



Perchlorate reduction during electrochemically induced pitting corrosion of zero-valent titanium (ZVT)

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ABSTRACT

Zero-valent metals and ionic metal species are a popular reagent for the abatement of contaminants in drinking water and groundwater and perchlorate is a contaminant of increasing concern. However, perchlorate degradation using commonly used reductants such as zero-valent metals and soluble reduced metal species is kinetically limited. Titanium in the zero-valent and soluble states has a high thermodynamic potential to reduce perchlorate. Here we show that perchlorate is effectively reduced to chloride by soluble titanium species in a system where the surface oxide film is removed from ZVT and ZVT is oxidized during electrochemically induced pitting corrosion to produce reactive soluble species. The pitting potential of ZVT was measured as 12.77 ± 0.04 V (SHE) for a 100 mM solution of perchlorate. The rate of perchlorate reduction was independent of the imposed potential as long as the potential was maintained above the pitting potential, but it was proportional to the applied current. Solution pH and surface area of ZVT electrodes showed negligible effects on rates of perchlorate reduction. Although perchlorate is effectively reduced during electrochemically induced corrosion of ZVT, this process may not be immediately applicable to perchlorate treatment due to the high potentials needed to produce active reductants, the amount of titanium consumed, the inhibition of perchlorate removal by chloride, and oxidation of chloride to chlorine.

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1. Introduction

Reduction of perchlorate (ClO_4^-) has been attempted with transition metal ions [1], zero-valent metals [2–5], and several metal electrodes [6,7]. However, perchlorate reduction occurs too slowly under ambient conditions for use in remediation and water treatment processes. A few studies have reported reduction of perchlorate at reasonable rates, but they were conducted at high temperature and pressure, or under strongly acidic conditions, or both [8–11]. It has been reported that the low reactivity of perchlorate is related to its high activation energy barrier in redox reactions [12]. This high activation energy originates from its structure and electronic configuration [1,12,13]. The structure of perchlorate is as a 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) [1]. During a reduction by electron transfer, the electron is received by the LUMO. However, unfilled orbitals in perchlorate are at too high an energy level to effectively interact with potential electron donors [1]. As direct electron transfer is difficult to perchlorate, it is typically reduced by removing one of its oxygen atoms [13]. However, this transfer can occur only when the electron-donor orbital of the reducing agent has appropriate symmetry and energy levels to effectively dissect the oxygen atom from the perchlorate [1] or when the reducing agent forms a stable “yl” oxidized product by forming $\text{M}=\text{O}^{n+}$ [13]. 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 and their partially oxidized dissolved metal species 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

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of the contaminants with bare metal, by reaction with partially oxidized dissolved metal ions, and by reaction with elemental hydrogen produced by reaction of water with the metal [3,14]. Iron [3,5], aluminum [4], zinc [5], and nickel [2] have been examined as reductants for perchlorate, but they showed very slow kinetics.

Titanium 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 [1,15–17]. Moreover, titanium has a high oxygen affinity and forms a “yl” oxidized product by forming TiO^{2+} [18]. This indicates that titanium compounds can effectively stabilize oxygen atoms transferred from perchlorate and promote perchlorate reduction. However, since zero-valent titanium (ZVT) 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 [19–21]. 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, induces rapid metal dissolution at the localized pitting site and the dissolved metal ions undergo hydrolysis reactions that develop a high concentration of H^+ inside of the pit [22–24]. Recent studies support the idea of oxide film removal via pitting corrosion to expose underlying reactive metal. Gaspar et al. [25] 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 by exposing the underlying metal or partially oxidized dissolved metal ions. 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 [26]. A similar effect is observed when the reactions occur in solutions with elevated concentrations of chloride [26]. However, pitting corrosion, especially for ZVT, 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 ZVT. However, application of an anodic potential can accelerate and maintain pitting corrosion.

In this part of the study, ZVT was examined for its ability to destroy perchlorate during electrochemically induced pitting corrosion. In the second part, evidence about the mechanism of perchlorate reduction will be presented. Pitting potentials of ZVT were determined with varying perchlorate concentrations. Various potentials, currents, surface areas of ZVT, 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 with various currents, chloride concentrations, and surface area concentrations of ZVT to identify possible application of this technology to remove perchlorate at the trace levels found in natural environments.

