FINAL REPORT

Removal of Perchlorate from Water and Wastewater by Catalytic Hydrogen Gas Membrane Systems

SERDP Project ER-1430

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Chapter 1: Introduction

1.1 Progress made in Year I

Year I work explored several methods for the reduction of perchlorate in water by 1) molecular hydrogen gas in the presence of catalysts, 2) elemental (or zero-valent) metals, 3) an indirect electrochemical system, 4) a catalytic mono-membrane, and 5) a catalytic dual-membrane system. More than 150 experiments were conducted to screen the best catalysts using gaseous or atomic hydrogen as the reducing agent. Appendix A summarizes catalysts and catalytic systems studied throughout the project period ending December 2005). Results showed that the extent and the rate of perchlorate reduction varied among the systems studied. Overall, two methods stood out as the most promising processes: the catalytic dual-membrane system and the indirect electrochemical system using a titanium electrode. These two methods were studied further during Year II.

For the catalytic dual-membrane system, it was found that perchlorate was removed completely at a rapid to moderately rapid rate. A total of 18 metallic catalysts from the first, second, and third rows of the periodic table were studied. In terms of the gross reaction rate constant, Ti (titanium) and Co (cobalt) from the first row and Sn (tin) from the second row were the most promising, with a rate constant of >9.5 μM-hr^{-1}. In terms of specific rate constant, i.e., rate constant per mass of catalyst, the following are the most promising catalysts: Sc (scandium) and Cr (chromium) from the first row, Mo (molybdenum) and Cd (cadmium) from the second row, and Pt (platinum) from the third row. The specific rate constant of the above metallic catalysts was >10 μM-hr^{-1}-mg^{-1} catalyst. In summary, we have discovered that Ti, Sn, Cr, Mo, Cd, and Pt are the most promising metallic catalyst for the reduction of perchlorate in dilute aqueous solutions.

For the indirect electrochemical reduction system we selected Ti as the electrode to which anodic current was applied. This material was selected because it is one of the most efficient metals in the reduction of perchlorate using both the dual-membrane and the zero-valent metal systems. Further, it is relatively inexpensive and non-toxic. It was found that perchlorate was readily reduced on the titanium electrode (note that the titanium electrode was an anode in this process) with a reduction efficiency of >90% at the initial perchlorate concentration of 245 pb-100 ppm and constant current of 20 mA. Results also indicated that nitrate did not inhibit perchlorate reduction; it was reduced at rates lower than that of perchlorate. Major cations such as Ca^{2+} and Mg^{2+} did not affect perchlorate reduction regardless of the relative concentration of perchlorate to these cations. When presence at concentrations two to three orders of magnitude greater than perchlorate, sulfate exhibited completive effect on perchlorate reduction apparently by poisoning the Ti electrode. No such competitive effect was observed by sulfate when the concentration of perchlorate and sulfate were of the same order of magnitude, however.

For the catalytic mono-membrane system, the reduction of perchlorate took place directly on the cathode (catalytic membrane) surface where hydrogen atoms were produced. The perchlorate reduction rate was generally slow. Nonetheless, it is an ideal system for studying the reaction mechanism during catalytic perchlorate reduction. This system was used to assess the reaction pathways of the catalytic membrane systems.

For the elemental (zero-valent) metal reduction system, it was found that perchlorate was reduced at a low rate, and various chlorine end products were generated, meaning an incomplete reduction reaction and the production of metal ions. The reduction was highly dependent on the temperature, pH and perchlorate concentration. This system was not studied further due to high material cost, low perchlorate removal efficiency, and production of secondary contamination, especially metal ions.

For the catalytic hydrogen gas reduction system, it was found that while it was possible to reduce perchlorate, the reduction rate was slower than the catalytic dual membrane and the indirect electrochemical Ti-TiO_2 methods under ambient and slightly above ambient conditions. Weak adsorption of perchlorate onto the metal surface and slow electron transfer from the hydrogen molecules to perchlorate ions appeared to be the reasons for the low reduction rate. This process was not studied further during Year II.

1.2 Progress made in Year II

Based on the original proposal and comments by the SERDP review panel, research activities were reorganized around the two most promising processes: the catalytic dual membrane and indirect electrochemical Ti-TiO_2 processes. Four specific tasks were carried out in Year II: 1) the kinetics of perchlorate reduction, 2) the reduction of perchlorate at extremely low (i.e., ppm levels) and ultra-low concentrations (i.e., ppb levels), 3) the effect of common ions on perchlorate reduction, and 4) preliminary economic analysis of the two most promising systems, catalytic dual membrane and indirect electrochemical Ti-TiO_2.

The kinetics of perchlorate reduction was observed for a period of less than 8 hours under various ambient conditions. In light of the difficulty in perchlorate reduction, it was agreed that if perchlorate could be reasonably reduced (e.g., with >90% removal efficiency) within 8 hours, it would be a great accomplishment and the project would be continued. The perchlorate concentration in most reported sites in the USA was low, in the range of several ppbs to ppms as reported by AWWA (American Water Works Association), who surveyed the contamination level of perchlorate in the water bodies of about 26 states and Puerto Rico. Therefore, we chose 2 ppm and 245 ppb as the representative low and ultra-low concentrations, respectively, in this study. The reduction of perchlorate was studied using both the catalytic dual membrane and the indirect electrochemical Ti-TiO_2 methods. The effect of common ions such as nitrate, sulfate, bicarbonate, chloride, Ca^{2+} and Mg^{2+} on perchlorate reduction reaction was investigated.

Based on the results obtained, a preliminary economic analysis was made of the two above processes. The analysis was made based on laboratory-scale semi-batch reactor and experimental conditions conducted during Year II. Results indicated that either process would be extremely competitive against any current perchlorate treatment technology, including ion exchange and biological methods.

1.3 Publications

During the project period from 2005 to 2006, the following papers were presented at national meetings:

1.“Catalytic Hydrogen Reduction of Perchlorate in Dilute Aqueous Solutions.” *Partners in Environmental Technology Technical Symposium & Workshop*, November 29–December 1, 2005, in Washington DC.
2 “Mono-metallic Nano-Catalysts for the Reduction of Perchlorate in Water.” *NSTI Nanotechnology Conference*, Boston, MA, May 2006.
3. “Comparison of Four Different Methods Investigated for Perchlorate Reduction.” *2006 Gordon Research Conference*, New Hampshire, June 2006.
4. “Removal of Perchlorate at Low Concentrations by Chemical Methods with Catalysts.” *Partners in Environmental Technology Technical Symposium & Workshop*, November 28–30, 2006, in Washington DC.

During the project period from 2005 to 2006, the following manuscripts were prepared and submitted to journal publications:

1. “Indirect Electrochemical Reduction of Perchlorate in Dilute Aqueous Solutions at the Titanium-Water Interface” (submitted to *Environmental Sciences & Technology*, 2007) (**Attachment 1**)
2. “Catalytic Reduction of Perchlorate by H_2 Gas in Dilute Aqueous Solutions” (submitted to *Separation and Purification Technology*, 2007) (**Attachment 2**)
3. “Reduction of Perchlorate in Dilute Aqueous Solutions by Catalytic Dual-membrane System ” (submitted to *Water Research*, 2007) (**Attachment 3**)
4. “Reduction of Perchlorate in Dilute Aqueous Solutions over Monometallic Nano-catalyst Exemplified by Tin” (submitted to *Separation and Purification Technology* 2007) (**Attachment 4**)
5. “Perchlorate Reduction in at the Ti-Water Interface in the Presence of Common Ions” (submitted to *Water Research, 2007*) (**Attachment 5**)

Chapter 2: Literature reviews

Perchlorate is an emerging contaminant. Therefore there have been escalating activities on the study of perchlorate in the environment. These research activities include the study of the occurrence, toxicity, regulation, and remediation technology of perchlorate. The chemistry of perchlorate in the aqueous solution was been studied exhaustively at the beginning of the last century. Appendix B lists publications related to treatment technology for perchlorate. This chapter highlights publications related to perchlorate treatment, with an emphasis on chemical methods in 2006 as a supplement to our 2005 Annual Report.

2.1 Chemical Methods

Chemical or electrochemical methods are among the most marketable processes for the removal of impurities from drinking water in terms of treatment efficiency, process “cleanness,” cost-effectiveness, and most of all public acceptance and policy buy-in. Physical and chemical processes and their combinations have dominated drinking water treatment methods as among the most publicly acceptable technologies. Hurley and Shapley (2006) [1] studied the reduction of perchlorate by hydrogen gas in the presence of catalysts (5% Pd/C powder and methyltrioxorhenium). They reported that perchlorate at an initial concentration of 2.0 mM (or 200 ppm) was reduced completely to chloride within 24 hours at room temperature under one atm of hydrogen gas. Gurol (2006)[2] reported that perchlorate can be reduced to chloride on the surface of metals as catalyzed by UV radiation at an initial perchlorate concentration of 1000 ppb and pH<2. They reported that the perchlorate was converted to 99% chloride and 1% chlorite. Oh, et al. (2006)[3] claimed that perchlorate could be reduced rapidly by elemental iron under extreme conditions. At room temperature and pH 7.4, only 40% of perchlorate was removed after 3 weeks at an initial perchlorate concentration of about 100 ppm. However, when the temperature was elevated to 200^{o}C by microwave radiation, the removal efficiency increased to >98% after 2 hours. Xiong and Zhao (2006) [4] investigated the reduction of perchlorate by stabilized zero-valent iron nanoparticles (average size 11 nm) and reported that temperature played a critical role in the process. They demonstrated that more than 90% of perchlorate should be removed after 6 hours at a temperature of about 95^{o}C.

Reduction of perchlorate by electrochemical methods using various electrode materials has also been studied. Rusanova, et al. (2006) [5] found a significant reduction of perchlorate at the Ni cathode and proposed that the deposition of a small amount of Pt onto the Ni cathode could enhance the reduction of perchlorate significantly at temperatures greater than 55^{o}C. No information on the removal efficiency was reported. Lee and Kramer (2006) [6] studied perchlorate reduction by polarization of Ti electrode and reported that more than 93% of perchlorate, at an initial concentration of 1000 ppb, was reduced at a constant current of 16 mA in 36 hours. Hassan (2006) [7] studied perchlorate reduction during Zn corrosion in a neutral medium using the voltametry method at room temperature and an initial concentration of 0.1 M (or 10 ppm) and reported the formation of an interior layer of ZnO as the mechanism of perchlorate reduction.

2.2 Biological Methods

Biological treatment of wastewater for the removal of perchlorate has already been pursued as a commercial technology. Research activities in this area have concentrated mainly on the mechanism and kinetics aspects of the processes. Shrout and Parkin (2006) [8] studied the influence of electron donor, redox potential, and dissolved oxygen on the biological reduction of perchlorate. They reported that the reduction of perchlorate was feasible under aerobic conditions in the presence of dissolved oxygen at appreciable concentrations. Nerenberg et al. (2006) [9] studied the kinetics of biological perchlorate reduction by bacterium, *Dechloromonas sp. PC1*. Wang et al. (2006) [10]investigated the parameters controlling the kinetics of biological reduction of perchlorate in batch systems with an emphasis on pH. Park and Marchand (2006)[11] studied inhibitory factors such as salinity on perchlorate reduction in a laboratory wastewater system. Yu et al. (2006) [12] and Son et al. (2006) [11] studied the enhancement on perchlorate reduction by the addition of zero-valent iron. Simon and Weber (2006) [13] investigated the biological reduction of perchlorate in natural systems. He et al. (2006) [14] studied perchlorate reduction in an anaerobic treatment system.

Biological reduction of perchlorate ion to chloride was reported in 1964[15, 16], and the function enzyme was identified to be the same as that for nitrate reduction, i.e., nitrate reductase (Hackenthal, E., 1964, 1965). It was found that anaerobic pre-incubation was needed for a reasonable rate of reduction. Since that time, an anaerobic environment has been maintained for reduction of perchlorate by bacteria. This condition precluded application to drinking water practice directly due to the secondary contamination issues associated with turbidity, residual chemicals, low pH, and odor. Furthermore, satisfactory removal efficiency was not achieved after several days, which translates into high treatment costs. The electron donor for perchlorate reduction in biological systems started with organic material and evolved to hydrogen gas and now zero-valent iron. There are about 20 bacteria reported to reduce perchlorate, and the electron donors were related to the bacterium species. The following inhibitory parameters of the biological system on perchlorate reduction have been studied: low concentration of oxygen, low pH, salinity, and secondary contamination.

2.3 Other Methods

The removal of perchlorate by adsorption process has been studied. Makris et al. (2006) [17] reported that alum sludge from drinking-water treatment is a potential adsorbent for perchlorate removal.

2.4 Regulatory Aspect and Chemical Analysis

As far as the regulatory action on perchlorate is concerned, although the National Academy of Engineers (NAE) has proposed a Drinking Water Equivalent Level (DWEL) value of 24.5 ppb based on the RfD value of 0.0007mg/kg/day in 2005, US EPA has not issued any Maximum Contamination Limit (MCL) value for perchlorate to this date. Ting et al (2006)[18] reported that the State of California is in the process of developing its MCL based on a Public Health Goal (PHG) value of 6 ppb together with a consideration of other factors such as economic impact and engineering feasibility.

EPA has published two methods on perchlorate analysis in drinking water. Method 314.0, which was issued in 1999, has a detection limit of 0.53 ppb using both AS11 and AS5 columns. EPA Method 314.1 provides standard procedures for the analysis of perchlorate in water. Method 314.1, which was published in 2005, has a detection limit of 0.14 ppb for the AS16 column and 0.13 ppb for the AS20 column. Methods for the analysis of perchlorate in various media such as milk[19, 20], plants[21], food [22, 23], fertilizer [24, 25] and sea water [26] are available also. Lamb et al (2006) [27] reported the determination of perchlorate in μg/L levels in the presence of a high concentration of chloride, sulfate, and carbonate by ion chromatography using macro cycle-based concentration and separation methods.

2.5 Summary

Based on the most recent literature, it can be concluded that:

- Currently, there is no physical-chemical technology capable of reducing perchlorate completely to chloride under ambient conditions for the treatment of either surface water or groundwater, with the exception of the two methods developed in this SERDP project;
- The application of biological treatment technology is still limited by high cost, secondary contamination, and low public-acceptance;
- No information is available on the effect of competing ions on perchlorate reduction except this SERDP project;
- The regulatory action on MCL for perchlorate contamination is pending due to the lack of appropriate technology. Although regulatory action is lacking mainly because of the uncertainty on RfD value, the unavailability of appropriate remediation technology remains the primary stumbling block.

Chapter 3: Catalytic Dual Membrane System

3.1 Introduction

A catalytic dual-membrane system consists of two membranes, an anion-exchange membrane permeable specifically to the perchlorate ion and a catalytic membrane onto which a specific metallic catalyst is deposited (or coated). The whole system can be divided into three components: the container, the reactor and the auxiliary part. The *container* holds water to be treated. It can be designed either as a bench or as a continuous flow system. The *reactor* consists of an anion exchange membrane (AEM), which is positively charged to facilitate the transport of anions, and a catalytic membrane (CM), which is negatively (cathodically) charged. The *auxiliary* component consists of two DC power supplies; one provides electricity for the transport of perchlorate ions across the AEM, the function of which is very much like electrodialysis (ED), and the other one provides electricity for the catalytic production of atomic hydrogen.

3.2 Materials and Apparatus

Figure 3.1 shows a photo and a schematic of a laboratory catalytic dual-membrane system. As can be seen from Figure 3.1, the reactor consists of two membranes; the upper one is the catalytic membrane (CM) coated with specific metallic catalyst and the bottom one is the anion exchange membrane (AEM).

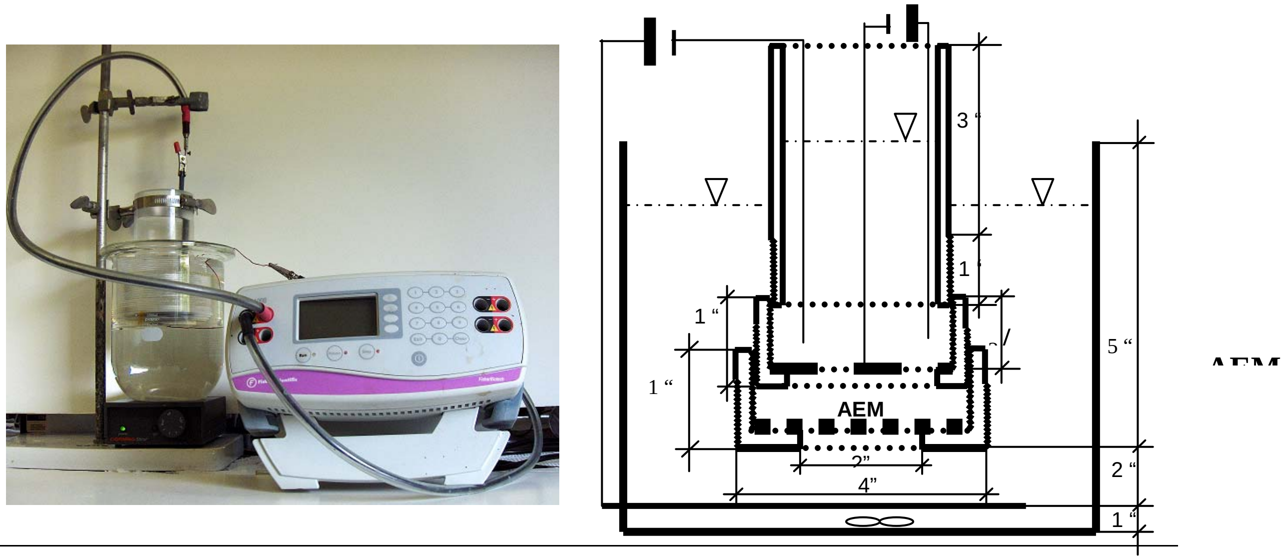


Figure 3.1 Experimental Setup of the Catalytic Dual Membrane System.

