} \tag{6.44}$$

$\equiv\mathrm{Ti(0)}^{\mathrm{dis}}$ is generated by electrochemically induced pitting corrosion and keep regenerated by electrochemical dissolution of Ti(0) to form Ti(II). Thus, as long as the current remains constant, $\equiv\mathrm{Ti(0)}^{\mathrm{dis}}$ remains a constant. Since the volume of pit is assumed a constant over time, $[\equiv\mathrm{Ti(0)}^{\mathrm{dis}}]_{\mathrm{p}}$ also becomes a constant. Then eq 6.44 can be simplified to

$$\gamma_{\mathrm{ClO4,p}} = \frac{k'_{\mathrm{ad,ClO4}}[\mathrm{ClO}_4^-]_{\mathrm{p}}}{[\mathrm{ClO}_4^-]_{\mathrm{p}} + K_{\mathrm{I}}[\mathrm{Cl}^-]_{\mathrm{p}}} \tag{6.45}$$

where $k'_{\mathrm{ad,ClO4}}$ ($=k_{\mathrm{ad,ClO4}}[\equiv\mathrm{Ti(0)}^{\mathrm{dis}}]_{\mathrm{p}}$).

A material balance on chloride in the pit is:

$$\frac{d[\mathrm{Cl}^-]_{\mathrm{p,net}}}{dt} = \frac{d[\mathrm{Cl}^-]_{\mathrm{p,\equiv Ti(0)}}}{dt} + \frac{d[\mathrm{Cl}^-]_{\mathrm{p}}}{dt} \tag{6.46}$$

where $d[\mathrm{Cl}^-]_{\mathrm{p,\equiv Ti(0)}}/dt$ is material balance on chloride on ≡Ti(0) and $d[\mathrm{Cl}^-]_{\mathrm{p}}/dt$ is material balance on chloride in pit solution. Then, a material balance for chloride on ≡Ti(0) is:

$$\frac{d[\mathrm{Cl}^-]_{\mathrm{p,\equiv Ti(0)}}}{dt} = \gamma_{\mathrm{prod,\equiv Ti(0)\cdot Cl,dis}} + \gamma_{\mathrm{prod,\equiv Ti(0)\cdot Cl,ox}} - \gamma_{\mathrm{loss,\equiv Ti(0)\cdot Cl,dis}} - \gamma_{\mathrm{loss,\equiv Ti(0)\cdot Cl,ox}} \tag{6.47}$$

where $\gamma_{\text{prod},\equiv\text{Ti(0)}\cdot\text{Cl,dis}}$ and $\gamma_{\text{prod},,\equiv\text{Ti(0)}\cdot\text{Cl,ox}}$ represent rates of $\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-$ and $\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{Cl}^-$ production, and $\gamma_{\text{loss},\equiv\text{Ti(0)}\cdot\text{Cl,dis}}$ and $\gamma_{\text{loss},\equiv\text{Ti(0)}\cdot\text{C,ox}}$ are rates of $\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-$ and $\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{Cl}^-$ loss. The $\gamma_{\text{prod},\equiv\text{Ti(0)}\cdot\text{Cl,dis}}$ and $\gamma_{\text{prod},,\equiv\text{Ti(0)}\cdot\text{Cl,ox}}$ are occurred by adsorption of perchlorate on $\equiv\text{Ti(0)}^{\text{dis}}$ and $\equiv\text{Ti(0)}^{\text{ox}}$.

$$\gamma_{\text{prod},\equiv\text{Ti(0)}\cdot\text{Cl,dis}} = k_2[\equiv\text{Ti(0)}^{\text{dis}}]_{\text{p}}[\text{Cl}^-]_{\text{p}} \tag{6.48}$$

$$\gamma_{\text{prod},\equiv\text{Ti(0)}\cdot\text{Cl,ox}} = k_4[\equiv\text{Ti(0)}^{\text{ox}}]_{\text{p}}[\text{Cl}^-]_{\text{p}} \tag{6.49}$$

The $\gamma_{\text{loss},\equiv\text{Ti(0)}\cdot\text{Cl,dis}}$ is caused by desorption and oxidative dissolution from $\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-$ and $\gamma_{\text{loss},\equiv\text{Ti(0)}\cdot\text{Cl,ox}}$ is by desorption and chloride oxidation from $\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{Cl}^-$.

$$\gamma_{\text{loss},\equiv\text{Ti(0)}\cdot\text{Cl,dis}} = k_{-2}[\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-]_{\text{p}} + k_{\text{ad,Cl}}[\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-]_{\text{p}} \tag{6.50}$$

$$\gamma_{\text{loss},\equiv\text{Ti(0)}\cdot\text{Cl,ox}} = k_{-4}[\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{Cl}^-]_{\text{p}} + k_{\text{Cl,ox}}[\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{Cl}^-]_{\text{p}} \tag{6.51}$$

Substitution of eqs 6.48, 6.49, 6.50, and 6.51 to 6.47 gives

$$\begin{aligned}\frac{d[\text{Cl}^-]_{\text{p},\equiv\text{Ti(0)}}}{d\text{t}} &= k_2[\equiv\text{Ti(0)}^{\text{dis}}]_{\text{p}}[\text{Cl}^-]_{\text{p}} + k_4[\equiv\text{Ti(0)}^{\text{ox}}]_{\text{p}}[\text{Cl}^-]_{\text{p}} - k_{-2}[\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-]_{\text{p}} \\ &\quad - k_{-4}[\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{Cl}^-]_{\text{p}} - k_{\text{ad,Cl}}[\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-]_{\text{p}} - k_{\text{Cl,ox}}[\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{Cl}^-]_{\text{p}}\end{aligned} \tag{6.52}$$

A material balance on chloride in the pit solution is

$$\frac{d[\text{Cl}^-]_{\text{p}}}{d\text{t}} = \gamma_{\text{prod,Cl,p}} - \gamma_{\text{loss,Cl,p}} \tag{6.53}$$

where $\gamma_{\text{prod,Cl,p}}$ represents the rate of chloride production and $\gamma_{\text{loss,Cl,p}}$ is the rate of chloride loss in the pit solution. There is a generation of chloride by perchlorate reduction. Thus, the $\gamma_{\text{prod,Cl,p}}$ is occurred by chloride desoprtion from $\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-$ and $\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{Cl}^-$, oxidative dissolution from $\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-$, and perchlorate reduction.

$$\gamma_{\text{prod,Cl,p}} = k_{-2}[\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-]_{\text{p}} + k_{-4}[\equiv\text{Ti(0)}^{\text{ox}}\cdot\text{Cl}^-]_{\text{p}} + k_{\text{ad,Cl}}[\equiv\text{Ti(0)}^{\text{dis}}\cdot\text{Cl}^-]_{\text{p}} + \gamma_{\text{ClO4,p}} \tag{6.54}$$

The $\gamma_{\mathrm{loss,Cl,p}}$ is caused by formations of $\equiv\mathrm{Ti(0)^{dis}}\cdot\mathrm{Cl^-}$ and $\equiv\mathrm{Ti(0)^{ox}}\cdot\mathrm{Cl^-}$.

$$\gamma_{\mathrm{loss,Cl,p}} = k_2[\equiv \mathrm{Ti(0)^{dis}}]_\mathrm{p}[\mathrm{Cl^-}]_\mathrm{p} + k_4[\equiv \mathrm{Ti(0)^{ox}}]_\mathrm{p}[\mathrm{Cl^-}]_\mathrm{p} \tag{6.55}$$

Substitution of eqs 6.54 and 6.55 to 6.53 gives

$$\begin{aligned}\frac{d[\mathrm{Cl^-}]_\mathrm{p}}{d\mathrm{t}} = \gamma_{\mathrm{ClO4,p}} + k_{-2}[\equiv \mathrm{Ti(0)^{dis}}\cdot\mathrm{Cl^-}]_\mathrm{p} + k_{-4}[\equiv \mathrm{Ti(0)^{ox}}\cdot\mathrm{Cl^-}]_\mathrm{p} + \\ k_{\mathrm{ad,Cl}}[\equiv \mathrm{Ti(0)^{dis}}\cdot\mathrm{Cl^-}]_\mathrm{p} - k_2[\equiv \mathrm{Ti(0)^{dis}}]_\mathrm{p}[\mathrm{Cl^-}]_\mathrm{p} - k_4[\equiv \mathrm{Ti(0)^{ox}}]_\mathrm{p}[\mathrm{Cl^-}]_\mathrm{p}\end{aligned} \tag{6.56}$$

Since $[\equiv\mathrm{Ti(0)}]_\mathrm{p}$ is much less than $[\mathrm{Cl^-}]_\mathrm{p}$, $d[\mathrm{Cl^-}]_{\mathrm{p,\equiv Ti(0)}}/d\mathrm{t}$ becomes much less than $d[\mathrm{Cl^-}]_\mathrm{p}/d\mathrm{t}$. Then, $d[\mathrm{Cl^-}]_{\mathrm{p,net}}/d\mathrm{t} \approx d[\mathrm{Cl^-}]_\mathrm{p}/d\mathrm{t}$ and summation of eqs 6.52 and 6.56 produces

$$\frac{d[\mathrm{Cl^-}]_\mathrm{p}}{d\mathrm{t}} = \gamma_{\mathrm{ClO4,p}} - \gamma_{\mathrm{Cl,p}} \tag{6.57}$$

where $\gamma_{\mathrm{Cl,p}} = k_{\mathrm{Cl,ox}}[\equiv\mathrm{Ti(0)^{ox}}\cdot\mathrm{Cl^-}]$. Following the same assumptions and procedures used in the derivation of perchlorate reduction in the pit, the rate of chloride oxidation in the pit can be described as:

$$\gamma_{\mathrm{Cl,p}} = \frac{k_{\mathrm{Cl,ox}}[\equiv \mathrm{Ti(0)^{ox}}]_\mathrm{p}[\mathrm{Cl^-}]_\mathrm{p}}{[\mathrm{Cl^-}]_\mathrm{p} + K_{\mathrm{I,ox}}[\mathrm{ClO_4^-}]_\mathrm{p}} \tag{6.58}$$

where $K_{\mathrm{I,ox}} = k_3k_{-4}/k_{-3}k_4$. Simplification of eq 6.58 by assuming constant $[\equiv\mathrm{Ti(0)^{ox}}]_\mathrm{p}$ gives

$$\gamma_{\mathrm{Cl,p}} = \frac{k'_{\mathrm{Cl,ox}}[\mathrm{Cl^-}]_\mathrm{p}}{[\mathrm{Cl^-}]_\mathrm{p} + K_{\mathrm{I,ox}}[\mathrm{ClO_4^-}]_\mathrm{p}} \tag{6.59}$$

where $k'_{\mathrm{Cl,ox}}$ $(=k_{\mathrm{Cl,ox}}[\equiv\mathrm{Ti(0)^{ox}}]_\mathrm{p})$.