2. Materials and methods

2.1. Chemicals

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 and pH was adjusted with NaOH (97%, Sigma). This was done to minimize effects of anions that would be added by using HCl, H_2SO_4 or HNO_3 to adjust pH. ZVT sheets (99.97%) were purchased from ESPI Corp. Inc. and cut to appropriate sizes for the experiments. The ZVT 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.

2.2. Pitting potential and 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 sodium chloride saturated calomel reference electrode that is guided by a bridge tube. The potential of the sodium chloride saturated calomel reference electrode is written as NaSCE [27] or SSCE [28] and its potential is 0.24 V negative of standard hydrogen electrode (SHE) [28]. All potentials are reported in this paper with respect to the SHE. Throughout all experiments, the working ZVT electrode had an effective surface area of 5.0 cm^2 and the counter electrode was Pt mesh with dimensions of 2 cm \times 2 cm. Electrode potential was controlled using a potentiostat (Solartron Analytical, Model 1287A).

Pitting potentials of ZVT were measured by the potentiodynamic polarization method in which the open-circuit potential (OCP) was swept to 14.7 V (SHE) 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 tip 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.

2.3. Constant current experiments

Electrochemical experiments on perchlorate reduction 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 ZVT sheets (99.97%) and constant current was supplied by a DC power supply (Kenwood, Model PW18-1.8AQ). The electrode 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 \times 5.1 cm \times 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 \times 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.

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 [3], 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. Results and discussion

3.1. Pitting potential of titanium

Fig. 1 shows that the pitting potential depends on the concentration of perchlorate. The pitting potential for a 100 mM solution of perchlorate is $12.77 \pm 0.04 \text{ V}$. Basame and White [29] reported that the pitting potentials are $9.61 \pm 0.43 \text{ V}$ for 100 mM chloride, $7.71 \pm 0.71 \text{ V}$ for 100 mM iodide (I^-) and $1.61 \pm 0.28 \text{ V}$ for 100 mM bromide (Br^-), respectively. A higher pitting potential for perchlorate than for other halide ions is consistent with what has been reported for Al, Fe, and Zr [30–32].

3.2. Influence of potential on perchlorate reduction

Experiments were conducted to evaluate perchlorate reduction during pitting corrosion and they were based on results of experiments to determine the pitting potentials. 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 (anode, ZVT) and the counter electrode (cathode, Pt mesh) as soon as potential was applied. Oxygen was expected to be formed at the ZVT electrode due to oxidation of water if ZVT was not being oxidized, while

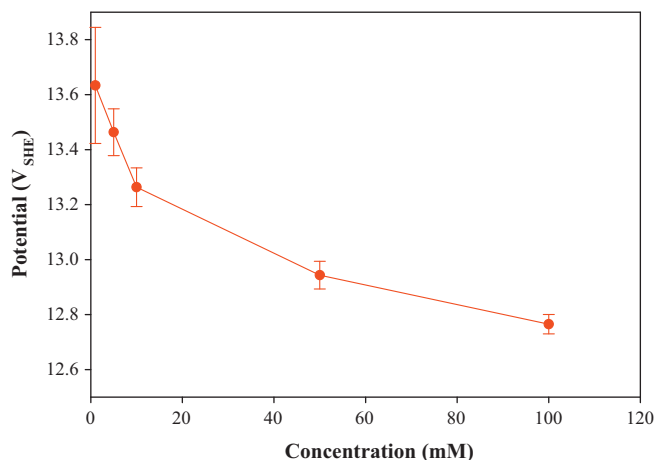


Fig. 1. Pitting potentials as a function of the concentration of perchlorate.

hydrogen was expected to be formed at the Pt electrode due to reduction of water. Gas bubbles slowly diminished over time and only small gas bubbles were observed coming from the ZVT electrode after pitting corrosion began. However, gas evolution from the Pt mesh counter electrode persisted over the course of the experiment. Fig. 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 12.2 V, which is less than the pitting potential (13.6 V, Fig. 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. The possibility that perchlorate was being reduced at the Pt counter electrode was considered. 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 14.7 V