The anion exchange membrane separates the bulk solution in the container and the electrolyte in the reactor and forms a Stern layer between the two membranes. When the auxiliary potential is applied across the AEM, perchlorate ions in the bulk solution migrate to the Stern layer after crossing the anion exchange membrane. The perchlorate ions become accumulated in the Stern layer due to electrical repulsion of the catalytic membrane, which is cathodically polarized. This extends the residence time of the perchlorate ions in the vicinity of the catalytic membrane, which eventually facilitates the reduction of perchlorate to its end product. The surface concentration of perchlorate is determined by the selectivity of the ion-exchange membrane, the applied potential, and the chemistry of the solution to be treated. The catalytic membrane can be readily prepared by depositing metallic catalysts onto the stainless steel membrane support. A detailed description on the preparation of the catalytic membrane has been reported previously (ref. 2005 Annual Report of this SERDP project).

Deionized and distilled water was prepared in the laboratory by a water-purification system (Mega-pure System, Model MP-290). Ammonium perchlorate (> 98%) was purchased from Sigma-Aldrich (Allentown, PA). Titanium sulfate (purified $Ti(SO_4)_2.9H_2O$) was purchased from Fisher Scientific (Pittsburgh, PA) and used as received.

3.3. Experiments

Three experiments were conducted: 1) reduction of perchlorate at low concentrations, 2) reduction of perchlorate at low concentrations in the presence of Ti^{4+}, and 3) concentration of perchlorate by ED.

3.3.1 Reduction of perchlorate at low concentrations

Reduction of perchlorate was examined at initial concentrations in the range of 8.3 to 79.2 ppm. The solutions were prepared by dissolving a given amount of ammonium perchlorate into 1.5 liters of deionized water. The ambient conditions were kept constant throughout the entire experimental process. Table 3.1 lists the detailed experimental conditions.

3.3.2 Reduction of perchlorate at low concentrations in the presence of Ti^{4+}

Attempts to reduce perchlorate at ultra-low concentrations were conducted in two sub-tasks. The first sub-task was conducted using the same catalytic dual-membrane reactor as the one shown in Figure 3.1. The initial perchlorate concentration was 2.3 ppm. Table 3.1 lists the detailed experimental conditions. The second sub-task was conducted in the presence of $Ti(SO_4)_2$ electrolyte. In order to facilitate the transport of Ti^{4+} ions toward the CM, a cation instead of the usual anion ion exchange membrane was used. An electrolyte, $Ti(SO_4)_2$, at a concentration of 0.01M was introduced in the container. It is expected that the cationic exchange membrane will increase the perchlorate reduction rate through the additional catalytic action of the Ti^{4+} ion that was added to the reactor for this purpose. For this reactor, the catalytic membrane was coated with Ti and brought into direct contact with the bulk solution. The cation-exchange membrane also separates the bulk solution from the supporting electrolyte. The Ti^{4+} ions that pass through the cation exchange membrane will be adsorbed on the negatively charge catalytic membrane. Table 3.1 lists the detailed experimental conditions.

3.3.4 Concentration of perchlorate by electrodialysis (ED)

The accumulation of perchlorate ions in the space between the two membranes was evaluated by lowering the working current to zero in the dual membrane system, i.e., by disconnecting the power supply to the catalytic membrane. A perchlorate solution was prepared at an initial concentration of 40 ppm and introduced to the container. The reactor was filled with the supporting electrolyte of NaOH solution at a concentration of 0.01M. The power supply was connected to the anion exchange membrane only, and the concentration of perchlorate ions in the reactor and the container was monitored. (Note: This experiment was similar to that of electrodialysis in that only one membrane was involved.)

Table 3.1 Experimental Conditions for Dual-membrane System.

Condition	Figure 3.2	Figure 3.3	Figure 3.4
System	Dual-membrane	Dual-membrane	Dual-membrane
Container volume (L)	2	2	2
Diameter of reactor (cm)	~3	~5	~5
Reactor volume (mL)	100	300	300
Membrane contact perchlorate solution	Anion-exchange	Anion-exchange	Catalytic membrane
Membrane contact supporting electrolyte	Catalytic membrane	Catalytic membrane	Cation-exchange membrane
Supporting electrolyte	0.01 M NaOH	0.01 M NaOH	0.01 M $Ti(SO_4)_2$
Initial concentration of perchlorate	8.3~79.2 ppm	2.3 ppm	1.0 ppm
Anode	Iron rod	Iron rod	Iron rod
cathode	Sn	Pt-Ti	Pt-Ti
Temperature (^oC)	25	25	25
pH	5.6~ 6.0	5.6	5.6
Current (mA)	10	10	5
Potential (V)	~10	~20	~10

3.4 Results and Discussions

3.4.1 Reduction of perchlorate at low concentrations

Figure 3.2a shows the change in perchlorate concentration with time at various initial perchlorate concentrations using the catalytic dual membrane system. Results indicate that the removal of perchlorate was related to the perchlorate concentration in the bulk phase. The higher the initial concentration, the higher the removal efficiency. The initial reaction rates were 6.9, 22.9, 61.3, and 76.5 M/hr for initial perchlorate concentrations of 8.3, 23.1, 61.3, and 79.2 ppm, respectively. The removal rate increased with an increase in initial perchlorate concentrations. Further analysis of the rate constants revealed that the perchlorate reduction could be described by the Langmuir-Hinshelwood equation, i.e., $-\left(\frac{dC}{dt}\right)_o = r_o = k_{obs}\frac{\Gamma_m C}{K+C}$, or $r_o = k'_{obs}\frac{C}{K+C}$, where k_{obs}, k'_{obs}, Γ_m, K, and C are the observed rate constant, apparent observed constant, perchlorate adsorption density at the monolayer level, adsorption constant, and residual perchlorate concentration, respectively. A linearized plot of the Langmuir-Hinshelwood equation (Figure 3.2b) yields slope and intercept from which the values of ($k_{obs}\Gamma_m$) and K were obtained (2.4×10^{-4} M/h and 1.9×10^{-3} M, respectively). Based on the adsorption constant, the free energy of perchlorate adsorption on the catalytic membrane was ~ -3.57 kCal/mol, which implies that the perchlorate adsorption onto the catalytic membrane surface was rather weak. The excellent fit of the rate constants with the initial perchlorate concentration clearly indicate that the reduction reaction was dependent on the surface concentration of perchlorate. The rate constant, k_{obs}, can be estimated from separate perchlorate adsorption experiments.

In summary, the perchlorate reduction rate is highly dependent on the concentration of adsorbed perchlorate ions, which is brought about by electrical transport processes across the ion exchange membrane. If a high concentration of perchlorate in the space between the ion exchange membrane and the catalytic membrane can be maintained, it is possible to remove the perchlorate by converting it to chloride using the catalytic dual membrane system.
The average perchlorate adsorption density on the above electrodes was about 10^{-9} mole-cm^{-2}.

With an assumed Γ_m value of 10^{-6}mol/cm^2, the k_{obs} would be $6x10^{-5}$ cm^{-1}-s^{-1}. (Note: The observed rate constant has the unit of specific surface area of the electrode volume of the solution per time, i.e., cm^2-cm^{-3}-s^{-1}.)

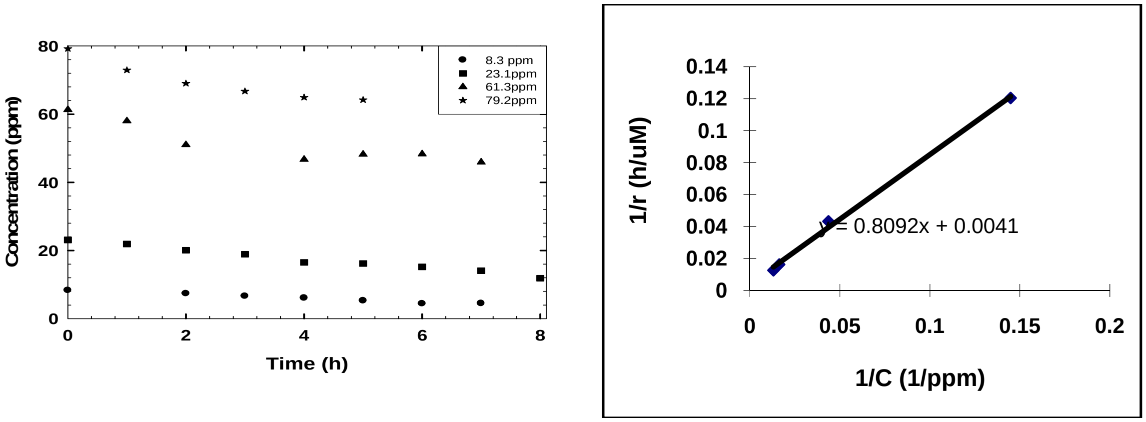


Figure 3.2 Removal of ClO4- at Various Initial Perchlorate Concentrations. (a) Change of Perchlorate Concentrations versus Reaction Time; (b) Langmuir-Hinshelwood plot.

Experimental conditions: Perchlorate concentration = 8.3 to 79.2 ppm; temperature = 25°C; pH = 5.6~6.0; anode = Fe; cathode = catalytic membrane coated with Sn; voltage applied = ~10 V; Current = 10 mA.

Figure 3.3 shows the results of the reduction of perchlorate at an initial concentration of 2.3 ppm using the same catalytic reactor as described above. It can be seen that the perchlorate concentration increased from 2.3 to 3.15 ppm quickly during the first hour, then decreased sharply from 3.15 to 1.4 ppm at the end of 21 hours. The reduction reaction followed almost a first-order rate expression with a rate of ca. 0.16 h^{-1} or 3.84 d^{-1}.

3.4.2 Reduction of perchlorate at low concentrations in the presence of Ti^{4+}

Figure 3.4 shows the results of perchlorate reduction using the cation exchange catalytic membrane reactor in the presence ot Ti^{4+} ions. It can be seen that the perchlorate reduction was rapid following a first-order kinetic with a rate constant of 0.22 h^{-1} or 5.33 d^{-1}. The concentration of perchlorate decreased drastically to 120 ppb in 9 hours, which is a 98% removal rate. The chloride concentration increased following the rapid reduction of perchlorate, then decreased when the reaction by-products such as chlorite (ClO_2^-) and chlorate (ClO_3^-) appeared. The total chlorine concentration, i.e.,, the sum of all chlorine-containing species, decreased with reaction time. This can be attributed to the formation of gaseous chlorine, which could escape from the solution.

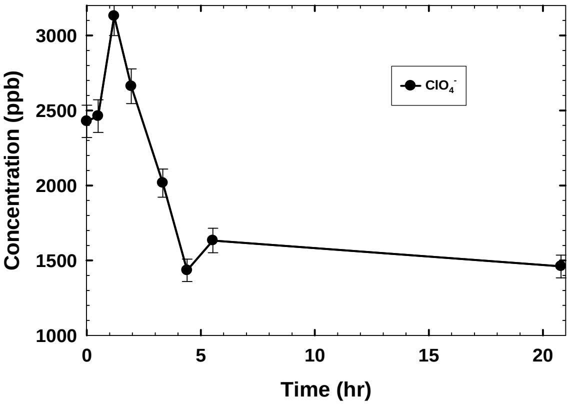


Figure 3.3 Reduction of ClO4- at Low Concentrations by Catalytic Dual-membrane System.

Experimental conditions: Perchlorate concentration = 2,300 ppb; CM membrane coated with Pt and Ti; ion-exchange membrane= anion membrane; temperature = 25°C; pH = 5.6; anode = Fe; cathode = catalytic membrane; voltage applied = ~20 V; current = 10 mA.

The results shown in Figure 3.4 represent a significant improvement of the catalytic dual-membrane system in that the Ti^{4+} did promote the perchlorate reduction significantly and the cation exchange membrane did facilitate the transport of cation Ti^{4+} species to the catalytic membrane. The accumulation of Ti^{4+} species at the catalytic membrane brought about additional perchlorate reduction via the reaction between the Ti^{4+} species and perchlorate in addition to reduction via atomic hydrogen. As indicated in Figure 3.3, the anion-exchange catalytic dual-membrane system failed to bring about a rapid reduction of perchlorate during the first hour, and the rate constant was slightly smaller than that in the presence of Ti^{4+} ions, 5.33 versus 3.84 d^{-1}. To facilitate perchlorate reduction, it is necessary to enhance the accumulation of perchlorate ions at the surface of the catalytic membrane, i.e., the reactive surface. The adsorption of perchlorate ions onto the metallic catalyst surface was weak with an adsorption energy of only -3.57 kCal/mol. The situation became worse when a negative potential was applied to the catalytic membrane, which tended to repel the perchlorate ions from approaching the catalytic membrane and the catalysts. As a result, most of the perchlorate ions would probably not even reach the catalytic membrane surface, and for those perchlorate ions that reached the surface, the small sticky coefficient did not allow them to stay on the surface for a time long enough for the reaction to complete. Furthermore, the negative polarity of the catalytic membrane surface was detrimental to the molecular distortion (or redistribution of electrons) of the perchlorate ion, i.e., the Cl-O bond, in lowering the activation energy barrier. Smaller molecular distortion or higher activation energy means a lower reaction rate.

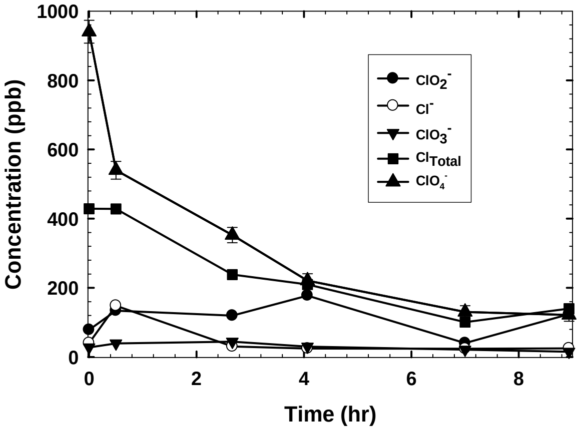


Figure 3.4 Reduction of ClO_4^- by Cation-exchange Catalytic Dual Membrane System.

Experimental conditions: Perchlorate concentration = 1000 ppb; CM = membrane coated with Pt-Ti; ion-exchange membrane = cation membrane; supporting electrolyte (in the reactor) = 0.01 M of $Ti(SO_4)_2$ in 0.1 M sulfuric acid solution; temperature = 25 ^oC; pH = 5.6; anode = Fe; cathode = catalytic membrane; voltage applied = ~10 V; Current = 5 mA.

A separate attempt to increase the surface concentration of perchlorate to enhance the collision frequency was made by pumping the solution through the catalytic membrane continuously. Intuitively, it seems that passing the flow of the bulk solution through the catalytic membrane would increase the contact between the perchlorate and the membrane surface. However, results demonstrated no significant improvement on the perchlorate reduction rate (data not showed). Apparently, a surface reaction, not mass transfer, was the rate-limiting step. Surface reaction, especially the accumulation of perchlorate on the membrane surface, is key to the rate of the reduction reaction as predicted by the Langmuir-Hinshelwood model as described above. In order to increase the surface concentration of perchlorate, improvements on the surface accumulation of the reacting species are necessary. The accumulation of perchlorate ions in the space between the anion exchange membrane and the catalytic membrane can be described by the expression: $\frac{dC}{dt} = J_e - J_i + r(C)$, where J_e is the mass transfer rate of perchlorate ions entering the reaction space, J_i is the mass transfer of perchlorate ions leaving the reaction space, and r(C) is the rate of perchlorate reduction at concentration in the reacting space. At high perchlorate concentration, i.e., $J_e >> J_i$, the reduction rate can be enhanced by the accumulation of perchlorate ions. However, when J_i is comparable to J_e as is the case of low perchlorate concentration, the reduction rate will be slow due to the low surface concentration of perchlorate at the catalytic membrane.

Perchlorate concentration at the catalytic membrane was enhanced with the use of a cation exchange rather than an anion exchange membrane in conjunction with the catalytic (anionic) catalytic membrane. In this system, the accumulation of perchlorate ions in the space between the ion exchange membrane and the catalytic membrane can be described by: $\frac{dC}{dt} = J_d - r(C)$,

where J_d is the mass transfer rate of perchlorate ions brought by enhanced diffusion, and r(C) is the rate of reduction at concentration of C.
It must also be mentioned that the surface property in the vicinity of the catalytic membrane was improved by the arrival of Ti^{4+} ions. The Ti^{4+} ions arrived at the catalytic membrane surface via passing through the cation-exchange membrane. As a result, the surface of the catalytic membrane can be rendered positive, i.e., charge reversal due to specific Ti^{4+} adsorption. These positively charged sites would facilitate the adsorption of perchlorate ions, which could increase the sticky coefficient between the perchlorate ions and the catalytic membrane surface. Finally, Ti^{4+} ions, in addition to enhancing the adsorption of perchlorate ions on the catalytic membrane surface, could contribute to the perchlorate reduction reaction when they were reduced to reactive Ti^{3+} or Ti^{2+} species on the cathodic membrane surface. The reaction between Ti^{3+} and/or Ti^{2+} species and adsorbed perchlorate ions was rapid. Consequently, the catalytic membrane surface was renewed quickly, which readied the catalytic membrane for resuming the perchlorate reduction in the next reaction cycles.