Perchlorate and chloride would accumulate in the pit to a great extent, because of the need to maintain electro-neutrality during production of metal cations such as $\mathrm{Ti^{4+}}$ and $\mathrm{TiO^{2+}}$ (*60, 62*). Several studies derived a simplified equation to predict anion concentrations in the pit relative to concentrations in solution (*158-163*). The simplified equation is derived from mass transport of equation of chemical species in the electrolytic solution neglecting convection during the electrochemical process (*158-163*).

$$J_i = -D_i\left(\frac{d\mathrm{C_i}}{d\mathrm{x}} + \frac{z_\mathrm{i}D_\mathrm{i}F}{RT}\mathrm{C_i}\frac{d\mu}{d\mathrm{x}}\right) = j\frac{v_\mathrm{i}}{nF} \tag{6.60}$$

where J_i represents flux of *i* chemical specie, D_i is diffusion coefficient, μ is electric potential, x is distance, *j* is current density and v_i is stoichiometric factor of *i* specie (i.e. if electrode reaction H_2.= $2H^+ + 2e^-$, $v_\mathrm{i} = +2$). If electrical charge is consumed only by metal dissolution, electrode reaction at the anode is $M \rightarrow M^+ + e^-$. Then, the stoichiometric factor for metal specie becomes +1 and electrochemically inactive anions that do not consume electric charge become zero. For electrochemically inactive anions, eq 6.60 become:

$$\frac{d\mathrm{C_i}}{d\mathrm{x}} = -\frac{z_\mathrm{i}D_\mathrm{i}F}{RT}\mathrm{C_i}\frac{d\mu}{d\mathrm{x}} \tag{6.61}$$

Then, integration of eq 6.61 with respect to distance (*x*) from bare metal surface to interface of pit and solution gives eq 6.62.

$$\mathrm{C_{p,i}} = \mathrm{C_{s,i}}\exp\left(-\frac{\Delta\mu z_\mathrm{i}F}{RT}\right) \tag{6.62}$$

where $\mathrm{C_{p,i}}$ represents anion concentration in the pit, $\mathrm{C_{s,i}}$ is anion concentration in the solution, $\mathrm{z_i}$ is valence of anion, *F* is faraday's constant, *R* is gas constant, *T* is temperature, and Δμ is the potential drop in the pit that is estimated from (*160*)

$$\Delta\mu = \frac{\mathrm{j_p ar}}{\kappa} \tag{6.63}$$

where j_p represents current density in the pit, r is radius of pit, a is geometric shape factor, and κ is conductivity of solution in the pit. Perchlorate is an electrochemically inactive anion, but chloride is believed to be electrochemically oxidized to chlorine in the pit, which consumes electrical current. However, amount of electrical current consumed by chloride oxidation is much less than the electrical current consumed for Ti(0) dissolution. The discussion in Chapter IV showed that chloride oxidation consumed less than 4 % of total electrical charge. This discussion was based on the assumption that inhibition of perchlorate reduction is caused by competitive adsorption of chloride. Thus, both perchlorate and chloride are assumed to be electrochemically inactive anions and their concentrations in the pit are estimated from their solution concentrations.

$$[\mathrm{ClO_4^-}]_\mathrm{p} = \alpha[\mathrm{ClO_4^-}]_\mathrm{s} \tag{6.64}$$

$$[\mathrm{Cl^-}]_\mathrm{p} = \alpha[\mathrm{Cl^-}]_\mathrm{s} \tag{6.65}$$

where α represents exp(ΔμF/RT). Then, the rate of perchlorate decrease in solution can be expressed using eqs 6.64 and 6.65 by assuming: 1) current density in the pit is a constant as long as a constant current is applied to Ti(0); 2) pit volume and geometric shape factor remain constant; 3) accumulation of anions and metal ions maintain constant conductivity in the pit and thereby potential drop (Δμ) within is relatively small compared to potential drop in the solution. Thus, Δμ within pit is assumed a constant; and 4) transport between pit and solution is sufficiently rapid and reaches equilibrium. Then, the rates of perchlorate and chloride concentration changes in the solution are proportional to their concentration changes in the pit.

$$\frac{d[\mathrm{ClO_4^-}]_\mathrm{s}}{d\mathrm{t}} = \frac{1}{\alpha}\frac{d[\mathrm{ClO_4^-}]_\mathrm{p}}{d\mathrm{t}} \tag{6.66}$$

$$\frac{d[\mathrm{Cl^-}]_\mathrm{s}}{d\mathrm{t}} = \frac{1}{\alpha}\frac{d[\mathrm{Cl^-}]_\mathrm{p}}{d\mathrm{t}} \tag{6.67}$$

Using eqs from 6.64 to 6.67, the rate of perchlorate removal ($\gamma_{\mathrm{ClO4,p}}$) and chloride oxidation ($\gamma_{\mathrm{Cl,p}}$) are rewritten to the rates of perchlorate removal ($\gamma_{\mathrm{ClO4,s}}$)and chloride removal ($\gamma_{\mathrm{Cl,s}}$) in the solution.

$$\gamma_{\mathrm{ClO4,s}} = \frac{k_{\mathrm{obs,ClO4}}[\mathrm{ClO_4^-}]_\mathrm{s}}{[\mathrm{ClO_4^-}]_\mathrm{s} + K_\mathrm{I}[\mathrm{Cl^-}]_\mathrm{s}} \tag{6.68}$$

$$\gamma_{\mathrm{Cl,s}} = \frac{k_{\mathrm{obs,Cl}}[\mathrm{Cl^-}]_\mathrm{s}}{[\mathrm{Cl^-}]_\mathrm{s} + K_{\mathrm{I,ox}}[\mathrm{ClO_4^-}]_\mathrm{s}} \tag{6.69}$$

Where $k_{\mathrm{obs,ClO4}} = k'_{\mathrm{ad,ClO4}}/\alpha$ and $k_{\mathrm{obs,Cl}} = k'_{\mathrm{Cl,ox}}/\alpha$. Then, material balance of perchlorate and chloride in the solution are

$$\frac{d[\mathrm{ClO_4^-}]_\mathrm{s}}{d\mathrm{t}} = -\gamma_{\mathrm{ClO4,s}} \tag{6.70}$$

$$\frac{d[\mathrm{Cl^-}]_\mathrm{s}}{d\mathrm{t}} = \gamma_{\mathrm{ClO4,s}} - \gamma_{\mathrm{Cl,s}} \tag{6.71}$$

Then, material balances of perchlorate and chloride in the solution described with solution concentrations of perchlorate and chloride are.

$$\frac{d[\mathrm{ClO_4^-}]_\mathrm{s}}{d\mathrm{t}} = -\frac{k_{\mathrm{obs,ClO4}}[\mathrm{ClO_4^-}]_\mathrm{s}}{[\mathrm{ClO_4^-}]_\mathrm{s} + K_\mathrm{I}[\mathrm{Cl^-}]_\mathrm{s}} \tag{6.72}$$

$$\frac{d[\mathrm{Cl^-}]_\mathrm{s}}{d\mathrm{t}} = \frac{k_{\mathrm{obs,ClO4}}[\mathrm{ClO_4^-}]_\mathrm{s}}{[\mathrm{ClO_4^-}]_\mathrm{s} + K_\mathrm{I}[\mathrm{Cl^-}]_\mathrm{s}} - \frac{k_{\mathrm{obs,Cl}}[\mathrm{Cl^-}]_\mathrm{s}}{[\mathrm{Cl^-}]_\mathrm{s} + K_{\mathrm{I,ox}}[\mathrm{ClO_4^-}]_\mathrm{s}} \tag{6.73}$$

Values of parameters used in the competitive adsorption model were obtained from regressions using experimental data. The value of $k_{\mathrm{obs,Cl}}$ was obtained by linear regression using Matlab function ‘regress’. Values of $k_{\mathrm{obs,ClO4}}$, K_{I} and $K_{\mathrm{I,ox}}$ were obtained by nonlinear regressions using Matlab function ‘nlinfit’ combined with Matlab function ‘ode45’. The ‘ode45’ function solved eqs 6.72 and 6.73, and the ‘nlinfit’ function estimated parameters by least squares regression. Confidence intervals of parameters were calculated with the ‘nlparci’ function. Eq 6.72 indicates that if there is only perchlorate present in the solution, the reaction becomes zeroth-order, and the rate constant ($k_{\mathrm{obs,ClO4}}$) can be obtained by linear regression on concentrations over time. However, since the final reduction product of perchlorate is chloride, the inhibition of perchlorate reduction by chloride is inevitable unless the value of K_{I} is small. However, chloride oxidation does not produce an inhibiting product when chloride is only present in the solution. Thus, if only chloride is present during the pitting corrosion of Ti(0), eq 6.73 becomes zeroth-order.

$$\frac{d[\mathrm{Cl}^-]_{\mathrm{s}}}{d\mathrm{t}} = -k_{\mathrm{obs,Cl}} \tag{6.74}$$

Then, $k_{\mathrm{obs,Cl}}$ can be obtained by linear regression of chloride concentrations over time using experimental data that were obtained from experiments only with chloride and various currents. Figure 6.6 shows that the rate constant for chloride removal from solution ($k_{\mathrm{obs,Cl}}$) is directly proportional to applied current per unit liquid volume ($\mathrm{I_v}$ (mA $\mathrm{L^{-1}}$)) and experimental data used are presented in Appendix C. Linear regression was conducted and it determined that the slope was $(2.18 \pm 0.10) \times 10^{-5}$ mM L $\mathrm{mA^{-1}}$ $\mathrm{min^{-1}}$.

Then, the observed rate constant for chloride removal from solution could be calculated from: $k_{obs,Cl} = (2.18 \times 10^{-5})\cdot I_v$ (mM min^{-1}).