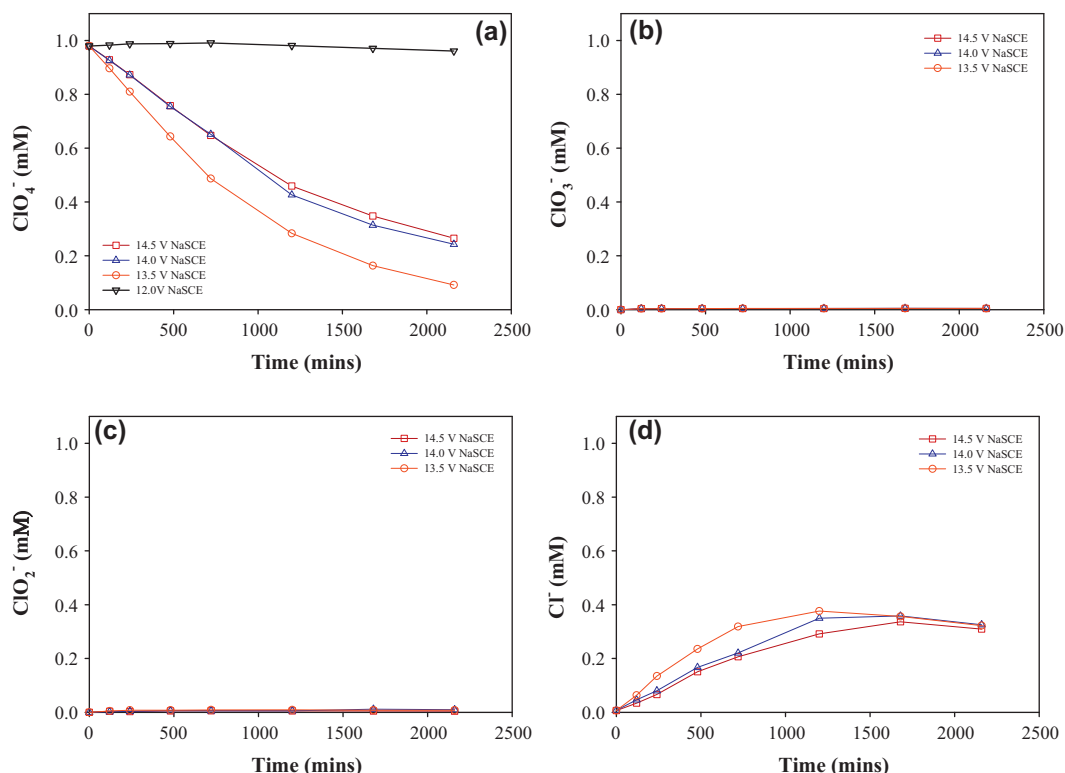


Fig. 2. Influence of imposed potential on removal of perchlorate and production of products. (a) perchlorate, (b) chlorate, (c) chlorite, and (d) chloride.

was imposed. The concentration of perchlorate did not change over time. Other potentials (14.2, 13.7, and 12.2 V) were also examined and showed no changes in perchlorate concentration. These results are presented in Supporting Information (Fig. S1). Additionally, previous studies [33–35] supported that electrocatalytic perchlorate reduction at the Pt surface is negligible.

Generally, it is expected that higher potentials would produce higher current and thereby more pitting corrosion. However, the perchlorate reduction rate decreased with increasing applied potential (Fig. 2a). Furthermore, the average current decreased (16.3, 11.5, and 9.4 mA) as potential increased (13.7, 14.2, and 14.7 V, respectively). This unusual behavior is caused by the formation of surface oxide films of different thicknesses. There is an apparent contradiction in the film growing and being broken down during pitting corrosion. However, pitting corrosion is a localized breakdown of the oxide film that promotes corrosion. The film can be simultaneously breached in one area while growing in another and increasing the imposed potential could increase the film growth. The thickness of the oxide film formed is directly proportional to the magnitude of the applied potential and this thickness can be estimated from the color of the surface oxide film on titanium [36]. 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 [36–38]. 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 pits and reduce the number of pits [32], thereby resulting in lower currents.