However, as shown in Figure 3.4, the perchlorate reduction reached a steady state at a perchlorate concentration of about 100 ppb. This could be attributed to the diffusion-limiting situation. When the perchlorate concentration in the bulk solution was ultra-low, the electrical double layer resistance effect became significant. That is, in a solution that contains only perchlorate at low concentration, the Debye length is extended, which impedes the approach of the counter ions, perchlorate in this case. Low perchlorate concentration at the catalytic membrane slowed the reduction. This situation can be drastically improved by the introduction of non-perchlorate electrolytes such as chloride into the perchlorate solution.

3.4.2 Concentration of perchlorate by electrodialysis (ED)

Figure 3.5 shows the increase in perchlorate concentration in the space between the catalytic and the anion exchange membrane under an electrical field. It can be seen that the single-membrane ED system can transport all perchlorate from the container to the reactor in 8 hours under an electric field of 2 V/cm. It is interesting to note that the perchlorate concentration decreased exponentially in the container. However, the loss of perchlorate in the container did not show up in the reactor. Rather, there was a lag time in the transport of perchlorate across the anionic membrane. Apparently, the anionic membrane retained the perchlorate ions briefly before their release after one hour. Once the perchlorate was freed from the anionic membrane, the perchlorate concentration increased exponentially in the reactor. A 100% rate of perchlorate transport was possible. Results clearly indicate that the application of electrodialytic transport of perchlorate toward the catalytic membrane surface is key to the perchlorate reduction reaction. The perchlorate concentration was boosted by 300 times over that in the reactor.

The surface reactions include the accumulation of perchlorate ions at the membrane surface and the subsequent reduction of the adsorbed perchlorate ions by the hydrogen atoms generated on the catalytic membrane surface. The molecular aspects of the surface reactions will be presented in Chapter 4, using the catalytic mono-membrane system. Several researchers have reported the adsorption of perchlorate on various electrodes. Goodrich and Schmid [28] studied the adsorption of perchlorate on an Au electrode by gravimetric method, i.e., weighing the gold electrode before and after contact with perchlorate solutions. Naneva et al [29] investigated the specific adsorption of perchlorate, nitrate and nitrite ions on a crystalline Cd surface and reported that the perchlorate ion was the weakest among all oxyanions studied. Niaura and Malinauskas (1991) [30] compared the adsorption of perchlorate and sulfate on a Cu electrode and reported that perchlorate was nonspecifically adsorbed, whereas sulfate was specifically adsorbed. Previous studies on the adsorption of perchlorate onto electrode surfaces provided no quantitative data on the adsorption density; rather, it was commonly agreed that the adsorption density of perchlorate at the surface of the catalytic membrane was very low when a negative potential was applied on the membrane.

In summary, the perchlorate reduction rate is highly dependent on the concentration of adsorbed perchlorate ions, which is brought by diffusion and/or electrical transport processes across the ion exchange membrane. If a high concentration of perchlorate in the space between the ion exchange membrane and the catalytic membrane can be maintained, it is possible to remove the perchlorate by converting to chloride using the catalytic dual membrane system.

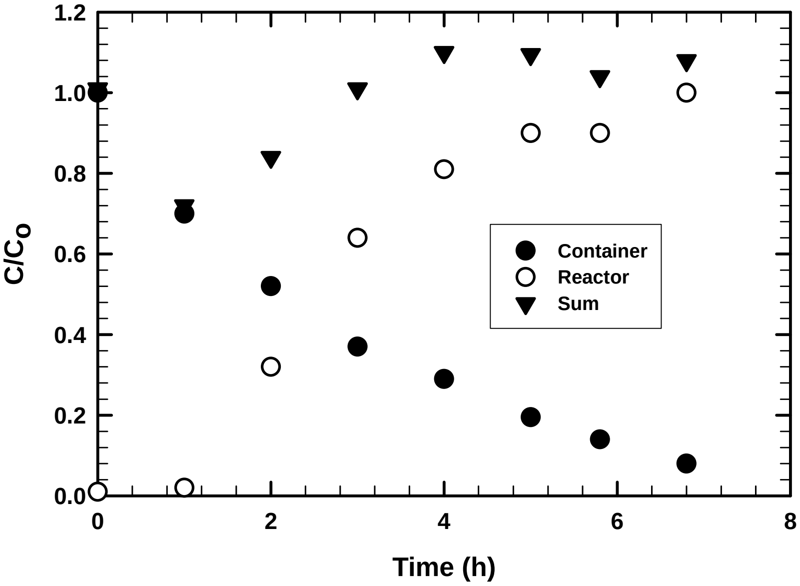


Figure 3.5 Concentration Process by Electrodialysis.

Experimental conditions: Perchlorate concentration = 40 ppm; ion-exchange membrane = anion membrane; temperature = 25 ^oC; pH = 5.6; anode = Fe; cathode = Fe; voltage applied = ~10 V; current = ~0 mA.

3.4 Reaction mechanism

As shown in Figure 3.6, the kinetics of perchlorate reduction in the catalytic dual-membrane system is a multiple-step reaction including the transfer (e.g., bulk diffusion), the accumulation, and the reduction of perchlorate at the membrane surface. Figure 3.6a shows the accumulation step of the reaction. When an electrical field was applied to the system, the perchlorate ions were transported into the space (Stern layer) between the catalytic membrane and the anion-exchange membrane. The selectivity of the ion-exchange membrane will determine the transport rate of the ions involved. With the accumulation of perchlorate ions in this space, its adsorption capacity was enhanced at the catalytic membrane surface. Reduction reaction then took place between the adsorbed perchlorate ions and the hydrogen atoms that were generated on the catalytic membrane as depicted in Figure 3.6b. Figure 3.6b depicts the structure of the adsorbed

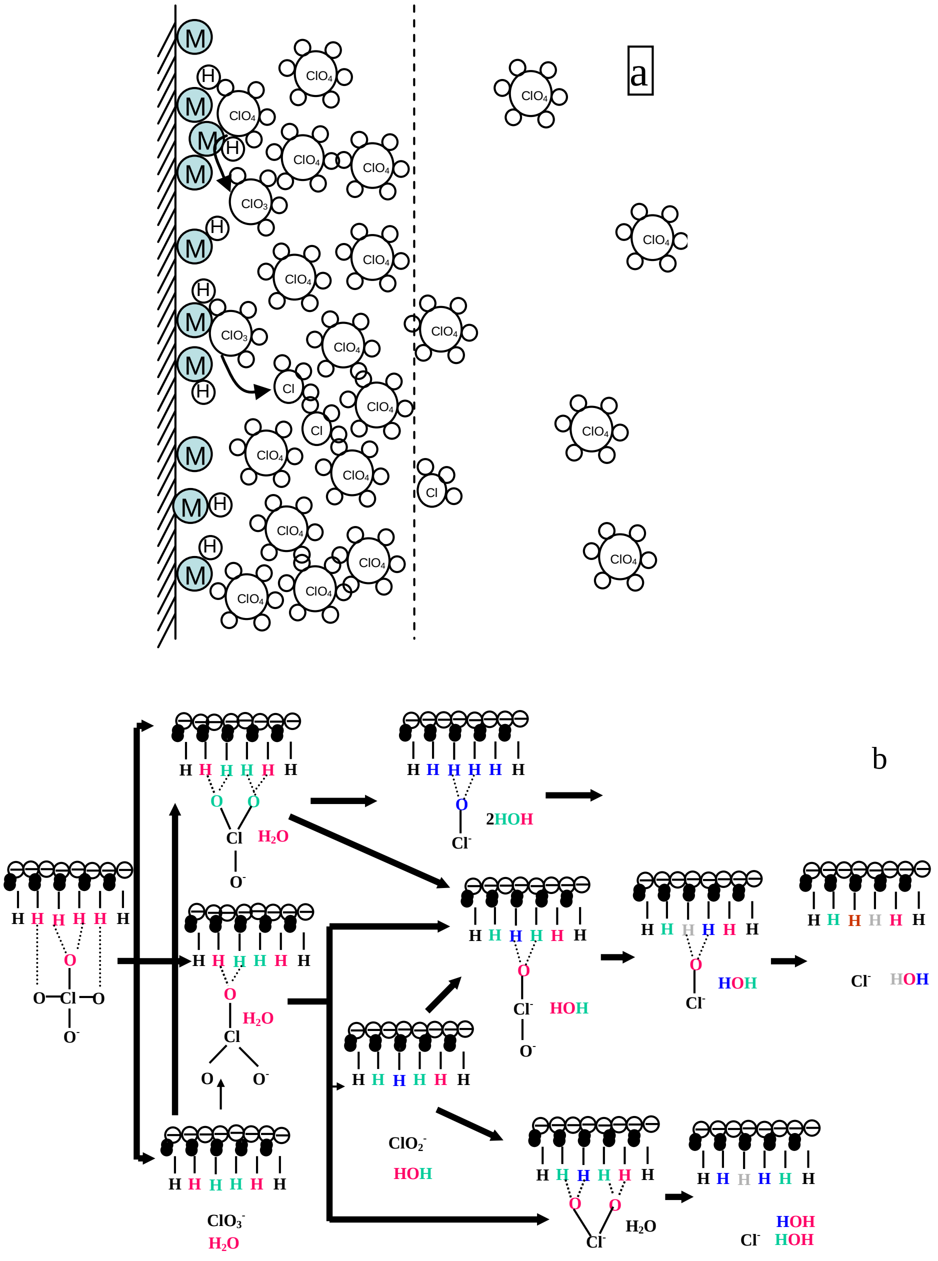


Figure 3.6 Sketch on Reaction Mechanism in Catalytic Dual-membrane System. (a) Surface activation stage, (b) Electro-transfer stage.

perchlorate ions, which occurs most favorably on the (111) surface. The (110) and (100) surfaces are not amenable to perchlorate ion adsorption, however [31]. When the catalytic membrane surface was occupied by perchlorate ions, the cathodically generated hydrogen atoms reduced them following a step-by-step fashion. However, depending on the site properties, some intermediates may diffuse into the bulk solution. The end product, i.e., chloride, eventually diffuses into the bulk solution. Naturally the reduction rate was dependent on the surface concentration of perchlorate. Therefore, a combination of the lowering of the activation energy and the concentration of perchlorate ions at the surface brings about rapid perchlorate reduction.

In summary, the kinetics of the catalytic dual-membrane system is a function of the following parameters: concentration of perchlorate in the bulk solution, ($[ClO_4^-]$), applied current or current density, (ρ), applied potential, (E), ion-exchange properties, (k_i), catalytic membrane properties, (k_m), catalyst, (k_c), pH, temperature (T), and mixing (ε). The kinetic equation can be written qualitatively as $-\frac{d[ClO_4]}{dt} = f([ClO_4^-], \rho, E, k_c, k_i, k_m, pH, T, \varepsilon)$.

Chapter 4: Catalytic Mono-membrane System

4.1 Introduction

The catalytic mono-membrane system is essentially the same as the catalytic dual-membrane system, except that it has only one catalytic membrane in the reactor. The entire system is divided into three components: the container, the reactor, and the auxiliary parts. The container holds the water to be processed. The reactor consists of a catalyst-coated membrane, i.e., stainless steel mesh, and can be designed as either a bench or a continuous type. The reactor is where the perchlorate ions are reduced. The auxiliary component is mainly the power supply, which provides electricity for the generation of atomic hydrogen necessary for the reduction reaction.

As far as the surface reaction is concerned, the reaction pathway for the reduction of perchlorate in the catalytic mono-membrane system is the same as that in the catalytic dual-membrane system (Figure 3.6b). The accumulation of perchlorate ions near the catalytic membrane was effected by mixing or molecular diffusion in the mono-membrane system, whereas electrical transport is the main driving force for the accumulation of perchlorate on the catalytic membrane. The first step of the surface reaction is the accumulation of perchlorate ions onto the catalytic membrane surface. The geometry of the attachment of perchlorate is believed to be affected by the surface structure. Figure 3.6b depicts the structure of the adsorbed perchlorate ions, which occurs most favorably on the (111) surface. The (110) and (100) surfaces are not amenable to perchlorate ion adsorption, however [31].

As reported in our 2005 Annual Report, the reduction rate was low for the catalytic mono-membrane system due to the low surface concentration of perchlorate. The reaction intermediates such as chlorate and chlorite easily diffused into the bulk solution and escaped from being reduced to the final product of Cl^-. Therefore, perchlorate could not be reduced to its final Cl^- product using the catalytic mono-membrane system.

Even though the performance of the catalytic mono-membrane system is not as good as that of the catalytic dual membrane system, the reaction mechanism is the same for both systems, the former system is a better tool for studying the mechanism of the surface reaction due to its simplicity in operation. Therefore, the catalytic mono-catalytic membrane system was used to study the surface reaction of perchlorate.

4.2 Catalytic Mono-membrane Reactor

Figure 4.1 shows the photo and the sketch of a laboratory bench top catalytic mono-membrane system used in this study. It can be seen that there is only one catalytic membrane in the reactor. Contrary to the catalytic dual-membrane reactor, there is no possibility of concentrating the perchlorate near the catalytic membrane. Perchlorate ions were in direct contact with catalytic membrane surface by diffusion. When perchlorate ions were adsorbed onto the membrane surface, reduction occurred while the end products back-diffuse to the bulk solution. As mentioned above, although the treatment efficiency of the catalytic mono-membrane system was relatively low, it is still a useful tool to investigate the surface reduction of perchlorate that occurred rather effectively in the catalytic dual-membrane system.

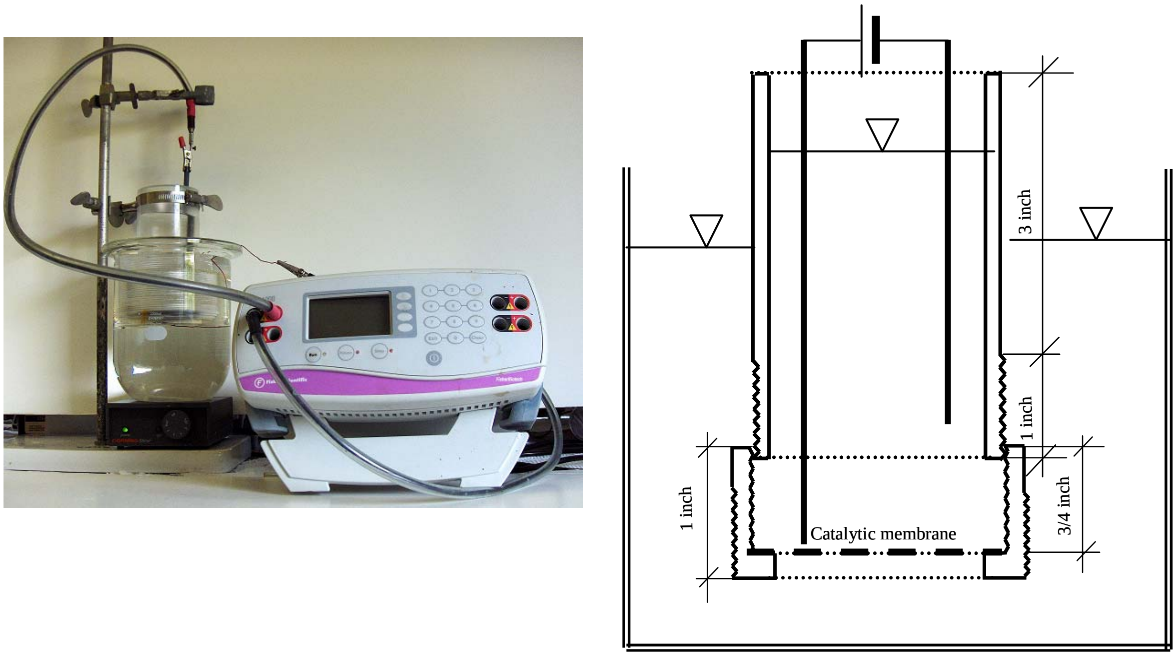


Figure 4.1 Mono-membrane Systems for ClO_4^- Reduction.

4.3 Surface Characterization of the Catalytic Membrane

The surface property of catalysts was examined by SEM/EDAX, XRD and XPS analyses. The SEM/EDAX analysis was performed by a JSM-7400 field scanning electron microscope with a resolution of 1 nm at 15kV. An XEDS detector was used to detect the elements of the solid product. X-ray diffraction (XRD) pattern of the solid byproduct was performed using a Rigaku D-Max B diffractometer, which is equipped with a graphite crystal monochromator operated with a Cu anode and a sealed x-ray tube. The 2θ scans were recorded using the Cu K_α radiation of wavelength of 1.5405 Å from 20^o to 80^o with a step size of 0.05^o. The chemical composition of the solid byproduct was studied by x-ray photoelectron spectroscopy (XPS) analysis. An SSI-M probe XPS employing Al K_α ($h\upsilon = 1486.6$ eV) excitation source was used. Peak positions were obtained with reference to the C 1s peak at 284.6 eV. The system pressure was maintained at $1\text{-}3 \times 10^{-8}$ Torr during the acquisition of the spectra.