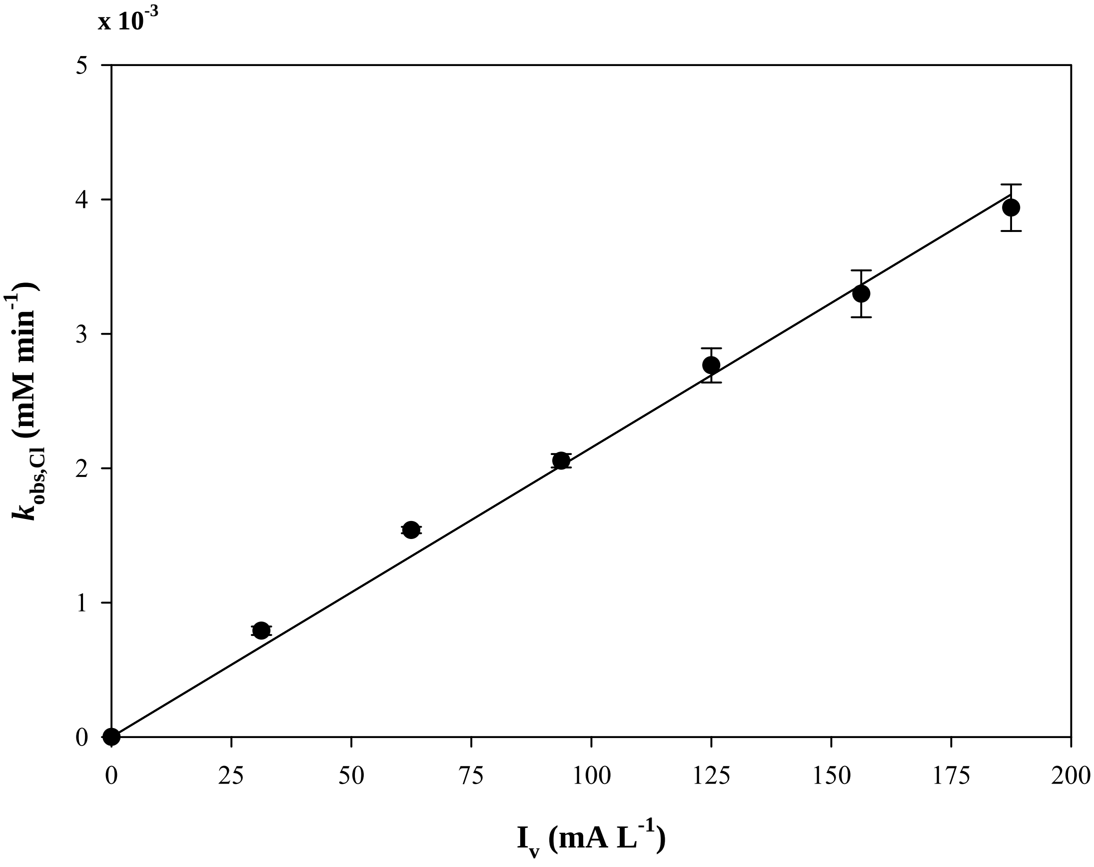


FIGURE 6.6. Rate constant for chloride oxidation as function of current. Initial chloride concentration was 1.05 ± 0.02 mM.

Values of $k_{\mathrm{obs,ClO4}}$, K_{I} and $K_{\mathrm{I,ox}}$ were obtained by conducting a nonlinear regression using experimental data that were obtained from experiments with initial concentration of 1.00 mM perchlorate and with various currents. The experimental data set contained perchlorate and chloride concentrations over time and they are presented in Appendix C. Nonlinear regressions of $k_{\mathrm{obs,ClO4}}$, K_{I}, and $K_{\mathrm{I,ox}}$ require that two ordinary differential equations (eqs 6.72 and 6.73) be solved. However, perchlorate concentration was observed to linearly decrease over time for most of the experiment, with only slight non-linear behavior at the end of the experiments. Thus, it is hard to accurately estimate values of $k_{\mathrm{obs,ClO4}}$, K_{I} and $K_{\mathrm{I,ox}}$ using only perchlorate concentrations. Chloride concentrations in experimental data set were used to estimate the rate of chloride removal in the solution ($\gamma_{\mathrm{Cl,s}}$) in eq 6.71. The rate of chloride removal in the solution is estimated by calculating amount of chloride loss during the experiments at each time.

$$[\mathrm{Cl}^-]_{\mathrm{t,loss}} = [\mathrm{ClO_4}^-]_{\mathrm{i}} - [\mathrm{ClO_4}^-]_{\mathrm{t}} + [\mathrm{Cl}^-]_{\mathrm{i}} - [\mathrm{Cl}^-]_{\mathrm{t}} \qquad (6.75)$$

where $[\mathrm{Cl}^-]_{\mathrm{t,loss}}$ represents concentration of chloride loss at a given time (t), $[\mathrm{ClO_4}^-]_{\mathrm{i}}$ and $[\mathrm{Cl}^-]_{\mathrm{i}}$ are initial perchlorate and chloride concentrations, and $[\mathrm{ClO_4}^-]_{\mathrm{t}}$ and $[\mathrm{Cl}^-]_{\mathrm{t}}$ are perchlorate and chloride concentrations at a given time. Figure 6.7 shows the amount of chloride loss over time and $[\mathrm{Cl}^-]_{\mathrm{t,loss}}$ was observed to linearly increase over time. Thus, the rate of chloride removal in the solution ($\gamma_{\mathrm{Cl,s}}$) in eq 6.71 is approximated with the slope obtained from linear regression of $[\mathrm{Cl}^-]_{\mathrm{t,loss}}$ over time.

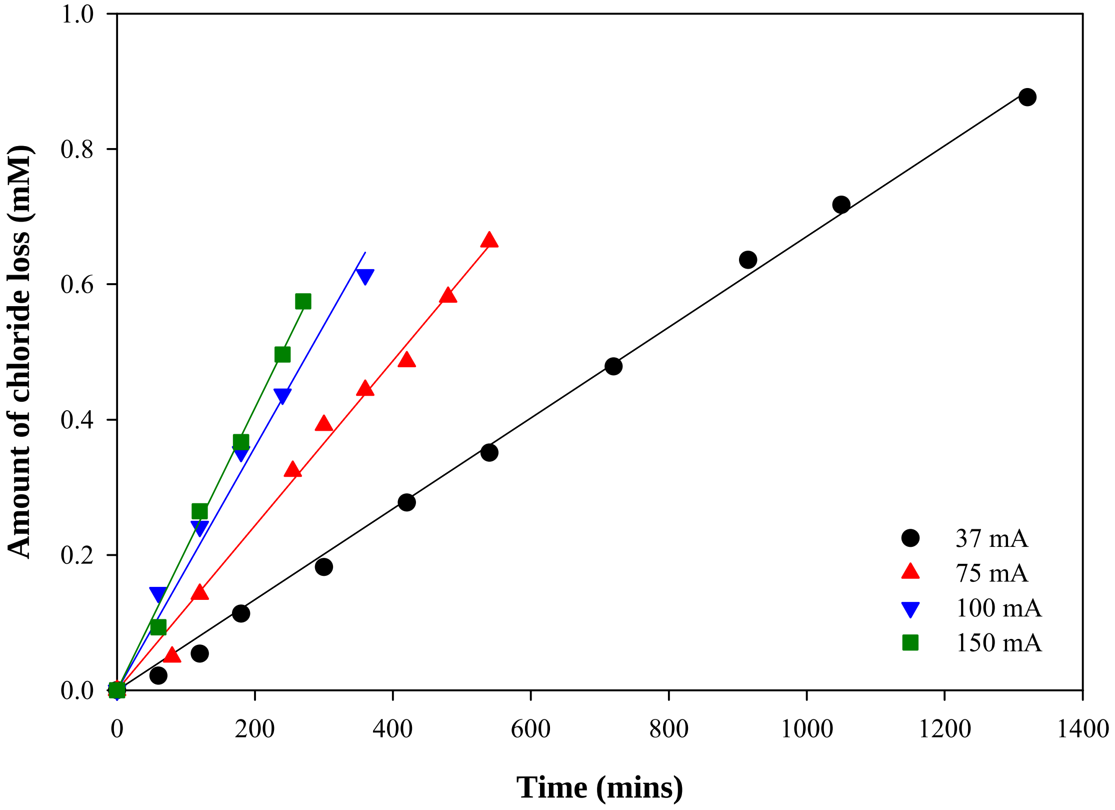


FIGURE 6.7. Amount of chloride loss in solution with various current during 1.01 ± 0.02 mM of perchlorate reduction.

Two nonlinear regressions were conducted on each experimental data set to determine $k_{obs,ClO4}$, K_I and $K_{I,ox}$ by solving two ordinary differential equations eq 6.72 and eq 6.73. First nonlinear regression on perchlorate concentrations was conducted by solving two ordinary differential equations eq 6.72 and eq 6.73 to determine $k_{obs,ClO4}$ and K_I, but $\gamma_{Cl,s}$ in eq 6.73 was replaced with the slope obtained from linear regression of $[Cl^-]_{t,loss}$ over time from experimental data. After determination of $k_{obs,ClO4}$ and K_I, another nonlinear regression on chloride concentrations was conducted to determine the value of $K_{I,ox}$ by solving eqs 6.72 and 6.73 ($\gamma_{Cl,s}$ was not replaced with the slope this time) using values of $k_{obs,ClO4,}$ K_I and $k_{obs,Cl}$ that were previously determined. The value for $k_{obs,ClO4}$ were obtained from experiments conducted at different current and were found to linearly increase with current per unit volume of solution as shown in Figure 6.8. A linear regression found that the value of the slope was $(2.61 \pm 0.27) \times 10^{-5}$ (mM L mA^{-1} min^{-1}). Then, values for the rate constant could be calculated from: $k_{obs,ClO4} = (2.61 \times 10^{-5}) \cdot I_v$ (mM min^{-1}). The values calculated for K_I did not show any dependence on current and their average value is 1.25 ± 0.62. $K_{I,ox}$ also was not dependent on current and its average value is 0.16 ± 0.09. These rate constants and inhibition coefficients are summarized on Table 6.3. If the oxidative dissolution of Ti(0) and chloride oxidation occur at the same site, K_I should be equal to $1/K_{I,ox}$. However, $1/K_{I,ox}$ is much greater than K_I. Therefore, the oxidative dissolution of Ti(0) and chloride oxidation would be developed at different site. Additionally, since K_I ($= K_{Cl}/K_{ClO4}$) is greater than 1, adsorption affinity of chloride is slightly greater than that of perchlorate at oxidative dissolution site ($\equiv Ti(0)^{dis}$). However, $1/K_{I,ox}$ is 6.25 and this indicates that adsorption affinity of chloride is much greater than that of perchlorate at the chloride oxidation site ($\equiv Ti(0)^{ox}$). Thus, perchlorate reduction is greatly inhibited by chloride, but chloride oxidation is only slightly inhibited by presence of chloride. According to Faraday's law, theoretical amount of Ti(II) that would be produced at $I_v = 1$ mA L^{-1} would be 3.11×10^{-4} mM min^{-1}, if the only redox reaction occurring at the electrode was the oxidative dissolution of Ti(0) to produce Ti(II). In order to completely reduce one mole of perchlorate, four moles of Ti(II) are required. Based on $k_{obs,ClO4,}$ the actual amount of Ti(II) consumed for perchlorate reduction in the absence of chloride would be 1.04 × 10^{-4} mM min^{-1} at $I_v = 1$ mA Then, the efficiency of perchlorate reduction during pitting corrosion of Ti(0) in the absence of chloride is 34 %. This value is expected to decrease as chloride concentration increases.