Fig. 2b–d illustrates how concentrations of the products of perchlorate reduction change with time. 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^-) ($<4.7 \mu\text{M}$) and chlorite (ClO_2^-) ($<11.7 \mu\text{M}$) 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 [27]. 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 13.7, 14.2, and 14.7 V, respectively. These low recoveries of Cl could be caused by oxidation of chloride to chlorine (Cl_2). The pitting potential of ZVT is greater than the standard oxidation potential for converting chloride to chlorine, so it is possible that this conversion occurs on the surface of ZVT.

3.3. Electrochemical chloride oxidation

Oxidation of chloride to chlorine, chlorite, chlorate, and perchlorate was further examined in experiments conducted with a solution of 1 mM chloride with an imposed current of 1 mA. Fig. 3 shows that the chloride concentration decreases over time, but the rate of chloride removal is different after pitting corrosion begins. Small amounts of chlorate ($<9.7 \mu\text{M}$) and chlorite ($<3.8 \mu\text{M}$), 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.

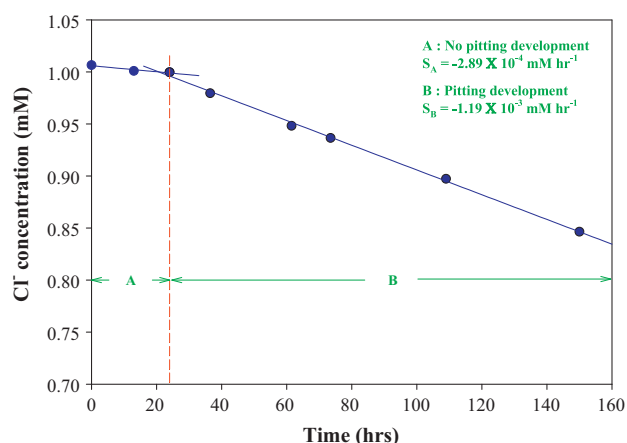


Fig. 3. Chloride concentrations over time during electrochemical experiments at 1 mA current.

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 that observed bromide (Br^-) oxidation on the ZVT surface supports the supposition that chloride is oxidized at the pitting site [21]. Scanning electrochemical microscopy (SECM) showed that bromide is oxidized to bromine (Br_2) at localized sites on ZVT that correspond to pitting sites. Therefore, the results in Figs. 2 and 3 indicate that both oxidation and reduction reactions take place simultaneously at pitting sites on ZVT. The oxidation occurs at the metal surface that forms the boundary of the pit, while the reduction occurs in the solution of the pit.

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. Fig. 4a shows that the rate of perchlorate reduction is increased by raising the current. Fig. 4a also shows that the experiments at high currents ended earlier, due to the earlier depletion of perchlorate and chloride, which results in higher voltages being necessary to sustain a constant current. The concentration of chloride oxidized is calculated using a material balance on Cl with the following assumptions: (1) perchlorate is only reduced to chloride (no accumulation of chlorate and chlorite) and (2) chloride oxidation is the only important mechanism of chloride removal. The concentration of chloride oxidized at a given time is calculated as follows.

$$[\text{Cl}^-]_{t,\text{ox}} = [\text{ClO}_4^-]_i - [\text{ClO}_4^-]_t + [\text{Cl}^-]_i - [\text{Cl}^-]_t \quad (1)$$

where $[\text{Cl}^-]_{t,\text{ox}}$ represents total chloride concentration oxidized at a given time (t), $[\text{ClO}_4^-]_i$ and $[\text{Cl}^-]_i$ are initial perchlorate and chloride concentration, and $[\text{ClO}_4^-]_t$ and $[\text{Cl}^-]_t$ are perchlorate and chloride concentrations at a given time. Fig. 4b presents the concentration of chloride oxidized over time with the lines representing linear regressions. The amount of chloride oxidized increases with increasing current. Fig. 4a shows that the perchlorate concentrations gradually decreased over time for all currents, but that 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,