Since Sn was one of the promising catalysts based on the results of the Year I (i.e., 2005) work, it was chosen as the typical catalyst for studying the surface properties of the catalytic membrane. Moreover, the mass of Sn coated onto the membrane was found to be easily controllable. After Sn was coated onto the membrane (stainless steel mesh), a small piece of the catalytic membrane was cut out and used to perform the surface analysis and characterization.

4.4 Results and Discussions

4.4.1 Surface Characterization

Figures 4.2 and 4.3 show the results of the XPS and XRD analyses, respectively. Results clearly indicate that the membrane surface was covered with films or nanoparticles of amorphous metal oxides. The presence of metal oxides was believed to be key to promoting the perchlorate adsorption onto the catalyst surface. Furthermore, the presence of amorphous metal oxides also increases the specific area of the catalytic membrane. These two factors explain why the reaction rate is more rapid for the catalyst-coated membrane than the bare membrane. Our results agree with those reported in the literature. Rusanova, et al (2006) [5] reported the enhancement of perchlorate reduction at a Ni electrode by the deposition of Pt. They indicated that the surface structure of the electrode was drastically modified upon the deposition of a small amount of Pt.

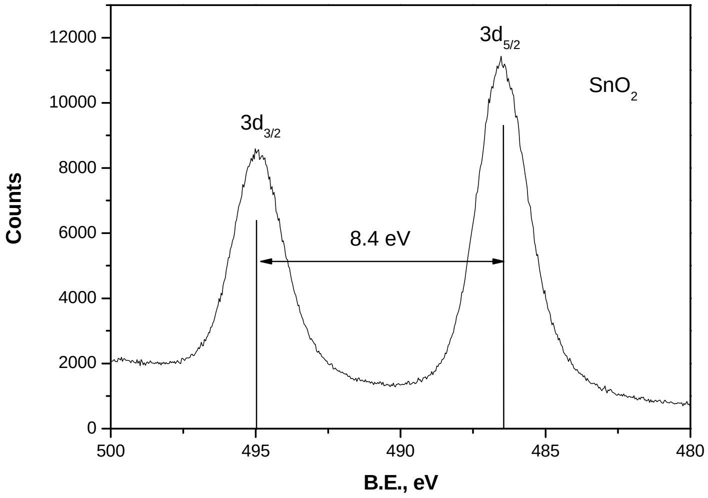


Figure 4.2 XPS analysis of Catalytic Membrane Coated with Sn.

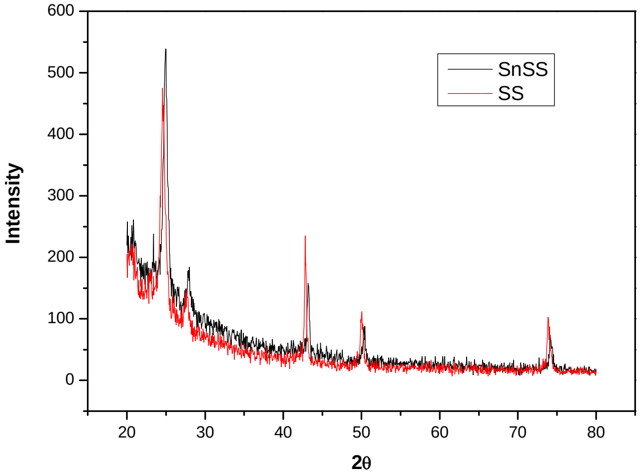


Figure 4.3 XRD analysis of Catalytic Membrane Coated with Sn.

4.4.2 Stability of catalytic membrane

In Year I work, we reported a slight loss of catalysts after the experiments. To minimize catalyst loss, annealing of catalyst was performed at different temperatures. After coating, a series of catalytic membranes was annealed by thermal treatment in a 10% hydrogen gas stream at the following temperatures: 300, 400, 500, 600 and 700^{o}C, respectively.

When the catalyst-coated membrane was in contact with water, hydrolysis reaction took place, which might render the metal oxides soluble, dependent mainly on the pH of the solution. This metal solubilization reaction can be minimized by applying a negative potential (i.e., cathodic) on the catalytic membrane. However, as reported in our 2005 Annual Report, there was a small amount of metal solution in the catalytic mono-membrane system (note: There was no metal dissolution in the catalytic dual membrane system because the catalytic membrane acts as cathode). It was postulated that a reduction reaction took place readily between the perchlorate ions and the metallic catalysts, which resulted in loosening the surface structure of the catalyst.

Figure 4.4 shows the percentage of mass loss of the catalyst as a function of the annealing temperature. Table 4.1 summarizes the elemental composition of the catalytic membrane treated at various temperatures. Results indicate that annealing at 500^{o}C, the catalyst suffered the most mass loss, whereas the mass loss was the lowest when annealing was carried out at 600^{o}C.

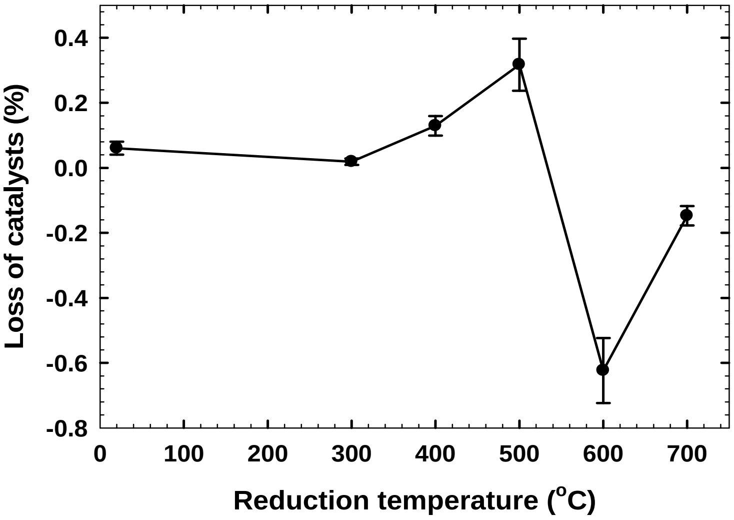


Figure 4.4 Loss of Catalyst that was Treated at Carious Annealing Temperatures.

Experimental conditions: Coated catalyst = Co (0.1~2.5 mg/g membrane); CM = annealed at different temperature in 10% hydrogen gas for 2 hours; contact time = 24 h in perchlorate solution with an initial concentration of 10 ppm.

From Table 4.1, it can be seen that after cobalt coating, the atomic O to Co ratio increased. This confirmed the XPS results that metallic catalyst was present as a metal oxide on the surface of the catalytic membrane. After annealing in 10% H_2 gas, the oxygen atom fraction decreased, whereas the Co fraction increased for most catalytic membranes. The oxygen atom fraction increased when the catalytic membranes were brought into contact with perchlorate solutions. Figure 4.4 shows that mass loss of the metallic catalyst was negligible at the annealing temperature of > 600^{o} C. It is believed that the decrease in perchlorate reduction rate is closely related to loss of catalyst mass.

Table 4.1 Element Composition of the Catalytic Membrane at Different Stages of Thermal Treatment.

Sample	Temperature (^{o}C)	Element composition (% in atom)							
		O	Si	Cr	Mn	Fe	Co	Ni	Mo
Post-coating	700	56.16	0.26	4.87	0.56	15.49	19.92	2.46	0.26
	600	14.62	0.68	15.34	1.59	54.88	1.99	9.8	1.1
	500	17.77	0.56	15.21	1.25	52.23	2.79	9.31	0.88
	400	25.19	0.63	13.02	1.29	45.44	5.56	7.96	0.92
	300	10.84	0.54	16.57	1.67	58.61	0.99	9.84	0.94
Post-annealing	700	27.94	0.81	14.93	1.48	37.15	11.79	5.29	0.61
	600	15.46	0.61	15.68	1.25	54.49	2.47	9.07	0.97
	500	11.99	0.54	16.42	1.39	58.19	0.51	9.86	1.09
	400	14.74	0.6	15.02	1.32	52.47	5.65	9.06	1.15
	300	11.11	0.56	16.78	1.52	58.34	0.51	10.15	1.04
Post-experiments	700	37.89	0.51	13.55	1.27	32.53	9.25	4.5	0.5
	600	22.57	0.62	14.34	1.3	49.3	2.24	8.74	0.89
	500	37.78	0.26	11.83	1.1	40.68	0.56	6.98	0.82
	400	12.27	0.81	16.18	1.5	57.14	0.97	10.21	0.92
Bare membrane	20	12.09	0.43	15.97	1.62	58.53	0.67	9.76	0.92

4.4.3 Surface reactions at low concentrations

It is expected that the perchlorate reduction rate will be slow in the catalytic mono-membrane system without improvement. As documented in our 2005 Annual Report, it was found that Pt was one of the best catalysts for rapid perchlorate reduction. To enhance the adsorption of perchlorate ions onto the membrane surface, Pt powder was added to the reactor. The variation in concentration of chlorine species was recorded as a function of reaction time.

For the catalytic mono-membrane system, the concentration enhancement at the catalytic membrane surface was negligible. To make up for the loss of reaction rate, it is desirable to minimize the loss of catalysts. Figure 4.5 shows the change of concentration of various chlorine species in the presence of Pt powders. Additionally, the catalytic membrane was coated with Pt without annealing.

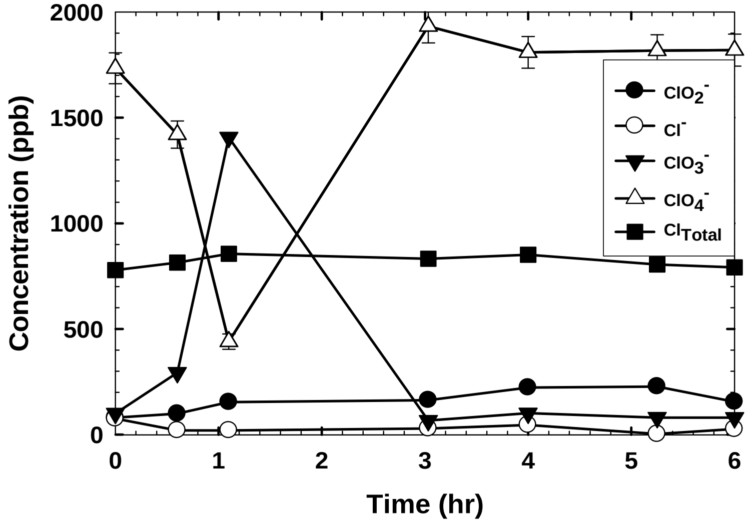


Figure 4.5 Reduction of ClO_4^- in Catalytic Mono-membrane System with Addition of Pt Powder.

Experimental conditions: Perchlorate concentration = 1700 ppb; CM = membrane coated with Pt-Ti; Pt powder added = 0.021g; temperature = 19.8 ^oC; pH = 7.0; anode = Fe; cathode = catalytic membrane; voltage applied = ~30 V; current = 5 mA.

The reduction of perchlorate took place rapidly during the first hour, and then increased. The decrease of perchlorate occurred simultaneously with the formation of chlorate, ClO_3^-. Chlorate was the major byproduct. The concentration of chloride remained small, however. The speculation that there might be a reaction between the Pt powder and the perchlorate ions was not conclusive. When Pt powder was dissolved in the reactor compartment, the multivalent cationic Pt species that was released formed a positively charged layer on the catalytic membrane surface, which significantly enhanced the adsorption of perchlorate ions. However, when the Pt powder was completely utilized, the perchlorate reduction halted and the electrochemical oxidation of chlorate ions occurred, which resulted in an increase in perchlorate concentration. As a result, the chloride concentration remained unchanged due to the rapid oxidation of chloride to chlorate then to perchlorate.

In summary, the kinetics of the catalytic mono-membrane system can be related to the following parameters: concentration of perchlorate in the bulk solution ($[ClO_4]$), applied current (I), or current density.(ρ), applied potential, (E), catalytic membrane properties, (k_m), catalyst (k_c), pH, temperature (T), and mixing (ε). The qualitative kinetics equation can be written as follows:

$$-\frac{d[ClO_4^-]}{dt} = f([ClO_4^-],\rho,E,k_c,k_m,pH,T,\varepsilon)\cdot$$

Chapter 5: Indirect Electrochemical Ti-TiO_2 System

5.1 Introduction

The Ti-TiO_2 system is a process that belongs to the indirect electrochemical reduction reaction. It is termed an indirect electrochemical reaction because perchlorate reduction takes place on the anode instead of the conventional cathode. The Ti-TiO_2 system is not a simple electrochemical cell per se. Once the Ti electrode is activated, a layer of TiO_2 is formed on the electrode surface. Since the Ti electrode is positively charged, the accumulation of perchlorate ions is enhanced on the Ti-electrode surface. As a result, perchlorate reduction occurs on the Ti electrode surface through a series of reactions between perchlorate ions and multi-valent Ti species, such as Ti^{2+} and Ti^{3+}. In this study, the research focused on the reactivity and mechanisms of the system.

5.2 Materials and Methods

5.2.1 Chemicals

The following chemicals were purchased from Sigma-Aldrich (Allentown, PA): perchlorate acid (purity 67~71%), sodium perchlorate (purity > 95%), ammonium perchlorate (purity > 98%), potassium chlorate (purity > 98%), sodium chlorite (purity > 80%), sodium chloride (purity >99.5%), sodium nitrate (purity > 98%). Titanium rods (purity 99.6%, Φ4x100 mm) were purchased from Goodfellow Company (Berwyn, PA). Graphite rods (Φ5x150mm) were purchased from Poco Company (Decatur, TX).

5.2.2 Electrochemical system

Figure 5.1 shows a photo (left) and a schematic (right) of the laboratory Ti-TiO_2 system. The working electrode was a Ti rod coated with TiO_2 and was the anode of the system. The electrochemical reactor was a Pyrex-glass beaker with a volume of 1500 mL. The anode was a Ti rod (Φ4x100 mm) with a total surface area of ca. 12.8 cm^2. The cathode was either an iron rod (Φ0.1x100 mm) or a graphite rod (Φ5x150mm). Both anode (Ti) and cathode (iron or graphite) were placed into the covered reactor and submerged in the solution at a depth of > 6 cm. The electrochemical reaction was initiated by the application of DC voltage to yield a specific constant current using a power supply (Model FB1000, Fisher Scientific Company, USA). A magnetic stirrer was used for mixing during the experiment.

5.2.3 Experiments

In order to elucidate the reaction mechanisms and the capability of perchlorate reduction at ultra-low to low concentrations under ambient conditions, the following experiments were conducted: 1) reduction of perchlorate in synthetic solutions, 2) reduction of perchlorate in tap water media, 3) reduction of perchlorate and nitrate in synthetic solutions, 4) effect of co-anions, 5) **effect of major cations,** 6) oxidation of chloride and chlorate, and 8) surface analysis and characterization of the Ti electrode and its solid products.

Figure 5.1 Ti-TiO$_2$ Systems for ClO$_4^-$ Reduction.

5.2.3.1 Reduction of perchlorate in synthetic solutions

Experiments on the reduction of perchlorate in synthetic solutions were conducted in three different initial concentrations: 100 ppm, 500 ppb and 150 ppb. The solutions were prepared by dissolving a given amounts of ammonium perchlorate in distilled water. For the solutions at 100 ppm of perchlorate, the applied potential was 10 and 15 V, which maintained a constant current of 20 and 50mA or current density of 3.8 and 9.5 mA/cm^2, respectively. Experiments on solutions containing 150 and 500 ppb perchlorate were conducted at an applied constant current of 10 mA or current density of 1.9 mA/cm^2. In order to maintain the necessary conductivity under such ultra-low perchlorate concentrations (e.g., 150 ppb), sodium chlorate at a concentration of 600 ppb was added to supplement the ionic strength.

5.2.3.2 Reduction of perchlorate in tap water media

Perchlorate reduction experiments were conducted with solutions containing 10 ppm of perchlorate. The solutions were prepared by introducing 18 mg of ammonium perchlorate into 1500 mL of tap water. After mixing for half an hour, the power supply was turned on to start the reduction experiments. Appendix C lists the chemical compositions of local tap water. Obviously the perchlorate concentration used in the experiment was small compared to that of the major common anions.

5.2.3.3. Reduction of perchlorate and nitrate in synthetic solutions

Experiments were conducted to study the co-reduction of perchlorate and nitrate using synthetic solutions. The experiments were conducted at two perchlorate concentration levels, i.e., the ppb and ppm ranges. For solutions in the ppm range, the initial concentrations of perchlorate and nitrate were 40 and 20 ppm, respectively. For solutions at the ppb level, the concentrations of perchlorate and nitrate were 90 ppb and 1000 ppb, respectively. All solutions were prepared from ammonium perchlorate and sodium nitrate salts, correspondingly. The applied potential was 10V, which was able to maintain constant currents of 20 and 50 mA (or current density of 1.9 and 9.5 mA/cm^2), respectively, for solutions containing perchlorate and nitrate at the low (e.g., ppm range) and ultra-low (e.g., ppb range) concentration levels, respectively.