TABLE 6.3. Estimated rate constants and inhibition coefficients for competitive adsorption kinetic model.

Rate constant		Inhibition coefficient	
$k'_{obs,ClO4}{}^{*}$ (mM L mA^{-1} min^{-1})	$k'_{obs,Cl}{}^{**}$ (mM L mA^{-1} min^{-1})	K_I	$K_{I,ox}$
$2.61 \pm 0.27 \times 10^{-5}$	$2.18 \pm 0.10 \times 10^{-5}$	1.25 ± 0.62	0.16 ± 0.09

* $k_{obs,ClO4}$ (mM min^{-1}) = $k'_{obs,ClO4} \times I_v$; ** $k_{obs,Cl}$ (mM min^{-1}) = $k'_{obs,Cl} \times I_v$

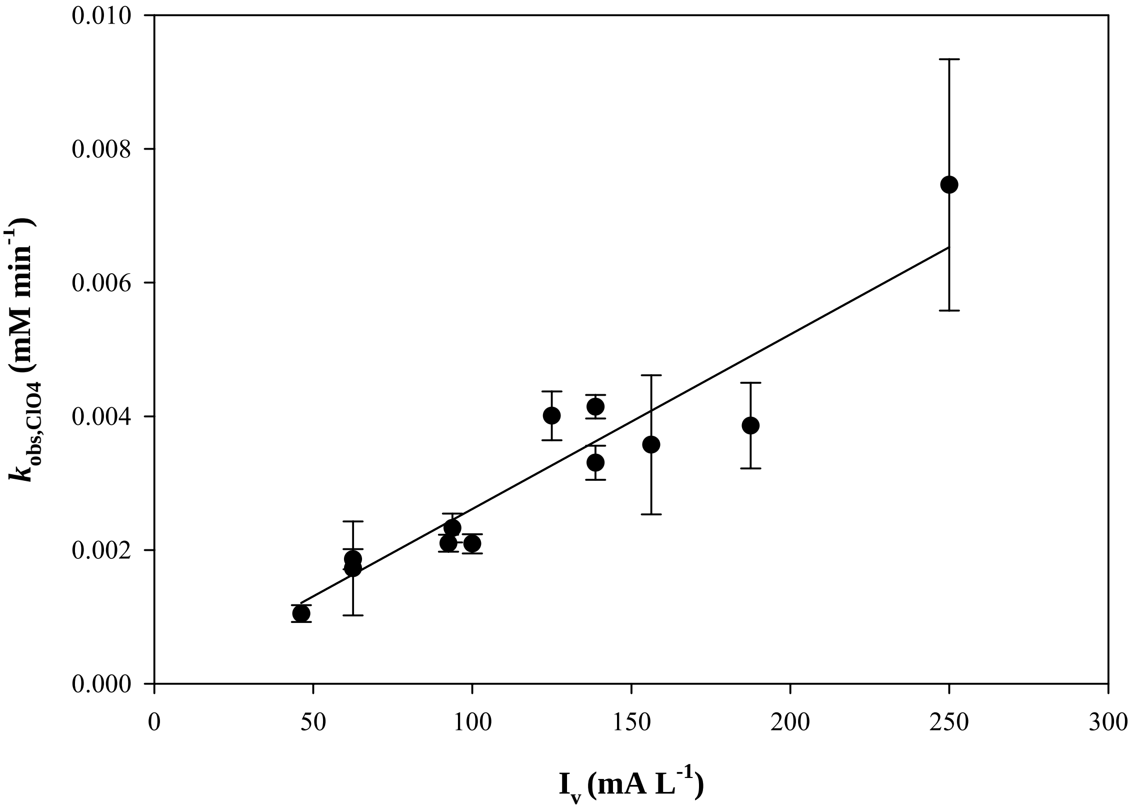


FIGURE 6.8. Rate constant for perchlorate removal as a function of current. Initial perchlorate concentration was 1.00 ± 0.03 mM.

6.3.4 Comparisons of Kinetic Models

Figure 6.9 shows a comparison of predictions made by the two kinetic models and experimental data that was not used to calibrate the models. Experimental data were obtained at different initial perchlorate concentrations, but at the same current. Both models well predict the behavior of perchlorate concentration in the experiments. Figure 6.10 compares predictions of the two kinetic models with another set of experimental data for concentrations of perchlorate and chloride obtained at a constant current. Both models well predict perchlorate concentration changes in the solution. However, the Ti(II) consumption model over predicts chloride concentration in the solution. Overprediction of chloride concentration is probably the result of under predicting the net conversion of chloride to chlorine. The net conversion is the difference between the chloride converted to chlorine and the chlorine converted to chloride by reaction with Ti(II). This would be strongly affected by the transport of chlorine from the pit to the solution, where it will not react with Ti(II). If transport to the solution is slow, most of the chlorine that is produced would be converted back to chloride, resulting in higher chloride concentrations in solution than observed. It was assumed that the transport of chlorine is developed by diffusion and no chlorine in solution is present. Using the pit volume and its radius, the transport coefficient was calculated and its value was 4.24×10^{-4} min^{-1}. However, transport coefficient of chloride was 5×10^{4} min^{-1} which was 10^{8} times greater than transport coefficient of chlorine. Higher transport coefficient of chloride might be a reasonable assumption. Because, high concentration of metal ions in the pit would produces higher rate of chloride ion transport to pit to maintain electroneutrality and electric current develops electromigration of chloride in the pit. Then, it might be possible that transport coefficient of chlorine to solution might be underestimated in this study. Thus, this might cause that most of chlorine is converted back to chloride in the solution. In order to solve overprediction of chloride concentration, it would be required additional investigations regarding chlorine begavior in the pit. Furthermore, it would be beneficial to develop a Ti(II) consumption kinetic model to support additional studies on chloride oxidation in the pit, especially the interaction of chloride with Ti(0). Therefore, it is very hard to judge whether the assumptions used to develop the two kinetic models are correct. However, it is clear that the competitive adsorption kinetic model did fairly well in predicting both perchlorate and chloride concentration changes during the pitting corrosion of Ti(0).

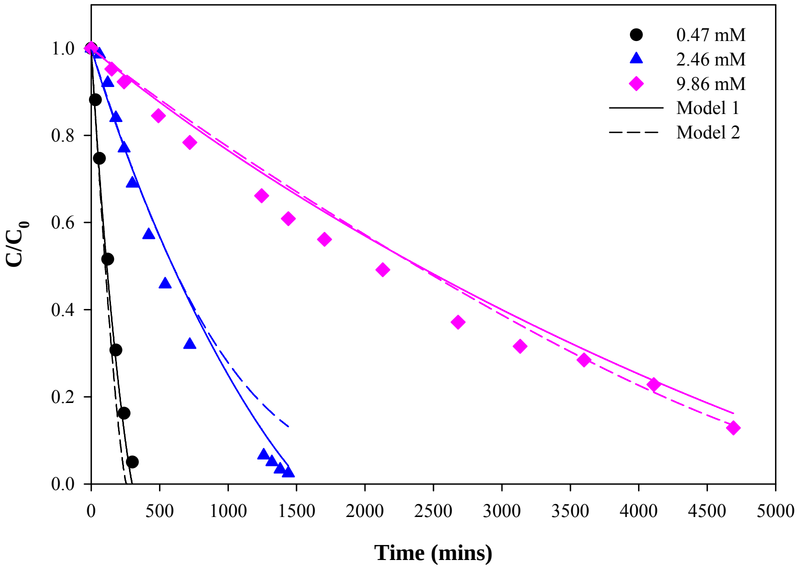


FIGURE 6.9. Comparisons of kinetic models with experimental data with different initial perchlorate concentrations at a constant current (80 mA). Model 1: Competitive adsorption model and Model 2: Ti(II) consumption model ($k_{\mathrm{trans}} = 5\times 10^4$ min^{-1}).

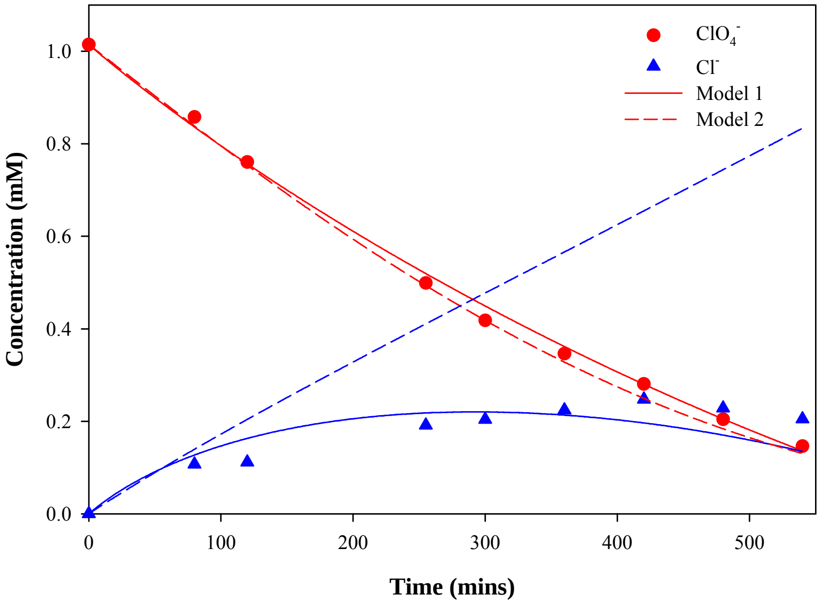


FIGURE 6.10. Comparison of kinetic models with perchlorate and chloride concentrations at constant current (75 mA); Model 1: Competitive adsorption model and Model 2: Ti(II) consumption model ($k_{trans} = 5\times 10^4$ min^{-1}).