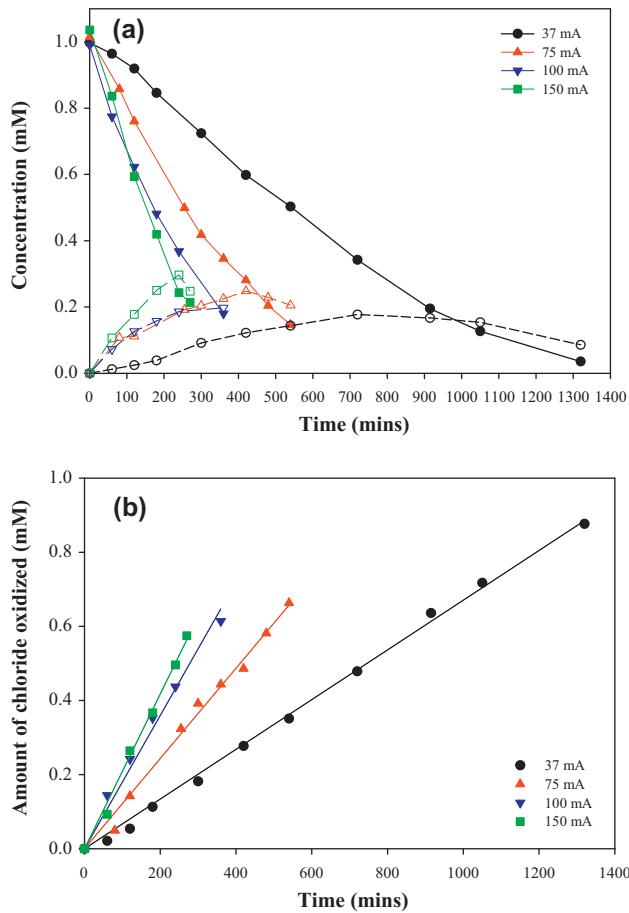


Fig. 4. Effect of current on perchlorate reduction and chloride production. (a) Perchlorate (filled points) and chloride (emptied points) concentrations and (b) amount of chloride oxidized. Surface area concentration was $92.5 \text{ cm}^2/\text{L}$.

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 [39].

$$m = \frac{Q_r}{nF} \quad (2)$$

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 ($96,485 \text{ C mol}^{-1}$), Q_r is total amount of electrical charge (C) that passed through the electrode. If current remains constant over time, then the total amount of charge passed is equal to the product of the current and time.

$$m = \frac{It}{nF} \quad (3)$$

where I is current (A), and t is overall reaction time (s). This relation indicates that higher current will cause electrochemical conversions to occur to a greater extent. In general, two electrochemical conversions can be developed at the ZVT anode during pitting corrosion. One is electrochemical oxidation of an external compound on the ZVT surface and the other is electrochemical dissolution of ZVT. Oxidation of chloride to chlorine is an example of the first type of reaction. Oxidation of ZVT to titanium ions is an example

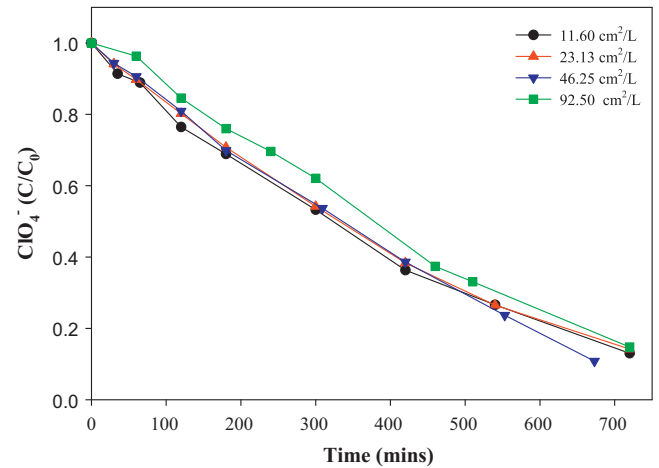


Fig. 5. Influence of surface area concentration of titanium electrode on perchlorate reduction. Initial perchlorate concentration was $0.98 \pm 0.017 \text{ mM}$ and current was 50 mA .

of the second. Perchlorate is reduced to chloride during the pitting corrosion of ZVT, so chloride is made available for oxidation at the electrode surface. Thus, it is inferred that higher currents increase the rate of pitting corrosion which results in higher the rates of titanium metal ion dissolutions (active reductants) at the pitting site and that may increase the 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 [32]. Thinner films and higher anion concentrations, potentials, and current densities result in shorter induction times. Since the current density is defined as the current divided by the surface area, shorter induction times are expected at higher currents when surface area is constant. Fig. 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.