5.2.3.4 Effect of co-anions

Perchlorate solutions were prepared by adding about 14 mg of ammonium perchlorate to 50 L of distilled water. The concentration of perchlorate in the solution was 245 ppb. Stock solutions containing competing ions were prepared by dissolving sodium chloride, sodium nitrate, sodium sulfate, and sodium bicarbonate in various amounts to one liter of distilled water to produce final anion concentrations from 10^{-3} to 1 M. The stock solutions were used to prepare the working solutions containing the competing anions at various concentrations while keeping the perchlorate concentration constant at 245 ppb. The typical concentration of the competing ions was in the range of 10^{-6} to 10^{-3} M. After mixing for 30 minutes, the power supply was turned on to start the reduction reaction. Samples were taken every hour, and the residual concentrations of perchlorate and competing ions were analyzed.

5.2.3.5 Effect of major cations

A stock solution of perchlorate was prepared as described above. Stock solutions containing the cations were prepared by dissolving a given amount of calcium chloride or magnesium chloride salts in distilled water. The working solutions were prepared by adding a given volume of the cation-containing stock solution to 1.5 liters of perchlorate solution containing 245 ppb of perchlorate to produce final cation concentrations in the range of 10^{-6} to 10^{-5} M while keeping the perchlorate concentration constant at 245 ppb. After mixing for 30 minutes, the power supply was turned on to start the experiments. Samples were taken hourly to analyze the residual concentration of perchlorate. The applied potential was 30 V, which was able to maintain a constant current of 10 mA (or current density of 1.9 mA.cm^2).

5.2.3.6. Oxidation of chloride and chlorite

In order to understand the mechanism of perchlorate reduction under ultra-low perchlorate concentrations (e.g., 100–245 ppb), the oxidation of chloride and chlorite was studied. The solutions were prepared by adding a given amount of sodium chloride in distilled water to yield a final chloride concentration of 6 ppm. The distilled water also contained about 260 ppb of residual chlorite. The applied voltage was 30 V, which maintained a constant current of 10 mA (or current density = 1.9 mA/cm^2). The changes in concentration of chloride, chlorite, chlorate, and perchlorate were monitored with time hourly.

5.2.3.7 Surface analysis and characterization of the Ti electrode and its solid products

The solid product on the Ti electrode surface was collected and characterized. The solid product was collected from the reactor and centrifuged at 2000 rpm (or 224 g) in a Hermle Z383k refrigerated centrifuge (Labnet International, Inc. Edison, NJ, USA). After air-drying for 24 hours, the solid was ground to fine particles using a marble motor and pestle. The fine particles were used to prepare samples for SEM/EDAX, XRD and XPS analyses. The SEM/EDAX analysis was performed by a JSM-7400 field scanning electron microscope with a resolution of 1 nm at 15kV. An XEDS detector was used to detect the elements of the solid product. The X-ray diffraction (XRD) pattern of the solid byproduct was performed using a Rigaku D-Max B diffractometer, which is equipped with a graphite crystal monochromator operated with a Cu anode and a sealed x-ray tube. The 2θ scans were recorded using the Cu $K_{□}$ radiation with a wavelength of 1.5405 Å from 20^{o} to 80^{o} with a step size of 0.05^{o}. The chemical composition of the solid byproduct was studied by x-ray photoelectron spectroscopy (XPS) analysis. An SSI-M probe XPS employing an Al K_{α} (hυ = 1486.6 eV) excitation source was used. Peak positions were obtained with reference to the C 1s peak at 284.6 eV. The system pressure was maintained at 1-3 x 10^{-8} Torr during the acquisition of the spectra.

5.2.4 Sampling and analytical methods

Samples were collected from the batch reactor with a 10-mL disposable syringe and filtered by membrane filter with a pore size of <0.2 μm (Fisher Scientific, CA). The analysis of residual perchlorate species was based on EPA method 314.0 [32] with slight modifications. Ion chromatography was the primary analytical technique used to detect perchlorate, chlorate, chlorite, chloride, nitrate, and nitrite. The IC system (Model ISC300, Dionex Co., Sunnyvale, CA, USA) was equipped with a GP50 pump, a conductance detector, and an EG 40 effluent generator. The species separation step was executed with a 4-mm Dionex AS-16 anion-exchange analytical column and guard column. The flow rate of sodium hydroxide effluent was 1.20 mL/min with a concentration gradient to assure a satisfactory separation and detection limit. For all experiments with an initial perchlorate concentration of >1 □M (or ca. 100 ppb), a 25-μL-injection loop was used for perchlorate analysis. For concentrations <1 □M, the injection loop was changed to 1000-μL.

5.3 Results and Discussions

5.3.1 Reduction of perchlorate in synthetic solutions

Figure 5.2 shows the reduction of perchlorate over a period of 8 h at an initial concentration of 100 ppm and constant current densities of 3.8 and 9.5 mA/cm^{2}. Perchlorate reduction took place readily and yielded 80 and 92% removal in 8 h at current densities of 3.8 and 9.5 mA/cm^{2}, correspondingly. Chloride ions dominated the reaction products. The reduction rate followed a first-order expression with rate constant of $4.6x10^{-5}$ s^{-1} (or 4.0 d^{-1}) and 3.47 $x10^{-5}s^{-1}$ (or 3.0 d^{-1}), at current density of 9.5 and 3.8 mA/cm^{2}, individually. Our rate constants were favorably competitive with other systems. Logan, et al. reported a maximum biokinetic constant of 1.2 d^{-1} for the degradation of perchlorate by two perchlorate isolates, e.g., "*Dechlorsoma*" sp. Strain KJ and PDX [33]. Cao, et al reported a rate constant of 0.3d^{-1} for the reduction of perchlorate by nano-ZVI at 25 ^{o}C and pH of 6-8 [34]. Yu, et al. studied perchlorate reduction using autotrophic bacteria in the presence of ZVI and reported a rate constant of 0.7 to 1.4 d^{-1} at pH 8 and 7, respectively [12].

Figure 5.3 shows the reduction of perchlorate at an initial concentration of 500 ppb and constant current of 10 mA. It is noted that the potential applied was much higher than that containing 100 ppm of perchlorate. It can be seen that the distribution of chlorine species was different from

Figure 5.2 due to the higher potential (~60V) applied. The rise of chlorate and perchlorate concentration during the first hour was brought about by the oxidation of chloride and chlorite in the solution. It is expected that residual chlorine species will be present in the distilled water used for sample preparation. However, once the reduction reaction started, the concentration of perchlorate and chlorate dropped readily, and the concentration of chloride and chlorite increased accordingly. The loss of total chlorine was significant, and chloride was not the dominant end product.

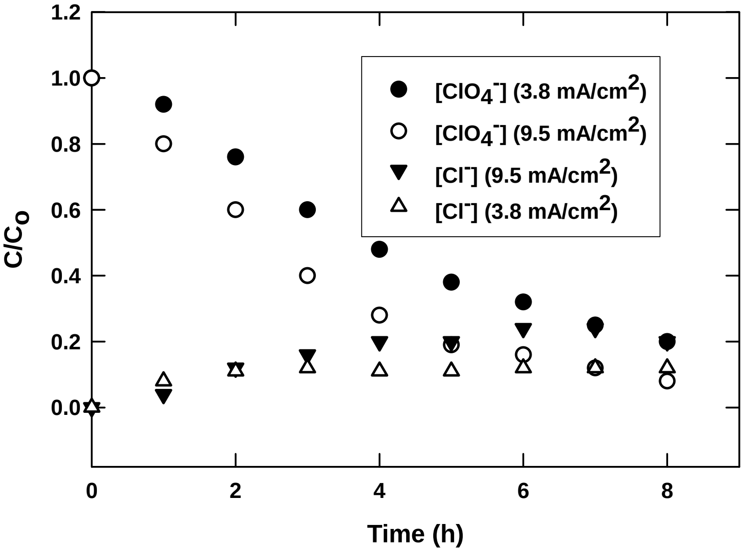


Figure 5.2 Reduction of ClO_4^- with Initial Concentration of 100 ppm.

Experimental conditions: Perchlorate concentration = 100 ppm; temperature = 25 ^{o}C; pH = 7; anode = Ti; cathode = Fe; voltage applied = 10 V; solid diamonds and open diamonds are for perchlorate and chloride respectively at current = 20 mA (or current density = 3.8 mA/cm^2). Solid triangles and open triangles are for perchlorate and chloride respectively at current = 50 mA (or current density = 9.5 mA/cm^2)

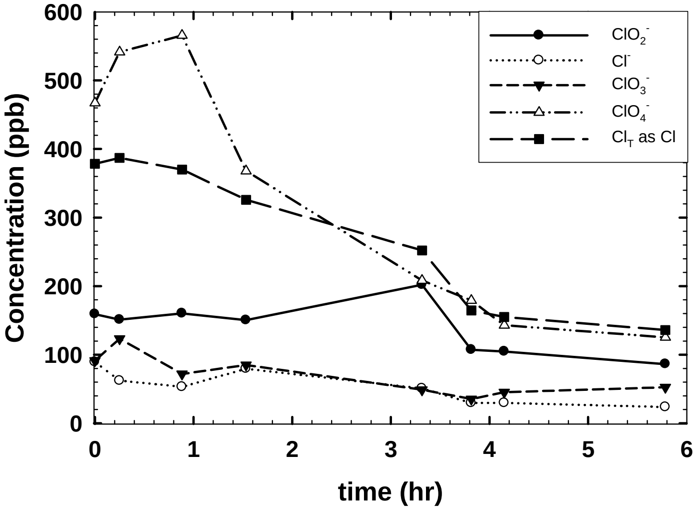


Figure 5.3 Reduction of ClO_4^- with Initial Concentration of 500 ppb.

Experimental conditions: Perchlorate concentration = 500 ppb; temperature = 25 ^oC; pH = 5.6; anode = Ti; cathode = Fe; voltage applied = ~60 V; current = 10 mA (or current density = 1.9 mA/cm^2).

Figure 5.4 shows the reduction of perchlorate at an initial concentration of 150 ppb in chlorate solution over a reaction period of 8 h. Results clearly indicate that it is possible to reduce perchlorate from 150 ppb to <20 ppb in hours. The perchlorate concentration increased initially by oxidation of chlorate to about 300 ppb at 2 h, then decreased to <20 ppb at 8 h. Intermediates, especially chlorite (ClO_2^-), increased during the first 6 h, reached a maximum value of 500 ppb, and then decreased to 200 ppb at 8 h. Chloride concentration remained low at 20 ppb during the first 2 h, then increased to about 200 ppb at 8 h. The total chlorine mass remained relatively constant during the first 5 h, then decreased to 200 ppb at 8 h. The decrease in total chlorine mass coincided with the reduction of chlorite and perchlorate, however. As will be discussed later, obviously at the onset of the electrochemical reaction, the Ti electrode was not activated, so the oxidation of chlorate to perchlorate took place on the un-activated Ti anode, which resulted in an instant increase of perchlorate. Once the Ti electrode was activated, reduction reactions occurred readily, which brought about reduction of all chloro-oxyanions, including perchlorate, chlorate, and chlorite. Overall, perchlorate reduction occurred readily even at initial concentrations of less than 1 ppm under ambient conditions.

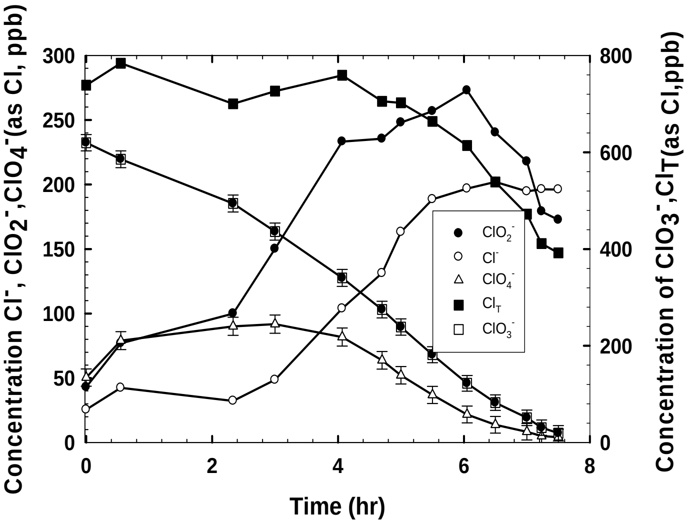


Figure 5.4 Reduction of ClO_4^- and ClO_3^- with Initial Concentration of 150 ppb.

Experimental conditions: Perchlorate concentration = 150 ppb; chlorate concentration = 600 ppb; temperature = 25°C; pH = 6.0; anode = Ti; cathode = Fe; voltage applied = ~20 V; current = 10 mA (or current density = 1.9 mA/cm^2)

5.3.2 Reduction of perchlorate in tap water media

Figure 5.5 shows the reduction of perchlorate with an initial concentration of 10 ppm in tap water. The reduction of perchlorate followed a zero-order expression. The removal efficiency of perchlorate was about 40% in six hours of reaction. The rate was estimated to be 6.7 $\mu M. h^{-1}$. It is also noted that sulfate was not removed, whereas, as expected, nitrate was removed at about the same rate as perchlorate. Obviously, these two species competed with each other in the reduction process.

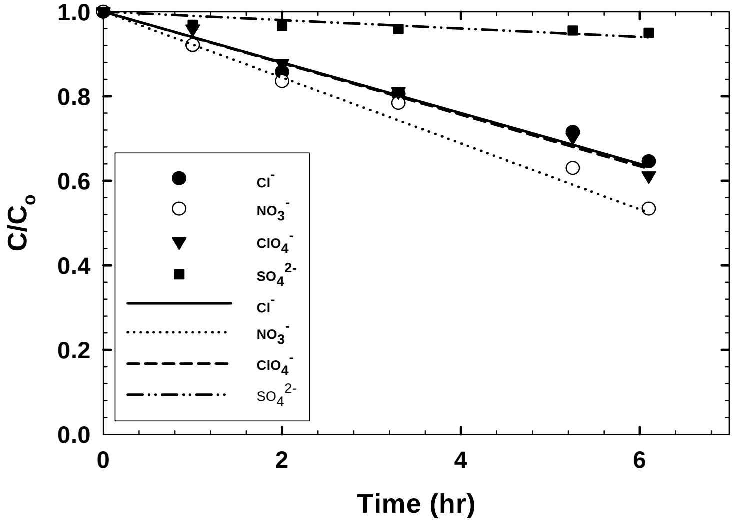


Figure 5.5 Reduction of ClO_4^- with Initial Concentration of 10 ppm in Tap Water.

Experimental conditions: Perchlorate concentration = 10 ppm in tap water; temperature = 25 °C; pH = 6.8; anode = Ti; cathode = Fe; voltage applied = ~10 V; current = 10 mA (or current density = 1.9 mA/cm^2)

5.3.3 Reduction of perchlorate and nitrate in synthetic solutions

Figure 5.6 shows the results of the co-reduction of perchlorate and nitrate at initial concentrations of 40 and 20 ppm, respectively. Results show that both perchlorate and nitrate were reduced effectively with removal efficiencies of 48% and 40% in 10 h for perchlorate and nitrate, respectively. Chloride was the major end product of perchlorate reduction, whereas there were no observable end products from nitrate reduction. The absence of nitrate reduction end products can be attributed in part to the formation of gaseous nitrogen and/or ammonia, which is volatile. It is interesting to note that the degree of chlorine mass balance in the perchlorate-nitrate system was better than that of the perchlorate-only system. This can be attributed to the completeness of perchlorate reduction. In the perchlorate-only solution, the degree of perchlorate reduction was complete with the production of chloride as the major end product; in contrast, in the perchlorate-nitrate solution, the degree of perchlorate reduction was incomplete with the production of intermediates such as hypochlorite and chlorine, which are volatile.

Figure 5.6 also shows results of the reduction of nitrate in a nitrate-only solution over a period of 6 h. As expected, nitrate reduction was effective following a linear decay rate expression. Nitrite, which constituted about 50% of the nitrate ions reduced, was the major end product. The imbalance in total nitrogen mass again can be attributed to the loss of nitrogen in the form of gaseous nitrogen or ammonia and the possible incorporation of nitrogen atoms into the Ti electrode surface, as will be discussed later.

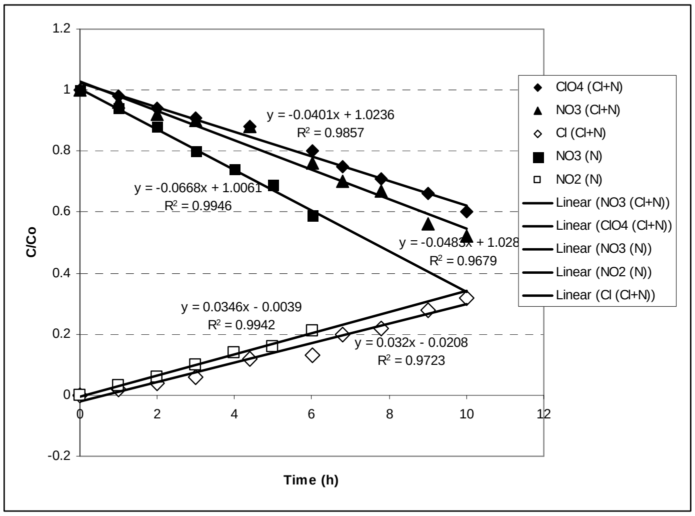


Figure 5.6 Reduction of ClO_4^- and NO_3^- in Distilled Water.