Figures 6.11 and 6.12 show additional comparisons of model predictions with experimental data that were not used to calibrate the models. Figure 6.10 shows the influence of chloride concentration on perchlorate reduction and predictions of it by the competitive adsorption model when the initial perchlorate concentration is about 0.48 mM. The rate of perchlorate removal decreases with increasing chloride concentration and the competitive adsorption model predicts this behavior well. Figure 6.11 presents experimental data and predictions of the competitive adsorption model at different chloride concentrations, but at a lower initial perchlorate concentration (0.99 µM). Again, experimental data shows that the rate of perchlorate removal decreases with increasing chloride concentration. The competitive adsorption model predicts concentrations of perchlorate that are slightly higher than experimental observations. However, this discrepancy between model prediction and experimental observation is caused by an initial delay in perchlorate removal that is caused by the induction time of pitting corrosion (*62*). The induction time is the time required to develop stable pitting corrosion.

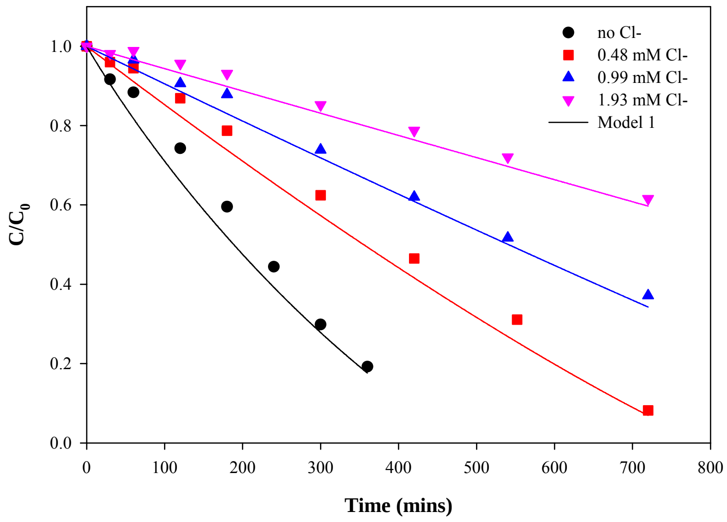


FIGURE 6.11. Influence of chloride concentration on rate of perchlorate reduction at constant current (50 mA) using predictions of competitive adsorption model. Initial perchlorate concentration was 0.48 ± 0.01 mM.

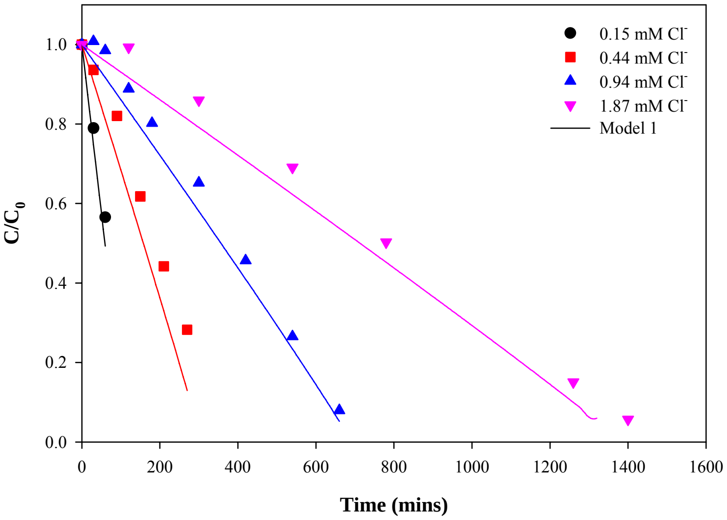


FIGURE 6.12. Influence of chloride concentration on rate of trace levels of perchlorate removal at constant current (50 mA); initial perchlorate concentration was 0.99 ± 0.05 μM and predictions by competitive adsorption model.

For removal of trace levels of perchlorate in presence of much higher concentrations of chloride, the competitive adsorption model has an analytical solution. Since the chloride concentration is greater than perchlorate concentration, $K_I[Cl^-]_s$ and $[Cl^-]_s$ are much greater than $[ClO_4^-]_s$ and $K_{I,ox}[ClO_4^-]_s$. Then, eqs 6.72 and 6.73 are simplified to

$$-\frac{d[ClO_4^-]_s}{dt} = \frac{k_{obs,ClO4}[ClO_4^-]_s}{K_I[Cl^-]_s} \tag{6.76}$$

$$-\frac{d[Cl^-]_s}{dt} = k_{obs,Cl} \tag{6.77}$$

Integration of eq 6.77 with initial values of $[Cl^-]_{s,i}$ and t = 0 produces

$$[\mathrm{Cl}^-]_\mathrm{s} = [\mathrm{Cl}^-]_\mathrm{s,i} - k_\mathrm{Cl,ox} \cdot t \tag{6.78}$$

Substitution of eq 6.78 to 6.76 and integration with initial values of $[\mathrm{ClO_4}^-]_\mathrm{s,i}$ and t = 0 produces

$$\ln\left(\frac{[\mathrm{ClO_4^-}]_\mathrm{s}}{[\mathrm{ClO_4^-}]_\mathrm{s,i}}\right) = \frac{k_\mathrm{ad,ClO4,s}}{k_\mathrm{Cl,ox} \cdot K_I} \ln\left(\frac{[\mathrm{Cl}^-]_\mathrm{s,i}}{[\mathrm{Cl}^-]_\mathrm{s,i} - k_\mathrm{Cl,ox} t}\right) \tag{6.79}$$

Since $k_\mathrm{ad,ClO4,s} = 2.61 \times 10^{-5} \cdot \mathrm{I_v}$ mM min^{-1}, $k_\mathrm{Cl,ox} = 2.18 \times 10^{-5} \cdot \mathrm{I_v}$ mM min^{-1}, and $K_\mathrm{I} = 1.25$ (dimensionless), $k_\mathrm{ad,ClO4,s}/(k_\mathrm{Cl,ox} \cdot K_\mathrm{I}) = 0.95$. Then, perchlorate concentration at a given time is:

$$[\mathrm{ClO_4^-}]_\mathrm{s} = [\mathrm{ClO_4^-}]_\mathrm{s,i} \left(\frac{[\mathrm{Cl}^-]_\mathrm{s,i}}{[\mathrm{Cl}^-]_\mathrm{s,i} - k_\mathrm{Cl,ox} t}\right)^{0.95} \tag{6.80}$$

6.4. Conclusions

This chapter developed two kinetic models to describe perchlorate concentration changes during the pitting corrosion of Ti(0). The kinetic models were developed based on two different assumptions about the mechanism of chloride inhibition of perchlorate reduction. The competitive adsorption model assumed that the primary mechanism was competitive adsorption of perchlorate and chloride on the surface of bare Ti(0). The Ti(II) consumption model assumed that the primary mechanism was consumption of Ti(II) by electrochemically generated chlorine. The competitive adsorption model showed that chloride has slight higher adsorption affinity to oxidative dissolution site of Ti(0) than that of perchlorate. However, the chloride showed much higher adsorption affinity to chloride oxidation site. Rate constants of perchlorate reduction and chloride oxidation were directly proportional to current. For Ti(II) consumption model, rate constant of Ti(II) production was directly proportional to current. Rate of chloride oxidation also seemed to proportional to current, but uncertainty prevents making conclusion with confidence regarding dependence of rate constant to current. Both kinetic models described changes in perchlorate concentration well. However, the Ti(II) consumption model was limited in its ability to predict chloride concentration. This might indicate that inhibition of perchlorate reduction was caused by competitive adsorption of perchlorate and chloride on bare Ti(0) surface. However, it cannot be ruled out that other factors caused the limitation of the Ti(II) consumption model. These factors could include computational limitations caused by a lack of available information on things like electrochemical oxidation of chloride on bare Ti(0), Ti(II) oxidation by chlorine, and over estimated transport coefficient of chloride or under estimated transport of coefficient of chlorine. This lack of information could result in calculation of inaccurate values of rate constants. Therefore, further studies required to evaluate kinetic models.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The results shown in this research demonstrate that pitting corrosion developed Ti(0) has the capability to chemically reduce perchlorate and thereby the application of Ti(0) may be possible by promoting pitting corrosion developments to abate contaminants in natural and engineered system. On the other hand, the results of this research imply that the application of pitting developed Ti(0) may not be immediately applicable by several factors including material and electricity costs and possible chloride oxidation. These results provide basic knowledge about Ti(0) process, especially electrochemical and environmental factors affecting perchlorate reduction, perchlorate reduction mechanism, influence of other aggressive and non-aggressive anion presences, and kinetic models that describe the rate of perchlorate reduction on pitting induced Ti(0). Furthermore, this knowledge could be used for further development of a new technology that can treat perchlorate present in natural and engineered system. The specific conclusions obtained from the research are as follows:

1) Perchlorate is a stable compound that is too slowly reduced by common chemical reductants and direct electrochemical reductions under ambient conditions. However, Ti(0) showed capability to reduce the perchlorate to chloride even in ambient natural conditions and the rate of perchlorate reduction was fast enough to be applied in treatment system. This faster perchlorate reduction by Ti(0) was observed only when pitting corrosion was developed on Ti(0). Pitting potential of Ti(0) was dependent on

perchlorate concentration and was 12.53 ± 0.04 V_{NaSCE} for a 100 mM solution of perchlorate. Main product of perchlorate reduction was chloride and relatively small amount of other products such as chlorate and chlorite were accumulated. The chloride concentration was increased by perchlorate reduction, but it was less than the decrease in perchlorate concentration. Besides, the chloride concentration began to decrease after a time that depended on experimental conditions. This chloride concentration changes were believed to be related to chloride oxidation on Ti(0) and its decrease was accelerated with pitting development.