3.5. Influence of surface area of ZVT and solution pH on perchlorate reduction

The surface area is usually an important parameter governing the rate of zero-valent metal and electrode reactions because it determines the number of surface sites available for reaction. However, the experimental results shown in Fig. 5 indicate that the influence of surface area concentration of ZVT on the rate of perchlorate reduction is negligible, even when it varies by a factor of 8 ($11.6\text{--}92.5 \text{ cm}^2/\text{L}$). The concentrations of perchlorate for the experiment conducted with a surface area concentration of $92.5 \text{ cm}^2/\text{L}$ 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. Increasing the surface area would probably increase the number of pitting sites, but the activity of each pitting site

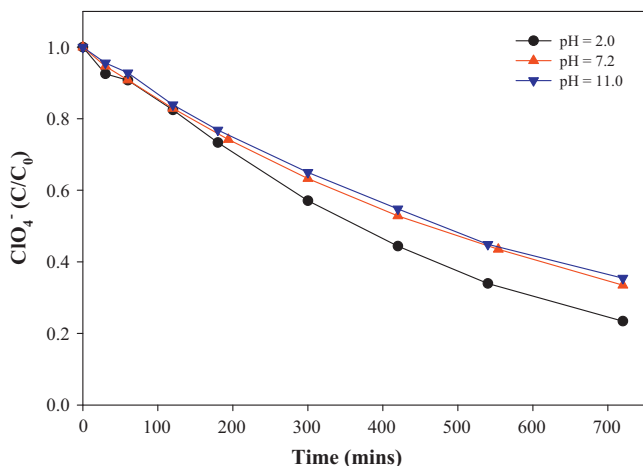


Fig. 6. Influence of solution pH on perchlorate reduction. Initial perchlorate concentration was 10.15 ± 0.35 mM, current was 370 mA, and surface area concentration of titanium electrode was 92.5 cm²/L.

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.

Fig. 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 [40]. 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.

3.6. Trace level of perchlorate removal

Perchlorate concentrations have been detected in groundwater and drinking waters generally at trace levels, i.e. at concentrations less than 1000 μ g/L. The literature on other metals indicates that it would be possible to develop pitting corrosion with trace levels of perchlorate [32]. However, pitting was not observed when constant potentials were applied to ZVT in contact with solutions that contained only trace levels of perchlorate and the current was observed to rapidly drop due to growth of a thicker surface oxide film on ZVT. Most natural waters contain chloride, which can promote development of pitting corrosion. Thus, the behavior of perchlorate at trace levels was examined in experiments that evaluated the effects of chloride concentration, current, and surface area concentration of ZVT.

Fig. 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 0.097 , 0.082 , 0.082 , and 0.082 mM 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 help induce pitting corrosion that is essential to the process of removing perchlorate, but it also inhibits the rate of perchlorate removal once pitting corrosion is initiated.

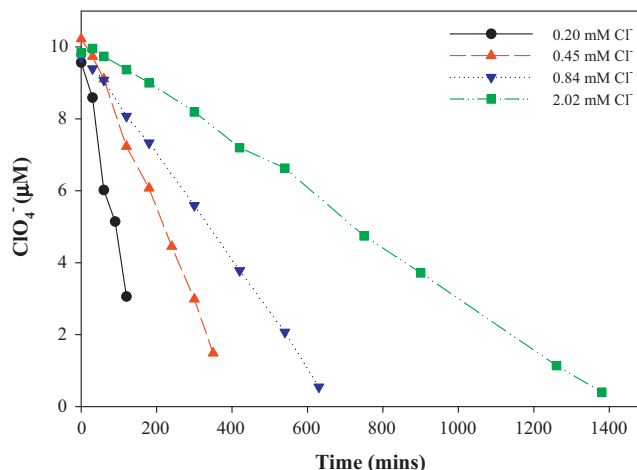


Fig. 7. Influence of chloride concentrations on reduction of trace levels of perchlorate. Current intensity was 50 mA and surface area concentration of titanium was 46.25 cm²/L.