Experimental conditions: Solid diamonds, solid triangles and open diamonds are perchlorate, nitrate and chloride respectively in the perchlorate plus nitrate system where the perchlorate concentration was 20 ppm and nitrate concentration was 40 ppm. Solid squares and open squares were nitrate and nitrite concentration respectively in the nitrate only system where the nitrate concentration was 10 ppm. All other experimental conditions were temperature = 25 ^{o}C; pH = 7; anode = Ti; cathode = Fe; voltage applied = 10 V; current = 50 mA (or current density = 9.5 mA/cm^2)

Figure 5.7 shows the results of the reduction of perchlorate and nitrate at initial concentrations of 90 ppb and 1000 ppb, respectively. It can be seen from Figure 5.7 that the residual concentration of perchlorate was less than 10 ppb after six hours with an initial concentration of 10 ppb. Nitrate was also reduced to less than 160 ppb with an initial concentration of 1000 ppb. The same is true with Figure 5.6; no end product of nitrate reduction was detectable during the experiment. Other chlorine species were detected, and chloride was found to be the dominant end product.

5.3.4 Effect of co-anions

Figure 5.8 shows the effect of anions, namely, sulfate, bicarbonate, and nitrate, on the reduction of perchlorate. It must be mentioned that the concentrations of these competing anions were at least 400 times that of perchlorate (in molar ratio). Results indicate that sulfate and chloride had the most severe effect on perchlorate reduction. In the presence of sulfate and chloride at a concentration 400 times that of perchlorate, the perchlorate concentration increased by 30 to 40% during the first hour of reaction. This increase in perchlorate can be attributed to the oxidation of residual chlorite in the distilled water. Perchlorate reduction in the presence of sulfate remained insignificant over the reaction time observed. However, the reduction of perchlorate increased gradually after one hour when chloride was present at an excessive concentration relative to that of perchlorate. The effect of nitrate was less significant compared to that of sulfate and chloride during the early phase of the reduction reaction. The increase in perchlorate was the highest in the presence of chloride due to the presence of both residual

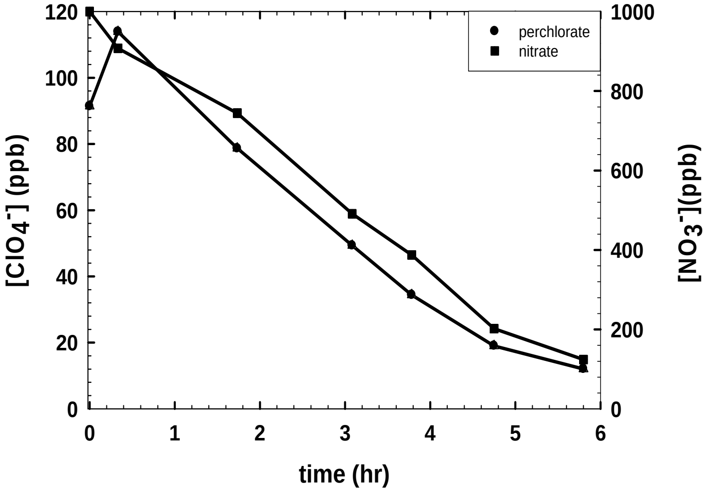


Figure 5.7 Reduction of ClO_4^- and Nitrate in a Ti-TiO_2 Surface System.

Experimental conditions: Perchlorate concentration was 90 ppb and nitrate concentration was 1000 ppb. All other experimental conditions were temperature = 25 °C; pH = 5.6; anode = Ti; cathode = Fe; voltage applied = 10 V; current = 10 mA (or current density = 1.9 mA/cm^2).

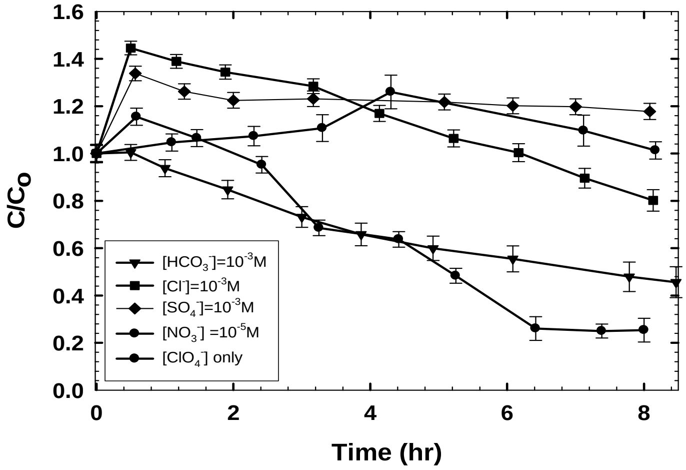


Figure 5.8 Anion Effects on Reduction of ClO_4^- at Ti-TiO_2 Surface.

Experimental conditions: Perchlorate concentration was 245 ppb and other ions were 10^{-3} M for bicarbonate, sulfate and chloride, 10^{-5}M for nitrate. All other experimental conditions were temperature = 25 °C; pH = 5.6~6.0; anode = Ti; cathode = Fe; voltage applied = 10 V; current = 10 mA (or current density = 1.9 mA/cm^2). chlorite and chloride, which can be oxidized to yield perchlorate. Nonetheless, once the electrode was fully activated as evidence of the formation of solid precipitates and subsequent dropping from the electrode surface, the perchlorate reductions occurred readily.

The time of maximum increase in perchlorate concentration was delayed from one hour in the presence of sulfate and chloride, to 4 hours in the presence of nitrate. This is because nitrate can be reduced simultaneously with perchlorate. During the early phase of the reaction, nitrate, not chlorite, occupied most of the activate sites on the Ti electrode. Once nitrate reduction started, the chlorite began to approach the Ti electrode. As a result, the concentration of perchlorate increased due to the oxidation of chlorite.

Figure 5.8 shows that nitrate, sulfate, and chloride have the greatest competing effect. Surface occupation and surface reduction are the major factors contributing to the competing effect of an anion. In the case of sulfate and chloride, surface occupation was the major factor. The adsorption of sulfate or chloride ions onto the anodically polarized Ti electrode surface, i.e., poisoning, impedes perchlorate reduction. In the case of nitrate, adsorption and surface reduction reaction plays the major role in inhibiting perchlorate reduction. Since bicarbonate has weak adsorption affinity toward the Ti-TiO_2 surface and it was not reactive with the Ti-TiO_2 surface, the effect of bicarbonate was insignificant.

Figure 5.9 shows the effect of nitrate on the reduction of perchlorate at various nitrate concentrations. The effect of nitrate on perchlorate reduction is unique in that at high nitrate concentrations, the reduction of perchlorate was severely inhibited, as discussed above. However, at low nitrate concentrations, e.g., $4x10^{-6}$ M, it enhanced the reduction of perchlorate. This enhancement resulted from two factors. The first factor is the interaction between nitrite and intermediates of perchlorate reduction, which will be discussed later. The second factor is the electrical double layer effect resulting from the specific adsorption of nitrate ions. Specific ion (e.g., nitrate, chloride) adsorption can modify the surface potential at the OHP by rendering the surface potential more negative. This will decrease the thickness of the electrical double-layer, which in turn will facilitate the interactions between perchlorate and the Ti-TiO_2 surface. The reaction rate will reach the maximum when these two effects make equal contributions. It should be noted that nitrate was reduced at the surface also. This reaction enables the surface to always remain active during the reaction.

Figure 5.10 shows the results of the effect of sulfate on perchlorate reduction as a function of sulfate concentration. It can be seen that even when the concentration of perchlorate and sulfate was of the same order of magnitude, the reduction of perchlorate was inhibited by sulfate. As will be discussed later (in the kinetics section), the formation of $TiOSO_4$ from the interaction between the adsorbed sulfate and the electrode surface will impede the contact between perchlorate and the active surface of the electrode. Upon the application of an anodic potential onto the Ti electrode, anodic reaction brought about corrosion, which yielded various titanium ions, e.g., Ti(II), Ti(III) and Ti(IV). These titanium species will react with sulfate to form a new surface of Ti-$TiOSO_4$. Unless the adsorption of perchlorate is comparable to that of sulfate, perchlorate reduction will be affected. It is generally agreed that sulfate is more absorbable than perchlorate on the Ti electrode.

Figure 5.11 shows the effect of chloride on perchlorate reduction as a function of chloride concentration. The effect was generally similar to that of nitrate except that there was an early surge in perchlorate concentration during the first hour of the reaction. Furthermore, the effect of chloride on perchlorate reduction might be brought about by a mechanism quite different from that of nitrate. It is known that nitrate can be reduced by the Ti-TiO_2 system; no such reaction was possible for chloride.

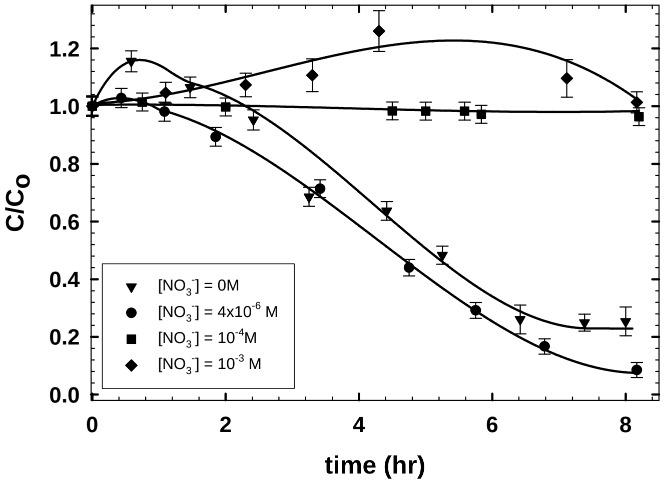


Figure 5.9 Nitrate Effects on Reduction of ClO_4^- at Ti-TiO_2 Surface.

Experimental conditions: The perchlorate concentration was 245 ppb and nitrate concentration was 0~10^{-3} M. All other experimental conditions were: temperature = 25 ^oC; pH = 5.6~6.0; anode = Ti; cathode = Fe; voltage applied = 6~30 V; current = 10 mA (or current density = 1.9 mA/cm^2).

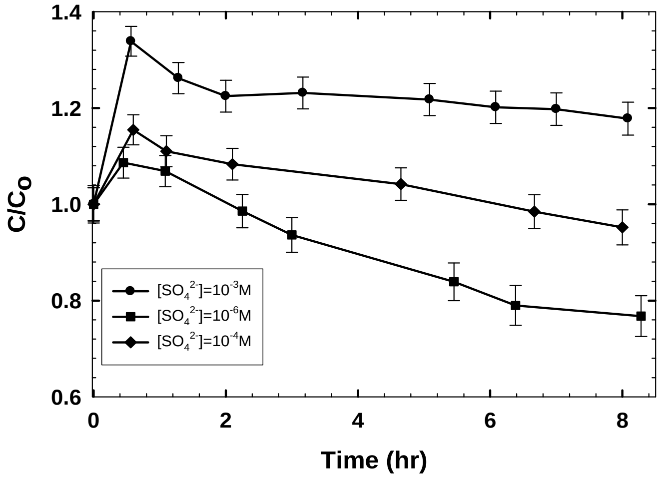


Figure 5.10 Sulfate Effects on Reduction of ClO_4^- at Ti-TiO_2 Surface.

Experimental conditions: The perchlorate concentration was 245 ppb and sulfate concentration was 0~10^{-3} M. All other experimental conditions were: temperature = 25°C; pH = 5.6~6.0; Anode = Ti; Cathode = Fe; Voltage applied = 6~30 V; Current = 10 mA (or current density = 1.9 mA/cm^2)

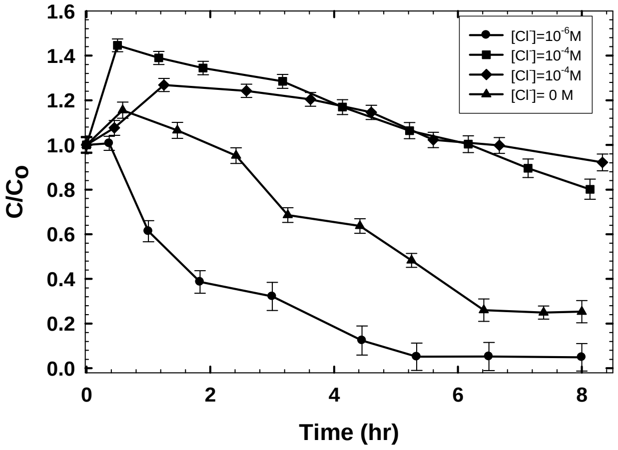


Figure 5.11 Chloride Effects on Reduction of ClO_4^- at Ti-TiO_2 Surface.

Experimental conditions: The perchlorate concentration was 245 ppb and sulfate concentration was 0~10^{-3} M All other experimental conditions were: temperature = 25°C; pH = 5.6~6.0; Anode = Ti; Cathode = Fe; Voltage applied = 6~30 V; Current = 10 mA (or current density = 1.9 mA/cm^2)

It is of great importance to note that the presence of chloride in trace concentrations was beneficial to perchlorate reduction. Results clearly indicate that the perchlorate reduction was much enhanced in the presence of chloride at a concentration of 4×10^{-6} M, which was about 100 times that of perchlorate (molar ratio). (Note: The perchlorate concentration was 2.45×10^{-8} M). Not only was there no early rise in perchlorate concentration, but the rate increased significantly also. A >95% perchlorate reduction was observed at 5 hours, whereas the percent perchlorate removal was ~80% in the absence of chloride. Due to the low electrolyte concentration of the solutions, the applied voltage varied between 6 and 30 V. When present at trace concentrations, the extent of chloride oxidation was at the minimum. Therefore, there was no increase in perchlorate concentration during the early phase of the reaction. The presence of chloride, even at a trace concentration, was adequate to enable the use of low applied voltage in the process. This will minimize the anodic oxidation of chloride and residual chlorite.

5.3.5 Effect of major cations

Figure 5.12 shows the effect of cations on the reduction of perchlorate in distilled water. Results indicate that the presence of Ca^{2+} at trace concentrations enhanced the reduction of perchlorate, whereas Mg^{2+} had no effect on perchlorate reduction. As discussed above, for any ion to exert an effect on perchlorate reduction, it must be reactive with the Ti-TiO_2 surface. In the absence of surface reactivity, the presence of ions can be beneficial, as they will contribute to the conductivity of the solution. An increase in electrical conductivity will decrease the applied voltage, which will minimize the oxidation of residual chlorite or chlorine. As a result, there is no rise in perchlorate and perchlorate reduction is enhanced. It is noted that the maximum increase of perchlorate was less than 5% with respect to the initial concentration in the presence of Mg^{2+}. No increase in perchlorate was observed in the presence of Ca^{2+}, however.

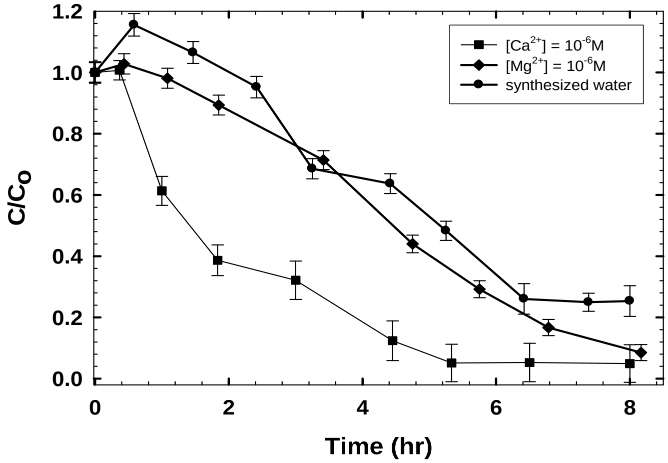


Figure 5.12 Cation Effects on Reduction of ClO_4^- at Ti-TiO_2 Surface.

Experimental Conditions: The perchlorate concentration was 245 ppb and Ca^{2+}, Mg^{2+} concentration was 10^{-6} M, respectively. All other experimental conditions were temperature = 25

^{o}C; pH = 5.6~6.0; Anode = Ti; Cathode = Fe; Voltage applied = ~30 V; Current = 10 mA (or current density = 1.9 mA/cm^2)

5.3.6 Oxidation of chloride and chlorate

To confirm the speculation that an increase of perchlorate during reduction experiments, under extremely low perchlorate concentrations, was brought by the oxidation of chloride and chlorite present in the media, experiments were conducted in solutions that contained only chloride ions. The initial concentrations of chloride and chlorite were 6 ppm and 260 ppb, respectively. The change in concentration of chloride, chlorite, chlorate, and perchlorate was monitored hourly.

Figure 5.13 shows the results of chloride oxidation at the Ti-TiO$_2$ surface. From the results, it can be seen that chloride concentration decreased with time due to oxidation, and other species such as chlorite, chlorate and perchlorate increased. The chloride ions were oxidized to chlorite, chlorate and perchlorate following a step-by-step manner. For the reducing Ti species, as discussed in the kinetics section, there was no change of chloride. So, oxidation of low-valent chlorine species into perchlorate occurred at high potential or inactive surfaces. As shown in both the reaction mechanism cartoon and the detailed reaction table, chloride will adsorb onto the surface and react with Ti(II) or Ti(III) to form TiClx, which will diffuse into the bulk solution due to the change of surface charge (from negative to neutral). However, TiClx is not stable in water; it will decompose into chloride and TiO$_2$ with reaction with water. So for chloride, there will be no change of concentration by the reducing site. For the oxidation site (TiO$_2$), chloride will be oxidized to chlorate and further perchlorate. In industry, the electrode is usually PbO$_2$-Pb surface; only oxidation occurs by applying positive potential. The difference of our system is that Ti(II) or Ti(III) can serve as the reducing agent.