2) Several electrochemical and environmental factors were examined to determine their effects on perchlorate reduction by pitting developed Ti(0). The rate of perchlorate reduction was not affected by imposed electrochemical potential as long as the potential was maintained above the pitting potential of Ti(0). However, the rate of perchlorate reduction was strongly dependent on the applied current. Other factors such as solution pH and surface area of Ti(0) electrodes showed negligible effects on perchlorate reduction. For trace levels of perchlorate reduction, the presence of chloride had both beneficial and adverse effects on perchlorate reduction. Since there was no pitting development only with trace levels of perchlorate in solution, the addition of chloride produced the pitting corrosion on Ti(0) and promoted perchlorate reduction. However, chloride inhibited the rate of perchlorate reduction and thereby the rate of perchlorate reduction was decreased by increasing chloride concentration. The rate of trace levels of perchlorate removal was also dependent on the applied current, but it was not dependent on surface area of Ti(0).

3) Several possible mechanisms were suggested based on literatures and evaluated based on experimental observations to explain perchlorate reduction during pitting corrosion of Ti(0). Direct reduction of perchlorate on bare Ti(0) was not appropriate mechanism. The direct reduction of perchlorate on bare Ti(0) was against thermodynamics due to higher anodic potential on Ti(0) that standard electrode reduction potential for ClO_4^-/Cl^-. Bare Ti(0) metal particles and direct reduction by high ohmic potential drop were also not supported by experimental results including optical microscopic observations, scanning electron microscope (SEM) and X-ray diffraction analyses of the precipitate, dissolution valence measurements and direct reduction of perchlorate on oxide film covered Ti(0) surface. Perchlorate reduction using Ti(II) and Ti(III) containing solution indicated that perchlorate reduction on pitting induced Ti(0) might be caused by dissolved titanium metals. The rate of perchlorate reduction was increased with higher dissolved titanium metal and H^+ concentrations.

4) A hypothetical mechanism that describes formation of uncommon metal ions during electrochemical dissolution of metals suggested that perchlorate reduction on pitting developed Ti(0) would be more likely caused by dissolved Ti(II) and dissolution valence measurements and molar ratio of Ti(0) consumed to perchlorate reduced ($\Delta Ti(0)/\Delta ClO_4^-$) supported the hypothetical mechanism. The hypothetical mechanism proposed that Ti(0) undergoes dissolution to Ti(II). Further oxidation of Ti(II) would be caused by reaction at the electrode surface or with dissolved oxidizing agents. Two hypothetical pathways of Ti(0) dissolution were proposed based on participation of aggressive anion on metal dissolutions. When Ti(0) undergoes dissolution to Ti(II),

aggressive anion is transported from solution to the bare Ti(0) surface through salt film in order to balance the positive charge and concentrated at the at the interface between the bare Ti(0) and salt film. The dissolution of Ti(0) would be accelerated by the adsorption of the aggressive anion on bare Ti(0) and Ti(0) undergoes dissolution with indirect and direct participation of aggressive anion on its dissolution process. Indirect participation pathway proposed that aggressive anion only stimulates oxidative dissolution of Ti(0). However, direct participation pathway suggested that aggressive anion promotes not only oxidative dissolution of Ti(0), but also aggressive anion forms dissolved complex with Ti(II). The salt film works as a barrier and accumulates dissolved Ti(II) at the interface between the salt film and bare Ti(0). The accumulated Ti(II) is oxidized by either oxidant or electrochemically on the surface of bare Ti(0) and possibly on salt film due to a lower potential drop across the salt film.

5) The rate of perchlorate reduction was not or slightly affected by the presence of nitrate, sulfate, and phosphate. These anions interacted with pitting corrosion and their concentrations decreased over time. Nitrate was chemically reduced to nitrite and ammonium and some of it may have formed gaseous compounds such as nitrogen, nitric oxide and nitrous oxide. Both sulfate and phosphate concentrations decreased during pitting. However, their concentration decreases were not related to chemical reduction nor to formation of titanium compounds that contained sulfur or phosphorous, but they were caused by adsorption onto precipitates formed during the reaction. Perchlorate reduction was inhibited by the presences of chloride and bromide, but other aggressive anions such as iodide and fluoride did not inhibit the perchlorate reduction. The

mechanism by which some anions inhibit perchlorate reduction was investigated based on the proposed dissolution mechanisms of Ti(0) to Ti(II). The dissolution mechanism of Ti(0) to Ti(II) with indirect participation of aggressive anion suggested that inhibition mechanism of perchlorate reduction would be caused by oxidation of dissolved Ti(II) by electrochemically generated chlorine and bromine. However, the dissolution mechanism of Ti(0) to Ti(II) with direct participation of aggressive anions proposed that inhibition of perchlorate reduction would be caused by b adsorption tendencies of aggressive anions that promotes pitting corrosion of Ti(0).

6) Perchlorate reduction kinetic by pitting induced Ti(0) was described by interactions of two domains (pit and solution). Two kinetic models were developed based on two possible inhibition mechanisms. Competitive adsorption model was developed based on surface coverage of perchlorate and chloride on bare Ti(0) surface and Ti(II) consumption model was developed based on Ti(II) oxidation by electrochemically developed chlorine. Both models well predicted perchlorate concentration changes in the solution. Competitive adsorption model showed that chloride has higher adsorption affinity on both oxidative dissolution of Ti(0) and chloride oxidation sites. Also, rate of perchlorate removal and chloride oxidation were directly proportional to current applied. For Ti(II) consumption model, the rate constant of Ti(II) production was dependent on current. The rate of chloride oxidation is also believed to be proportional to current. However, uncertainty prevents making conclusion with confidence regarding dependence of rate constant to current. Both kinetic models described changes in perchlorate concentration well. However, the Ti(II) consumption

model was limited in its ability to predict chloride concentration. This limitation was probably caused by a lack of available information on things like electrochemical oxidation of chloride on bare Ti(0), Ti(II) oxidation by chlorine, and over estimated transport coefficient of chloride or under estimated transport of coefficient of chlorine. Further investigations are required to develop Ti(II) consumption based model.

CHAPTER VIII

RECOMMENDATION FOR FUTURE WORKS

It has been shown that perchlorate is rapidly reduced to chloride during pitting corrosion of titanium and it is believed to be caused by reaction with by dissolved Ti(II). The rate of perchlorate reduction is sufficiently rapid for application as a treatment process. However, there are several limitations which restrict its immediate application to treatment systems. These limitations are: 1) high energy costs, 2) chloride oxidation, and 3) unwanted titanium dissolution during treatment of trace levels of perchlorate. These limitations seem to be caused by different problems. However, these restrictions are associated with the high potential required to develop the pitting corrosion on titanium, which is over 12.0 V. Thus, this high pitting potential causes the high energy cost and promotes oxidation of chloride to chlorine. Moreover, high electrical energy input dissolves more titanium than needed to reduce perchlorate. Therefore, lowering the pitting potential of titanium is a key to overcoming the high cost of the electrochemical titanium process and makes it feasible for field application. Furthermore, it would be advantageous for field applications if the titanium were to undergo dissolution without any electrical energy input.

Several modifications could possibly affect the pitting potential of a metal and they can be classified as being environmental or internal factors (*62*). Environmental factors important in developing a water treatment process include solution composition, solution temperature, and solution flow. Changing the solution composition by adding aggressive anions, especially Br^-, could greatly decrease the pitting potential (*62, 67*). However, this study has shown that Br^- decreases the rate of perchlorate reduction, possibly by competing with perchlorate for sites on Ti(0) or Ti(II) consumption by electrochemically produced Br_2. Moreover, the presence of Br^- can produce secondary contamination by the oxidation of Br^- to BrO_3^- by reaction with O_3 (*164, 165*). Increasing the solution temperature also decrease the pitting potential of titanium (*62, 166-168*), but this will greatly increase the energy costs. Slowing the solution flow (*62, 169, 170*) has only a minor effect on lowering the pitting potential of titanium.

A promising methodology for lowering the pitting potential of titanium would be the alloying titanium with other metals and this is the primary internal modification method. It has been known that adding alloys to a metal can have beneficial effects on increasing corrosion resistance, while it can also have detrimental effects such as increasing susceptibility to corrosion. For titanium, the additions of niobium and zirconium increased corrosion resistance (*171*). However, the additions of aluminum (*172, 173*) and iron (*172*) greatly decreased the corrosion resistance. For example, pure titanium required a potential of approximately 10.0 V_{SCE} in 0.5 N NaCl solutions to begin pitting corrosion. However, additions of aluminum to titanium greatly lowered the pitting potential and the extent of the decrease depended on the amount of aluminum added. Aluminum has a pitting potential of −0.70 V_{SCE} in 0.5 N of NaCl solutions. The pitting potentials of different mixtures of titanium and aluminum in 0.5 N NaCl have been reported: 1.5 to 1.8 V_{SCE} for Ti_3Al, −0.02 V_{SCE} for TiAl, and −0.46 V_{SCE} for $TiAl_3$. (*173*). Iron also showed similar behavior. Increasing iron contents up to 25 % of total weight dropped the pitting potential 0.72 V_{SCE} in Hank's solution (*172*). Thus, the adding iron or aluminum to titanium is a promising solution to the problem of high pitting potentials for titanium.

Recent environmental forensic studies reported that perchlorate often coexists with organic contaminants such as trichloroethene (TCE), tetrachloroethene (PCE), and vinyl chloride (VC) (*174*) as well as with nitrate, which is a common inorganic contaminant in groundwater (*9, 175*). Several studies have suggested that zero-valent iron and aluminum can abate chlorinated organic compounds and inorganic contaminants (*176-181*) by chemical reductions through direct contact at metal surface, as well as by reaction with dissolved metal ions and elemental hydrogen produced by the zero-valent metals (*83, 182*). Therefore, the alloying titanium with iron or aluminum could possibly achieve not only the removal of perchlorate, but also removal of co-contaminants such as TCE, PCE, VC and NO_3^-.

For electrochemically controlled system such as using DC power supply and potentiostat, alloyed titanium with iron and aluminum would be dissolved non-selectively. However, there is a possible problem associated with the alloying titanium with iron or aluminum during its dissolution without electrochemical control. Titanium has a more electropositive potential than iron and aluminum, so it is possible that less noble metals, such as iron and aluminum, would preferentially dissolve. This selective leaching is called demetalification and is an example of micro-scale bimetallic corrosion. When two metals having different electrode potentials are alloyed, current would flow from the metal whose potential is more electronegative to the metal whose potential is more electropositive (*59, 60*). Thus, it is possible that the iron and aluminum could work as anodic metals with titanium as a cathodic metal, which means that only iron and aluminum would undergo dissolutions. However, the selective leaching can be minimized by mixing (not alloying) or contacting a more noble metal such as graphite when alloys undergo chemical dissolution (*60*), and controlling electrochemical potentials when alloys undergo electrochemical dissolution (*183, 184*).