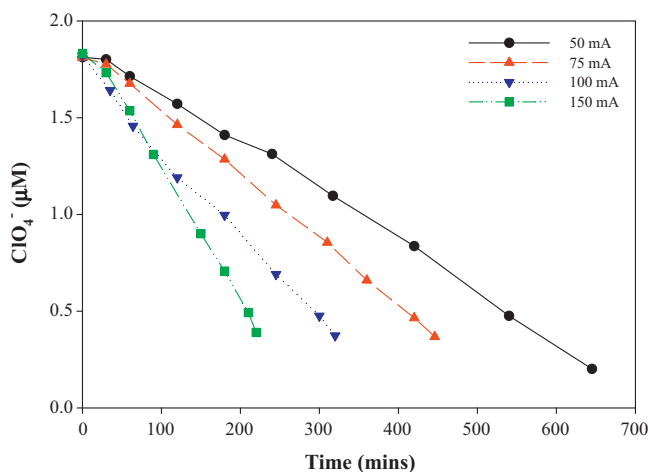


Fig. 8. Influence of current on reduction of trace levels of perchlorate. Initial chloride concentration was 1.06 ± 0.02 mM and surface area concentration of titanium electrode was 46.25 cm²/L.

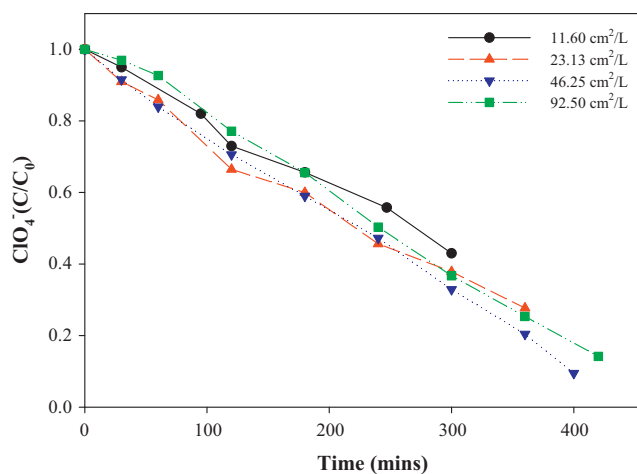


Fig. 9. Influence of surface area concentration of titanium electrode on removal of trace levels of perchlorate. Initial perchlorate concentration was 4.82 ± 0.17 μ M and current was 80 mA.

Fig. 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 Fig. 4. Effects of surface area concentrations were also investigated over the range from 11.6 cm²/L to 92.5 cm²/L. Results of these experiments showed that surface area concentration had negligible influence on the rates of removal of trace levels of perchlorate (Fig. 9).

4. Conclusions

A new methodology to reduce perchlorate to chloride has been presented. It is based on using electrochemically induced pitting corrosion of titanium metal. Results of experiments have been presented to evaluate the effects of imposed potential, current, solution pH, and surface area concentration of ZVT electrode on rates of perchlorate reduction. Surface area of ZVT electrodes showed negligible effects on perchlorate reduction and lower solution pH may promote perchlorate reduction to some extent. Reduction of perchlorate was not dependent on the imposed electrode potential as long as the potential was maintained above the pitting potential of ZVT. 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. However, the requirement of high potentials needed to produce active reductants, the amount of titanium consumed, the inhibition of perchlorate removal by chloride, and chloride oxidation to chlorine restrict its immediate application in treatment systems. Therefore, methodologies are needed to lower the pitting potential of ZVT and to minimize the effects of chloride before the process can be applied to treatment systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.09.072.

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