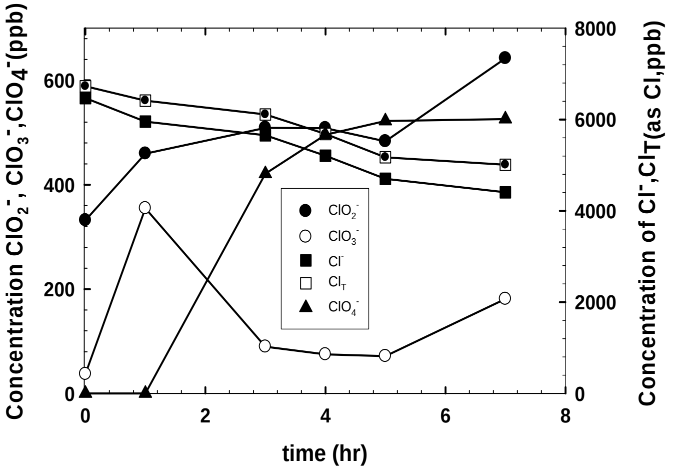


Figure 5.13 Oxidation of Chloride at a Ti-TiO$_2$ Surface.

Experimental conditions: The chloride concentration was 6000 ppb. Other ions initial exist in distilled water. All other experimental conditions were: temperature = 25 ^{o}C; pH = 5.6; Anode = Ti; Cathode = Fe; Voltage applied = ~30 V; Current = 10 mA (or current density = 1.9 mA/cm^2)

5.3.7 Surface analysis and characterization of the Ti electrode and its solid products

Particulate material was produced during the reduction of perchlorate at the Ti-TiO_2 surface. Although the amount of this by-product was small (less than 200 mg in a 1.5-liter solution per experiment), important information can be obtained by characterizing the solid. The solid particles that were dropped from the reaction site, i.e., the Ti-TiO_2 surface, provide excellent insights into the reaction mechanism.

The first observation of the particulate by-product was the difference in color of solid particles obtained from the various experiments described above. The commercial pure $TiO_{2,}$ e.g., P25, is white. The solid particles obtained from the reduction of nitrate in synthetic solutions were yellowish green. The solid particles derived from the reduction of perchlorate in tap water media were gray. The color of the solid particles from the reduction of perchlorate using hydrogen gas in distilled water was black. The difference in color among these solid materials collected from the above reactions strongly implies the presence of solid products of different chemical composition or crystal structure. The elemental composition of these solid particles was examined by EDX. Table 5.1 shows the EDX analysis of various solid products collected from the above experiments and compared with that of the pure commercial TiO_2. The results clearly indicate that there were differences in elemental composition of the solid particles resulting from the reduction of perchlorate and nitrate on the Ti-TiO_2 surface.

The crystal property of the solid end products was studied. It was found that all solid samples collected from reduction experiments were amorphous. No peak was found in the XRD spectra. However, after annealing at 700^{o}C, the amorphous particles did become crystallized. This is a reasonable scenario, as it is extremely probable that the solid end products were formed at ambient temperature via reaction of low-oxidation-number Ti species with water, perchlorate or electrochemically generated oxygen.

Table 5.1 summarizes the element composition of solid end products collected under various reaction conditions. The results clearly show that there were differences in elemental composition among the samples. Sample #1 was the pure commercial P25 TiO_2 from Degussa Company. Note that the commercial TiO_2 sample was supposed to be free of N or Cl atoms. The mass fractions of Ti and O were 18.48% and 80.86%, respectively. Other chemical species constituted about 0.66%, probably from impurities in the carbon tape used for sample preparation. Note that the Ti:O ratio was 1:4 instead of the stoichiometric value of 1:2. This can be attributed to oxygen uptake by the commercial TiO_2 sample due to exposure to oxygen during sample handling. Sample #2 was the P25 that was derived from the perchlorate adsorption experiment. The adsorption experiment was performed for 24 hours at ambient temperature and low perchlorate concentration and pH 5.6. The Ti:O ratio was 1:2.5 with a trace amount of Cl atoms, i.e., 0.17%. The atomic fraction of N was 10.13% resulting from ammonium perchlorate; however, there was uncertainty regarding the amount of N atom contributed from the distilled water used to prepare the perchlorate solutions. Sample #3 was derived from the P25 used in the nitrate adsorption experiment. The experimental condition was the same as above in perchlorate adsorption. The contribution of N (11.45%) was obvious, with the atomic ratio increased significantly compared with samples #1 and #2. Although we believe that most of the nitrate ions were adsorbed onto the particle surface, the ratio of Ti:O was not close to 2 seemingly with some loss of O atoms in the sample for unknown reasons. Sample #4 represented the solid

particles derived from the nitrate reduction experiment. The Ti:O ratio was 2:3, which was smaller than the stoichiometric value of pure TiO_2. However, the Ti: (N+O) ratio was 1:2. This could be attributed in part to the doping of N into the TiO_2 structure. The doping of N was further evidenced by the light-green color of the particles. Samples #5 and #6 were the solid particles collected from perchlorate reduction in the tap water medium. Sample #6 was prepared by washing the particulates first with distilled water before drying, whereas sample #5 was tested directly without distilled water rinsing. Results indicated that there was a significant increase in the concentration of both N and Cl atoms. The increase in surface Cl concentration can be attributed to the adsorption of Cl or un-reacted perchlorate ions that remained adsorbed on the TiO_2 surface. Results also showed that the surface concentration of Cl was one order of magnitude greater than that of the TiO_2 sample used in perchlorate adsorption, i.e., 1,22-2,18% versus 0.17%. It is speculated that Cl doping occurred during perchlorate reduction. This is further evidenced by the high surface Cl concentration upon washing with distilled water.
In order to support the above speculation, solid products were characterized using the XPS technique. Figures 5.14a, b and c show the Ti ($2p_{1/2}$, $2p_{3/2}$), O (1s), C (1s), N (1s), and Cl (2p) surveys of the solid particles collected at the end of the reaction using XPS. Peak positions were referenced to C (1s) peak at 284.6 eV. Figure 5.14a shows the Ti 2p peaks of the solid products. It clearly shows the shift of the binding energy of the 2p electron in TiO_2. The position of the 2p electron and their binding energy difference is the signal of intrusion of other species into the chemical bond. The Ti $2p_{1/2}$ and Ti $2p_{3/2}$ peaks were positioned at 463.58, 457.76 and 463.96, 458.23, respectively. And the peak separations (Ti 2p1/2 and 2p3/2) were 5.82 and 5.73 eV, respectively. The peak positions and peak separations of the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ in both cases agreed well with results of our earlier work on the synthesis of TiO_2 by metalorganic chemical vapor deposition (MOCVD) [35] and those reported by others[36, 37]. A slight shift toward higher binding energy suggested that titanium in the $TiO_{(2-x)}Cl_x$ structure was more oxidized compared to that in nitrate reduction ($TiO_{(2-x)}N_x$) due to the higher electron affinity of Cl ions in Ti-Cl than N ions in Ti-N bonding.

Figure 5.14b compares the binding energy of N (1s) for nitrate reduction and perchlorate reduction. Since the presence of ClO^- and ClO_2^- species might promote the transformation of NO_3^- more toward gaseous N_2 than to NO_2^-, the binding energy of N (1) at 399.5 ± 0.2 suggests that the N atoms were doped into TiO_2 lattice as $TiO_{(2-x)}N_x$ formation [36, 38]. An additional N (1s) peak was found in the nitrate reduction experiment at 406.2 eV. This suggests the adsorption of NO_2^- onto $TiO_{(2-x)}N_x$ particle surfaces because metallic titanium was not found in the particles.

Figure 5.14c shows the binding energy Cl 2p for the solid reaction products. A broad 3.3 eV full-width-of-half-maximum (FWHM) suggests the presence of Cl species at multi-valance states. D'Hennezel et al. (2001) [39] reported Cl (2p) binding energy at 199.7 eV for perchloronated TiO_2 surface. Our results on both XPS and IC also showed the presence of ClO_4^-. In addition, ClO_2^- and $TiO_{(2-x)}Cl_x$ species were suspected to be present in the solid end products. It can be seen that lower binding energies of Cl (2p) were also observed. Results clearly indicate that both N and Cl were doped into TiO_2 lattice with a formation of $TiO_{(2-x)}$, Cl_x $TiO_{(2-x)}N_x$, or $TiO_{(2-x-y)}N_xCl_{y,}$.

Table 5.1 Chemical Composition of Various TiO_2 Products.

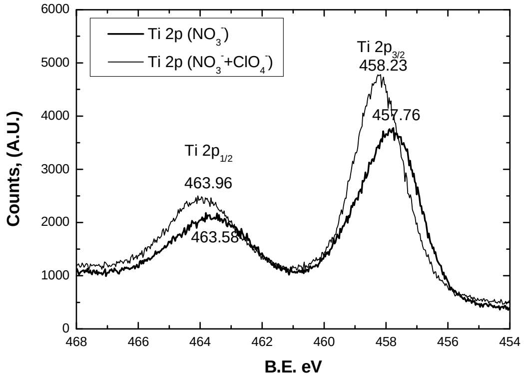
Sample		Atomic ratio of different element (%)					
		Ti	O	N	Cl	Other	total
#1	P25	18.48	80.86	0	0.0	0.66	100
#2	P25-ClO_4^- adsorption	27.45	61.88	10.13	0.17	0.37	100
#3	P25-NO_3^- adsorption	32.48	54.28	11.45	0.0	1.79	100
#4	Reduction of NO_3^-	32.68	50.38	15.12	0.0	1.82	100
#5	Treatment of tap water	19.42	66.38	10.06	1.22	2.92	100
#6	Treatment of tap water*	26.98	55.97	11.61	2.18	3.26	100

* Washing with distilled water before drying the particles

5.4. Perchlorate reduction mechanism

5.4.1 Description of the removal process

The removal of contaminants at the Ti-TiO_2 surface system can be simplified into three steps, i.e., adsorption, reaction and desorption. Adsorption is the first and critical step for this process. It is the step during which contaminants diffuse from the bulk solution and are adsorbed onto the surface. From the results discussed above, it can be found that the adsorption of perchlorate on the metals was so small that it severely affected the reduction rate. To improve the reaction rate, adsorption needs to be enhanced first.



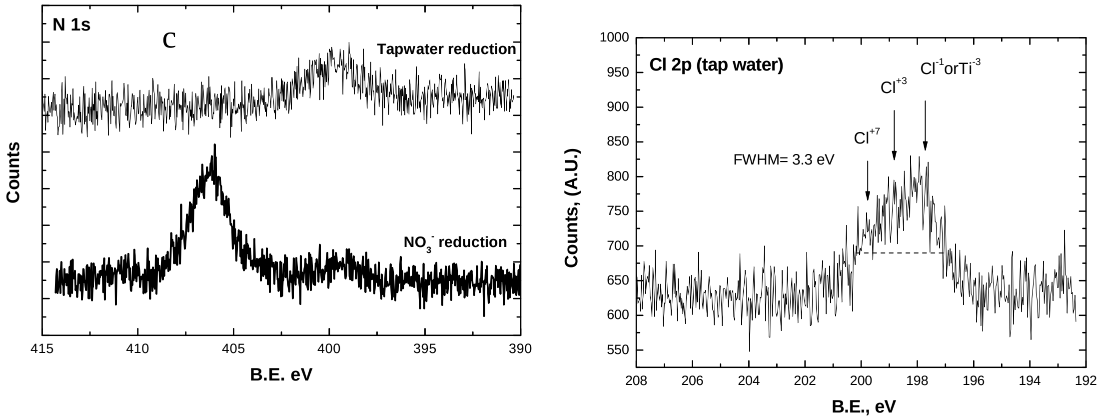


Figure 5.14 XPS Analysis of the Particulate by-products. (a) Ti; (b) N; (c) Cl.

From Gibbs adsorption isotherm, $-d\gamma = \sum_i \Gamma_i d\bar{\mu}_i$, the adsorption of perchlorate can be enhanced by applying potential on the surface. In ultra-high voltage conditions, the adsorption of perchlorate on several metals such as Au, Re is specific, but with water molecules introduced into the system, adsorption became non-specific. However, other researchers have argued that at positive potentials, the adsorption of perchlorate may be specific. The consistent conclusion is that perchlorate adsorption capacity will be enhanced by applying positive potential on the surface. Jusys and Bruckenstein (2000)[40] estimated the adsorption of perchlorate at Au electrode to be 8% of adsorbed molecules at the double-layer region. The adsorption of perchlorate increased with the increase of applied potential. The second step is the reaction of adsorbed ions with the reducing agent at the Ti-TiO_2 surface. The reaction is complex if more than one kind of ion is adsorbed onto the surface. The surface reaction was initialized by the erosion of the electrode, which produced a reducing agent such as Ti(II) and Ti(III). The last step is desorption of the products from the surface. Usually, the product is positively charged or neutral, which enhances desorption. The rates of desorption are different for different products.

5.4.2 Reduction of perchlorate in synthetic solutions

Figure 5.15 illustrates the reaction mechanism of perchlorate reduction. The surface reactions are described below.

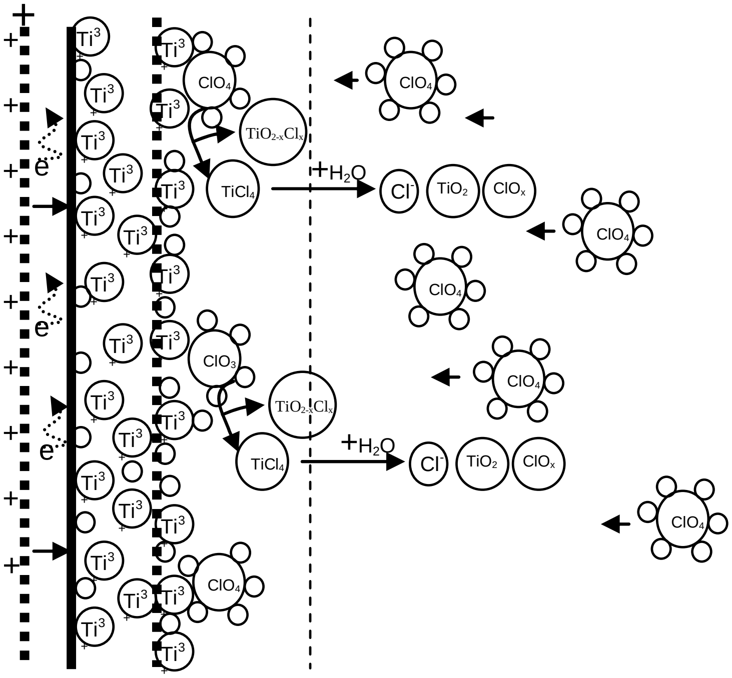
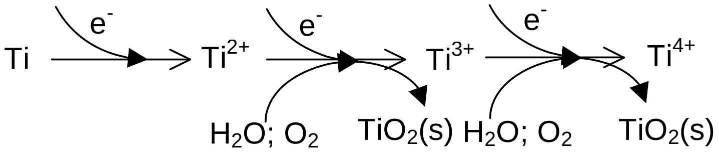


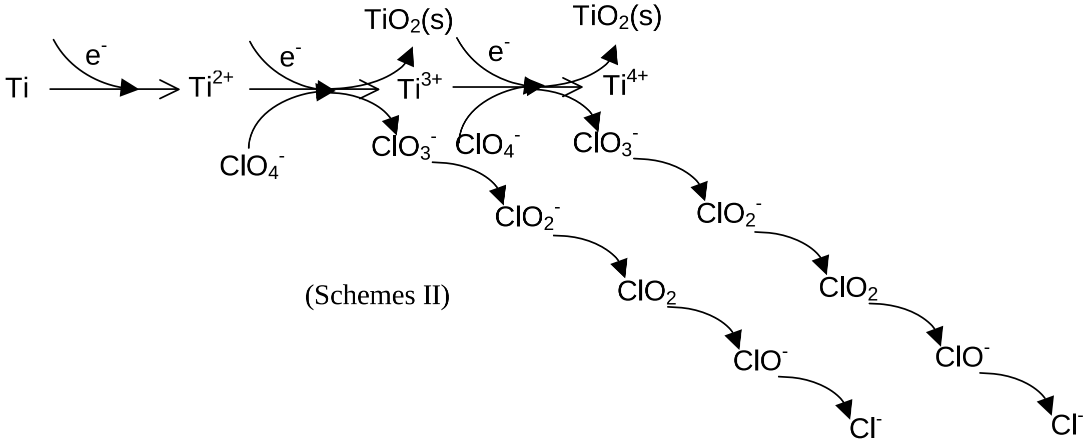
Figure 5.15 Sketch of the Mechanism on Reduction of ClO_4^- in Distilled Water.