Future research to extend this dissertation study should focus on the application of the alloying iron and aluminum with titanium in order to overcome the disadvantages of electrochemical titanium process such as high energy cost, chloride oxidation and inefficiency in removing trace levels of perchlorate. Furthermore, it will be worthwhile to investigate how well organic and inorganic co-contaminants are removed by the modified treatment process.

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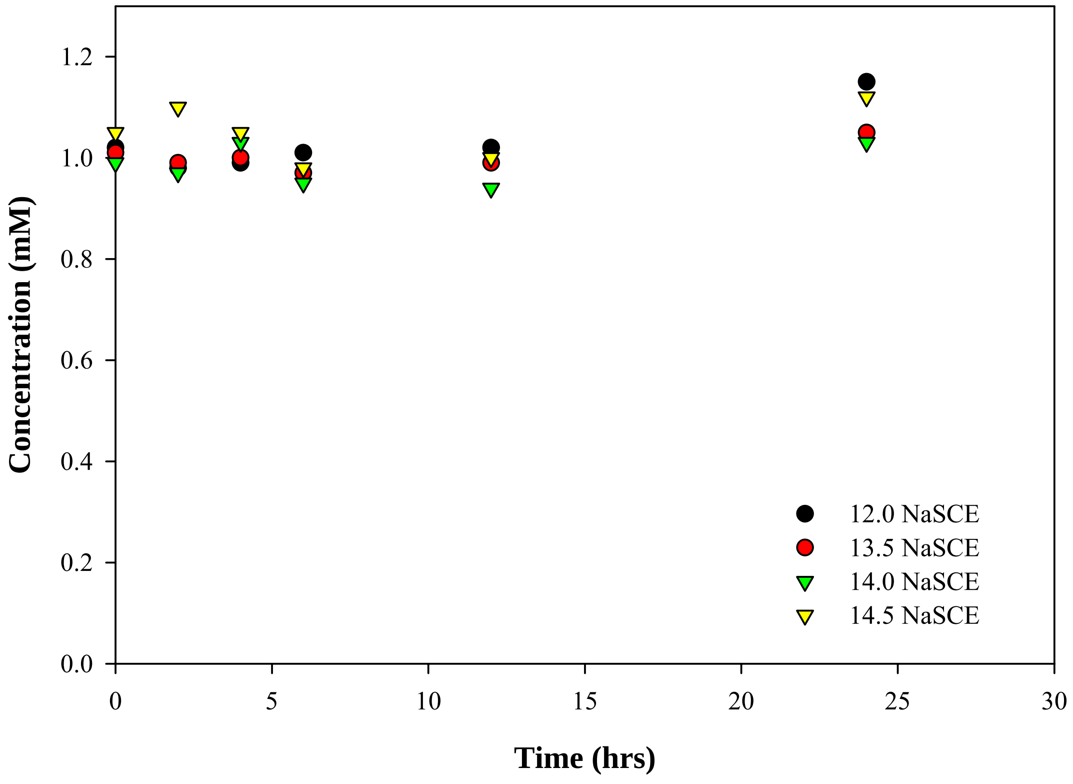
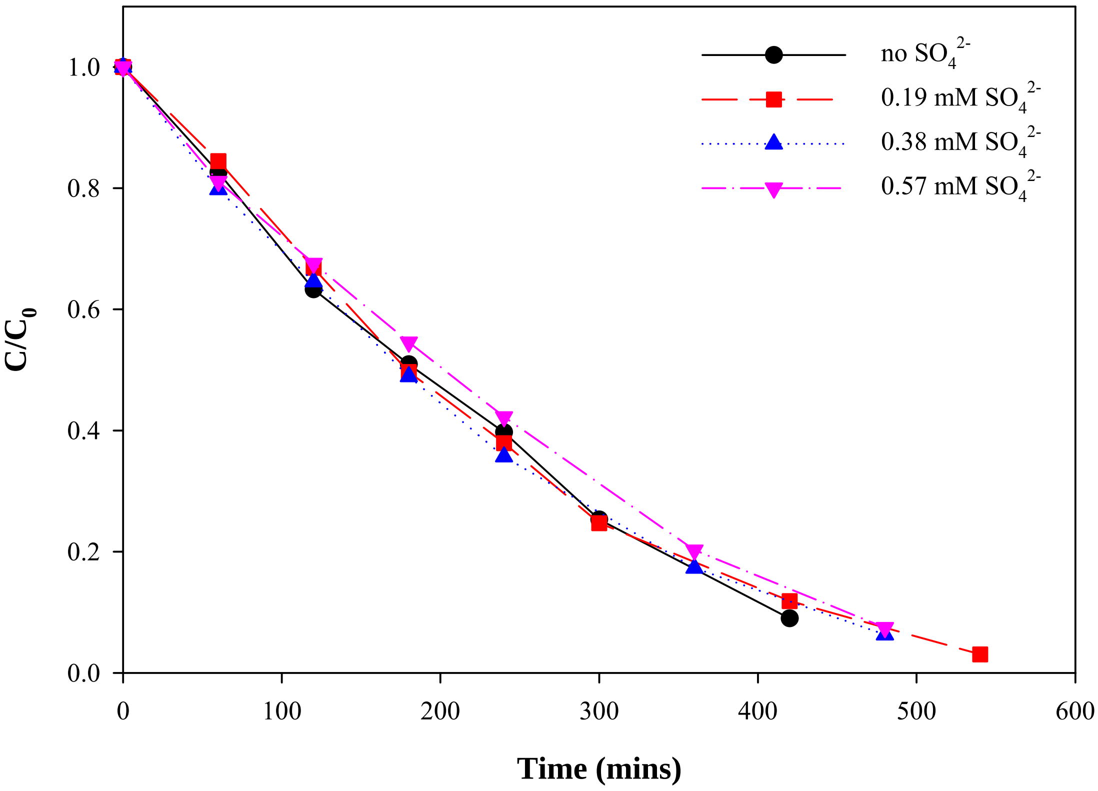
APPENDIX A

ADDITIONAL FIGURES



.1

APPENDIX A.1 Examinations of possible perchlorate reduction at Pt cathode. Anode was graphite.



APPENDIX A.2. Effect of sulfate on perchlorate reduction with some data shifted in time. Data for 0.38 and 0.57 mM sulfate shifted 60 min and data at lower times eliminated.

APPENDIX B

MATLAB PROGRAM

B.1 COMPUTER PROGRAM (MATLAB®) TO PREDICT RATE CONSTANT AND INHIBITION CONSTANTS FOR COMPETITIVE ADSORPTION BASED MODEL

```
global I ClO_0 Cl_0 K beta1 KII

load File name.txt % load data file
matrix= File name;%assign loaded data as matrix
I=50; % current
t_data=matrix(:,1);%assign the time
ClO_data=(matrix(:,2)); % assign perchlorate data
Cl_data=(matrix(:,3)); % assign chloride data

ClO_0=ClO_data(1); % initial concentration of perchlorate
Cl_0=Cl_data(1); % initial concentration of chloride

Cl_removed=(ClO_0-ClO_data+Cl_0-Cl_data); % removed chloride concentration
[b,bint]=regress(Cl_removed,t_data); % conduct linear regression
Cl_removed_model=b*t_data; % obtain model data
K=b; % assign slope to K

KI_guess=[2.71e-5/0.8*I 2.8734e-001]; % initial guess

[beta,r,j]=nlinfit(t_data,ClO_data,@Kobs_cal_1,KI_guess);
% nonlinear regression with nlinfit function to obtain kobs,ClO4 & KI
ci=nlparci(beta,r,j); % 95% confidential interval
beta1=beta;

[beta_1,r_1,j_1]=nlinfit(t_data,Cl_data,@Kobs1_cal_1,[0.15]);
% nonlinear regression with nlinfit function to obtain KI,ClO4
ci_1=nlparci(beta_1,r_1,j_1);
KII=beta_1;
ci_1;

[t_out,C_out]=ode45(@Kobs_cal_3, [0:0.5:t_data(end)], [ClO_0,Cl_0],[],[I]);
% solve ode and obtain model values
```

```
plot(t_data,ClO_data,'o',t_out,C_out(:,1),'-',t_data,Cl_data,'*',t_out,C_out(:,2),'--')
% compare model values with experimental data
```

……

```
function  clo_out=Kobs_cal_1(beta,t)

global ClO_0 Cl_0
tspan=t ;
[tout,cout]= ode45(@Kobs_cal_2, tspan, [ClO_0,Cl_0],[],beta); % solve ode with nlinfit
clo_out=cout(:,1);



function  dcdt=Kobs_cal_2(t,c,beta)

global I K

Kobs=beta(1); %kobs,ClO4
KI=beta(2); % KI

ClO=c(1);
Cl=c(2);

r=Kobs*ClO/(ClO+KI*Cl); % calculate perchlorate with ode function

dcdt(1)=-r; % calculate perchlorate concentration
dcdt(2)=r-K; % calculate chloride concentration
dcdt=dcdt';
```

……

```
function  dcdt=Kobs_cal_3(t,c,beta)

global I K beta1 KII

I=beta;

ClO=c(1);
Cl=c(2);
Kobs=beta1(1);
KI=beta1(2);
kcl=2.18e-5/0.8;
% rate of chloride concentration decrease in solution (0.8=solution volume)
```

```
r=Kobs*I*ClO/(ClO+KI*Cl);% perchlorate concentration

dcdt(1)=-r;
dcdt(2)=r-kcl*I*Cl/(Cl+KII*ClO);% chloride concentration
dcdt=dcdt';
```

B.2 COMPUTER PROGRAM (MATLAB®) TO PREDICT RATE CONSTANTS FOR TI(II) COMSUMPTION BY CHLORINE BASED MODEL

```
load File Name.txt % load data file
matrix=File Name;%assign loaded data as matrix
a=50; % current
t_data=matrix(:,1);%assign the time
ClO_data=(matrix(:,2)); % assign perchlorate data
Cl_data=matrix(:,3); % assign chloride data

ClO_0=ClO_data(1); % initial perchlorate concentration in the solution
Cl_0=Cl_data(1); % initial chloride concentration in the solution


K_guess=[16.487  , 42.881,  1.49e+005 ,1.35e+001 ]; % initial guesses
[beta,r,j]=nlinfit(t_data,ClO_data,@K1_cal_1,K_guess);
% nonlinear regression with nlinfit function
ci=nlparci(beta,r,j);% 95% confidential level

kcl=beta(1); %rate constant chloride oxidation in the pit
kcl2=beta(2); % rate constant of Ti(II) odixation by hlorine
K=beta(2); % rate constant of perchlorate reduction
kprod=beta(3); % rate constant of Ti(II) production

[t_out,C_out]=ode23s(@K1_cal_3,[0 t_data(end)],[ClO_0, ClO_0,Cl_0,
Cl_0,0,0],[],beta);
plot(t_data,ClO_data,'o',t_out,C_out(:,1),'-',t_data,Cl_data,'*',t_out,C_out(:,3),'--')

…………………………………………………………………………………………
function  ca=K1_cal_1(beta,t)

global ClO_0 Cl_0
tspan=t;
[tout,cout]= ode23s(@K1_cal_2, tspan, [ClO_0, ClO_0, Cl_0,Cl_0, 0, 0],[],beta);
cout
ca=cout(:,1);

…………………………………………………………………………………………

function  dcdt=K1_cal_2(t,c,beta)

global ClO_0 Cl_0 Vp a
```

```
kcl=beta(1); %rate constant chloride oxidation in the pit
kcl2=beta(2); % rate constant of Ti(II) odixation by hlorine
K=beta(2); % rate constant of perchlorate reduction
kprod=beta(3); % rate constant of Ti(II) production

ClO=c(1); % perchlorate in solution
ClOp=c(2); % perchlorate in the pit
Cl=c(3); % chloride in solution
Clp=c(4); % chloride in the pit
Cl2=c(5); % chlorine in the pit
Ti=c(6); Ti(II) concentration

Vp=0.0001; %pit volume
Vs=0.8; % solution volume
Vp1=Vp*1000; % %pit volume in cm3 scale
radius=(Vp1*3/2*pi)^(1/3); % radius of pit
kcltrans=50000;% mass transfer rate of perchlorate and chloride

r=K*Ti*ClOp;

dcdt(1)=-Vp/Vs*r; %d[ClO4-]/dt perchlorate concentration in solution
dcdt(2)=kcltrans*(ClO-ClOp)-r; % d[ClO4-]p/dt perchlorate concentration in the pit
dcdt(3)=Vp/Vs*(-kcl*Clp+r+B*2*kcl2*Ti*Cl2);
% d[Cl-]s/dt chloride concentration in the solution
dcdt(4)=kcltrans*(Cl-Clp)-kcl*Clp+r+B*2*kcl2*Ti*Cl2;
% d[Cl]p/dt chloride concentration in the pit
dcdt(5)=kcl*Clp-B*kcl2*Ti*Cl2-T*3*8.4e-4/(radius^2)*Cl2;
% d[Cl2]/dt chlorine concentration in the pit
dcdt(6)=kprod-r-B*kcl2*Ti*Cl2;
%d[Ti]/dt Ti(II) concentration in the pit

dcdt=dcdt';
```

…………………………………………………………………………………………

```
function  dcdt=K1_cal_3(t,c,beta)

global ClO_0 Cl_0 Vp a

kcl=beta(1); %rate constant chloride oxidation in the pit
kcl2=beta(2); % rate constant of Ti(II) odixation by hlorine
K=beta(2); % rate constant of perchlorate reduction
kprod=beta(3); % rate constant of Ti(II) production
```

```
ClO=c(1); % perchlorate in solution
ClOp=c(2); % perchlorate in the pit
Cl=c(3); % chloride in solution
Clp=c(4); % chloride in the pit
Cl2=c(5); % chlorine in the pit
Ti=c(6); Ti(II) concentration

Vp=0.0001; %pit volume
Vs=0.8; % solution volume
Vp1=Vp*1000; % %pit volume in cm3 scale
radius=(Vp1*3/2*pi)^(1/3); % radius of pit
kcltrans=50000;% mass transfer rate of perchlorate and chloride

r=K*Ti*ClOp;

dcdt(1)=-Vp/Vs*r; %d[ClO4-]/dt perchlorate concentration in solution
dcdt(2)=kcltrans*(ClO-ClOp)-r; % d[ClO4-]p/dt perchlorate concentration in the pit
dcdt(3)=Vp/Vs*(-kcl*Clp+r+B*2*kcl2*Ti*Cl2);
% d[Cl-]s/dt chloride concentration in the solution
dcdt(4)=kcltrans*(Cl-Clp)-kcl*Clp+r+B*2*kcl2*Ti*Cl2;
% d[Cl]p/dt chloride concentration in the pit
dcdt(5)=kcl*Clp-B*kcl2*Ti*Cl2-T*3*8.4e-4/(radius^2)*Cl2;
% d[Cl2]/dt chlorine concentration in the pit
dcdt(6)=kprod-r-B*kcl2*Ti*Cl2;
%d[Ti]/dt Ti(II) concentration in the pit

dcdt=dcdt';
```

APPENDIX C

TABULATED DATA USED FOR KINETIC MODEL CALIBRATIONS

Table C.1 Chloride oxidation with different current

Current = 25 mA		
Time (min)	Cl^- (mg/L)	Cl^- (mM)
0	38.1	1.08
60	37.6	1.06
120	36.6	1.03
195	35.0	0.99
240	33.6	0.95
300	30.9	0.87
420	28.1	0.79
540	23.9	0.67
720	18.5	0.52
900	14.4	0.41
1080	8.8	0.25
1360	1.70	0.05

Current = 50 mA		
Time (min)	Cl^- (mg/L)	Cl^- (mM)
0	38.0	1.07
30	36.8	1.04
60	35.4	1.00
120	31.7	0.89
180	28.5	0.80
240	25.2	0.71
307	21.2	0.60
420	15.1	0.43
540	8.0	0.22
645	3.1	0.088

Current = 75 mA		
Time (min)	Cl^- (mg/L)	Cl^- (mM)
0	37.1	1.05
30	34.9	0.98
60	33.0	0.93
120	27.8	0.79
180	23.8	0.67
245	17.7	0.50
310	14.7	0.42
360	11.7	0.33
420	7.1	0.20
446	4.5	0.13

Current = 100 mA		
Time (min)	Cl^- (mg/L)	Cl^- (mM)
0	37.2	1.05
35	34.0	0.96
64	29.1	0.82
120	23.6	0.66
180	19.9	0.56
245	13.2	0.37
300	8.5	0.24
320	6.3	0.18

Table C.1 Continued

Current = 125 mA			**Current = 150 mA**		
Time (min)	Cl^- (mg/L)	Cl^- (mM)	Time (min)	Cl^- (mg/L)	Cl^- (mM)
0	36.5	1.03	0	37.9	1.07
30	33.4	0.94	30	36.2	1.02
60	29.2	0.82	60	30.0	0.85
90	25.5	0.72	90	25.3	0.71
120	19.7	0.56	150	16.7	0.47
190	15.2	0.43	180	13.0	0.37
240	8.9	0.25	210	9.0	0.25
265	5.8	0.16	220	6.4	0.18

Table C.2 Perchlorate reduction with different current

Current = 37 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	1.01	0.006
30	0.99	0.013
60	0.98	0.012
120	0.94	0.023
180	0.90	0.037
300	0.77	0.075
420	0.63	0.109
547	0.48	0.137
720	0.31	0.146

Current = 50 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	1.00	0.01
30	0.94	0.02
60	0.89	0.03
120	0.80	0.06
180	0.71	0.09
294	0.54	0.14
420	0.38	0.17
540	0.26	0.18
720	0.14	0.17

Current = 50 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	1.00	0.000
60	0.96	0.037
120	0.85	0.072
180	0.76	0.108
240	0.70	0.139
300	0.42	0.219
460	0.37	0.225
510	0.23	0.218
780	0.15	0.222
960	0.06	0.160

Current = 74 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	0.99	0.005
30	0.91	0.022
60	0.85	0.029
120	0.76	0.044
180	0.69	0.066
300	0.54	0.101
420	0.40	0.124
540	0.27	0.128
720	0.10	0.078

Current = 75 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	1.01	0.000
80	0.86	0.107
120	0.76	0.112
255	0.50	0.192
300	0.42	0.204
360	0.35	0.225
420	0.28	0.248
480	0.20	0.229
540	0.15	0.205

Current = 80 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	0.94	0.007
30	0.89	0.022
60	0.84	0.037
120	0.70	0.076
180	0.59	0.115
300	0.38	0.160
420	0.22	0.172
540	0.10	0.128
660	0.02	0.053

Table C.2 Continued

Current = 100 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	0.99	0.000
60	0.77	0.073
120	0.62	0.126
180	0.48	0.158
240	0.37	0.186
360	0.18	0.198

Current = 100 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	1.03	0.005
30	0.88	0.035
60	0.79	0.054
120	0.60	0.126
180	0.44	0.164
240	0.31	0.182
300	0.21	0.195
360	0.13	0.159

Current = 111 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	0.99	0.008
30	0.90	0.029
60	0.81	0.050
120	0.63	0.095
180	0.46	0.133
300	0.20	0.146
420	0.04	0.061

Current = 125 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	1.02	0.000
60	0.77	0.089
120	0.65	0.170
180	0.50	0.227
240	0.33	0.257
300	0.21	0.241

Current = 150 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	1.04	0.000
60	0.84	0.107
120	0.59	0.178
180	0.42	0.250
240	0.24	0.248
270	0.21	0.297

Current = 200 mA		
Time (min)	ClO_4^- (mM)	Cl^- (mM)
0	0.99	0.004
30	0.79	0.045
60	0.63	0.086
90	0.51	0.104
120	0.35	0.144
180	0.17	0.138

APPENDIX D

MOVIE FILES

Video Clip D.1 Observation of hydrogen gas evolution from pitting site (25 mM perchlorate)

Video Clip D.2 Observation of hydrogen gas evolution from pitting site (25 mM chloride)

Video Clip D.3 Observation of initial pitting development in perchlorate solution

Video Clip D.4 Observation of initial pitting development in chloride solution

VITA

Chun Woo Lee was born in YoungChun, Korea. He received his B.S. degree in environmental engineering from Pukyung National University in Korea in 1999 and a M.S. degree in civil engineering from Texas A&M University in College Station in 2003. His research interests include physico-chemical treatments of contaminants including coagulation, zero-valent metal treatment, and the electrochemical process. Also, he is interested in the fundamental aspect of chemical kinetic and equilibrium models for water and wastewater treatment. His permanent address is 1-206 Gu-Il Apt, Jae Song 2Dong, Haeundae Gu, Busan, Korea.