In the presence of an electrostatic field, corrosion of the titanium electrode (an anode) took place to form multivalent Ti ions, e.g., Ti^{2+}, Ti^{3+} and Ti^{4+}. This is termed *electrode activation*. Both Ti^{2+} and Ti^{3+} are strong reducing agents that can react with a host of adsorbed species, including perchlorate, hydroxyl ions, and water. Once in the form of Ti^{4+}, electron transfer reaction stops, which leads to the formation of TiO_2. TiO_2 is stable under neutral pH conditions (Scheme I):



(Scheme I)

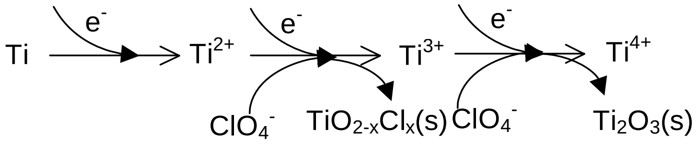
The reactions between perchlorate and Ti^{3+} and Ti^{2+} can be complex. Direct reaction between Ti^{3+} and Ti^{2+} and ClO_4^- takes place to yield various intermediate chloro-oxyanions and finally chloride (Scheme II).



(Schemes II)

It must be mentioned that both Ti^{3+} and Ti^{2+} can also migrate into bulk solution and participate in a series of redox reactions involving perchlorate. Many researchers have studied the reduction of perchlorate by Ti^{3+} and its complexes[41-45] in homogeneous solutions. Our results agree well with those reported by Duke et al. [45] in terms of order of reaction, except that the rate constant of this study was larger than those reported for otherwise similar homogenous reductions. This is because the perchlorate and titanium ions on the surface in our system were much higher than those reported.

The enhancement of perchlorate concentration particularly in heterogeneous systems such as the present study is attributed to the adsorption of perchlorate on the polarized Ti electrode surface during the early phase and the formation of TiO_2 on the Ti electrode at a later time. Several authors have suggested that complex formation between titanium ions, e.g.,Ti^{2+} and Ti^{3+}, and perchlorate induces electron transfer, which leads to the reduction of perchlorate ions [42, 45]. In the absence of literature information, based on the XPS results, the formation of $TiO_{2-x}Cl_x$ (s) or Ti_2O_3(s) complexes can be speculated (Scheme III):



(Scheme III)

Duke and Quinney reported a pseudo first-order reaction with respect to Ti^{3+} concentration of an inhomogeneous reduction [45]. We have observed an increase in soluble titanium concentration at high current density.

Results also indicate that the end product was mainly chloride in solution, albeit a lack of chlorine mass balance. The loss of total chlorine can be attributed to the following. First, there was possible formation of gaseous chlorine on the anode surface and loss to the electrode surface due to doping. The higher the current, the greater the chlorine mass imbalance, which is indicative of gaseous chlorine formation. Second, chlorine species once formed might be adsorbed on the electrode surface. In addition to perchlorate ions, other anions such as chlorate and chloride can be adsorbed on the surface of electrodes as reported by various authors [46-49].

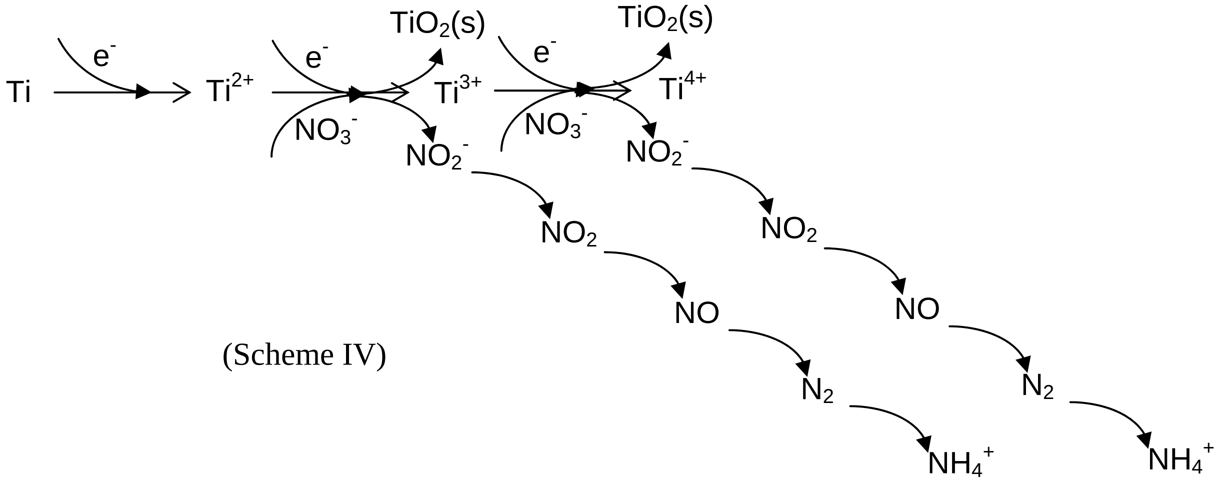
Results of perchlorate reduction at ultra-low concentration (i.e., <150 ppb) indicate that the process was highly dependent on the competitive adsorption of oxy-chloro species and the properties of the electrode surface. As shown in Figure 5.3, perchlorate concentration increased during the initial three hours when the adsorption of chlorate was dominant. Some surface sites were covered by TiO_2 where chlorate was oxidized to perchlorate. With prolonged reaction time, all electrode surfaces were renewed (or activated); the sites became occupied by Ti^{3+} and Ti^{2+}, and the reduction of chlorate and perchlorate occurred simultaneously.

The end product of chloride resulted from the diffusion of neutral TiClx species. When they arrived in the bulk solution, they decomposed into chloride and solid TiO_2.

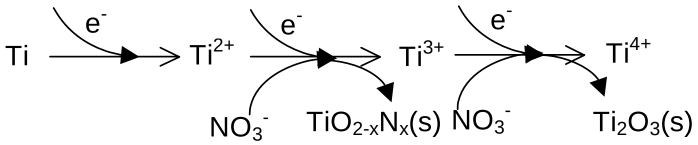
5.4.3 Reduction of nitrate in distilled water media

Reduction of nitrate at the Ti-TiO_2 surface also occurred readily, as shown in Figures 5.6 and 5.7. The removal process is sketched in Figure 5.16. Dikusar et al. (1981)[50] reported the reduction of nitrate by anodic dissolution of titanium electrodes. Chavdarova (1973) [51] also investigated the reduction of nitrate by catholically generated Titanium (III) at temperatures higher than 70°C. Our results agreed with what was reported, i.e., that the reduction of nitrate would produce gaseous nitrogen.

The reaction mechanism proposed above for the reduction of perchlorate can be implied for nitrate reduction as well. Following Scheme I, adsorption of the nitrate, the surface reaction of Ti^{3+} or Ti^{2+} with adsorbed nitrate took place as described in schemes (IV) and (V)



(Scheme IV)



(Schemes V)

From Schemes IV, we know that different intermediates are produced by nitrate reduction. However, the selectivity of the surface will determine the dominant end product, which is actually a topic in catalysis studied in chemical engineering. As shown in Figure 5.6, the end product is nitrite at this Ti-TiO_2 surface.

From Schemes V, the adsorbed nitrogen species can intrude into the TiO_2 lattice. The doping effect was confirmed by both EDX and XPS analysis as described in section 5.3.7.

The reaction mechanism proposed above for the reduction of perchlorate can be implied for nitrate reduction as well. Following Scheme I, adsorption of the nitrate, the surface reaction of Ti^{3+} or Ti^{2+} with adsorbed nitrate took place as described in schemes (IV) and (V).

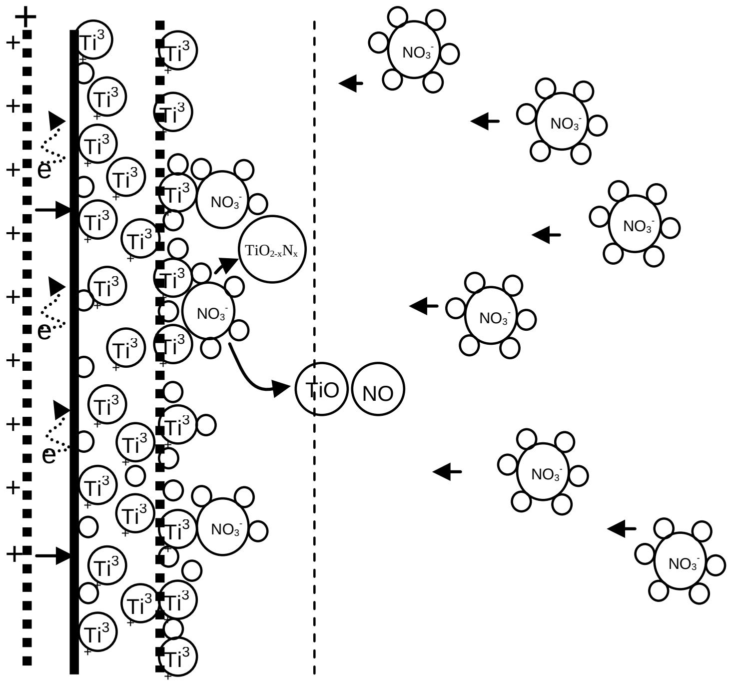


Figure 5.16 Sketch of the Mechanism on Reduction of Nitrate in Distilled Water.

5.4.4 Reduction of perchlorate and nitrate in synthetic solutions

Figure 5.17 is a sketch of the mechanism of perchlorate and nitrate reduction simultaneously. When both nitrate and perchlorate exist in the solution, it was found to be a complex reaction. They may be reduced independently as process ① and ②, as shown in Figure 5.17. They can also be reduced with interaction between each other as process ③ shown in Figure 5.17. It is interesting to note that the chlorine mass balance in the perchlorate-nitrate system was better than that of the perchlorate-only systems by comparing Figure 5.7 to Figure 5.3. The interaction between chlorine species and nitrogen species may explain the difference in generation of end product and mass balance shown in Figures 5.7. In the reduction of perchlorate, the intermediates may be chlorate, chlorite, hypochlorite and other chlorine compounds with the ultimate end product of chloride. For nitrate, they may be nitrite, nitrogen oxides with nitrite ion and/or molecular nitrogen and ammonia as the end products. Nitrite is easily oxidized by hypochlorite with a rapid rate and by chlorite at a relative slow rate . Nitrite cannot be detected as shown in Figure 5.7 during the reduction of perchlorate and nitrate at the same electrode due to back oxidation of nitrogen species to nitrate by chlorite and/or hypochlorite. The following two reactions may occur concurrently at the very same titanium electrode: $2NO_2^- + ClO_2^- = 2NO_3^- + Cl^-$ and $NO_2^- + ClO^- = 2\ NO_3^- + Cl^-$. Both reactions favor the production of chloride, which was confirmed by the results showed in Figure 5.3.

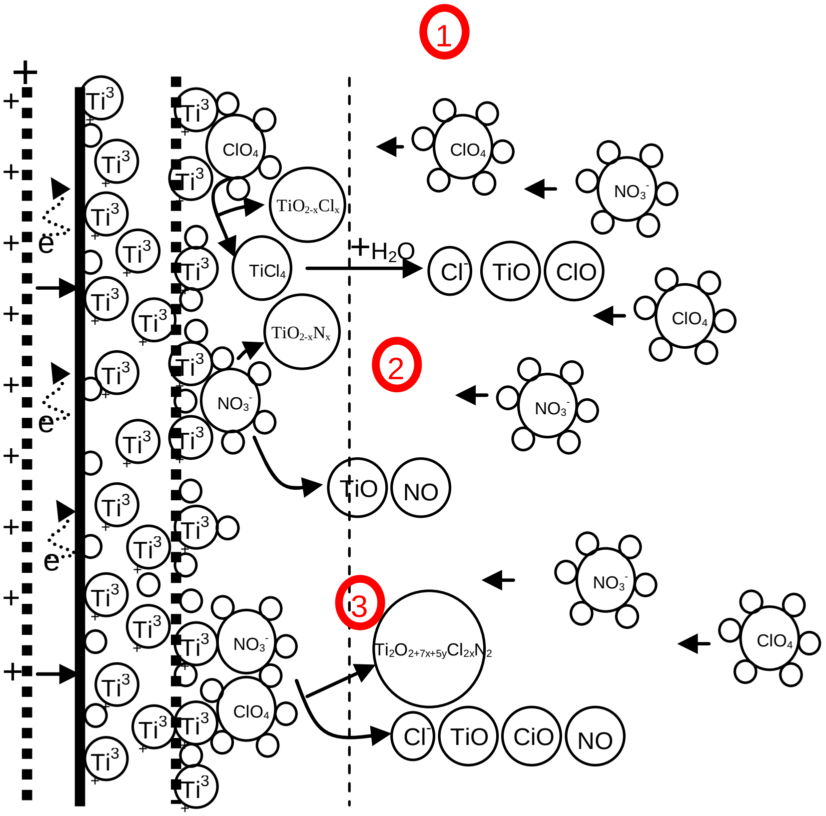


Figure 5.17 Sketch of the Mechanism on the Reduction of ClO_4^- and NO_3^- in Distilled Water.

Compared to simple systems such as perchlorate-only or nitrate-only solutions, such as process ③ shown in Figure 5.17, the solid phase that was formed when both perchlorate and nitrate were present simultaneously could be quite complicated in composition. Results appear to indicate the co-doping of both N and Cl onto theTiO_2 surface. Doping of both N and Cl was verified by the analysis of the particles with EDX and XPS. The Ti:O ratio in EDAX analysis, and the character of the Ti, Cl, N peak in XPS results clearly indicated doping contribute the imbalance of both the chlorine and nitrogen family.

5.4.5 Reduction of perchlorate in tap water media

In local tap water system, as shown in Appendix C, dominant anions with effect were Cl^-, SO_4^- and NO_3^-. Four species including the added perchlorate would be competitively adsorbed at the positively charged Ti-TiO_2 electrode surface. In addition to the reactions of chloride and nitrate discussed above, another effect is the reaction of sulfate at the Ti-TiO_2 surface.

No reduction of sulfate is detectable at the surface. However, the proposed formation of particulate $TiOSO_4$ interfered with the reduction process and the mass balance of sulfate ions. $Ti(SO_4)_2$ didn't affect the concentration of sulfate. It decomposed simultaneously as sulfate, and the particle was actually TiO_2 without any sulfur detectable in XPS analysis. There was also no end product ion found in the solution.

5.4.6 Preliminary kinetics

In summary, the kinetics of the Ti-TiO_2 surface system would include but not be limited to the following parameters: concentration of perchlorate in the bulk solution, $[ClO_4^-]$; applied current, I, applied potential, E, reaction conditions, pH, T and mixing. The kinetics equation can be semi-qualitatively written as $-\frac{d[ClO_4^-]}{dt} = f([ClO_4^-], I, E, pH, T)$.

Chapter 6: Preliminary Process Evaluation

6.1 Progress to date

During the project period, we have developed successfully two innovative processes for the removal (total destruction) of perchlorate from water for potable purposes: the catalytic dual-membrane and indirect electrochemical Ti-TiO_2 systems.

The following describe the merits of both systems. The major merits of the catalytic dual-membrane system are as follows:

- **High removal efficiency:** In terms of system operation, the catalytic dual-membrane system is similar to the popular electrodeionization (EDI) process except that the catalytic membrane system does not need any ion-exchange resin and it can reduce the perchlorate directly. In contrast, the EDI system requires an anion exchange resin and it only separates and concentrates perchlorate from water. The EDI process has already been applied to produce high-quality water in the high-tech industry due to its high ion separation efficiency. The catalytic dual-membrane systems developed in this SERDP project can treat water that contains perchlorate in the ppm level to the ppb range effectively.
- **Cost effective**: The main cost items of the catalytic dual-membrane system are electricity, catalyst and ion-specific membrane with electricity being the major O&M cost item. Electricity is needed to generate hydrogen atoms and also to transport perchlorate ions across the ion-specific membrane toward the catalytic membrane. Theoretically, the current requirement is negligible due to the ultra-low perchlorate concentration of most contaminated waters, e.g., groundwater and surface water. As shown later, the total annual cost of the catalytic dual-membrane will be less than \$5 per 1000 gallons. This is extremely attractive compared to any current perchlorate treatment technology.
- **Clean process:** The catalytic dual membrane process is a clean operation that requires no chemicals and generates no secondary contaminants. Compared to current perchlorate treatment technologies, the catalytic dual membrane process converts the perchlorate to chloride as the end product at the expense of only a small amount of electricity current.
- **High public acceptance:** The catalytic dual-membrane technology will have wide public acceptance because it is operated based on the same principle as EDI, a technology that has already been widely used in the production of high-quality water in the high-tech industries. Furthermore, the voltage applied in the catalytic dual membrane system is at least two to three orders of magnitude less than what is needed in the operation of the EDI system. The lower the applied voltage, the cheaper and the safer the operation. Cheap and safer operation will boost public acceptance of the technology.

The following are the advantages of the indirect electrochemical (Ti-TiO_2) system:

- **Currently it is the only method capable of treating water containing ultra-low concentration of perchlorate**: The Ti-TiO_2 system is the only current technology that can reduce perchlorate to less than the DWEL levels, i.e., <25 ppb in water. We have conducted a thorough literature search on technology related to the removal of perchlorate from aqueous solutions. Appendix B lists all publications related to the study on the removal of perchlorate from water. Although various authors have reported that perchlorate can be chemically reduced in homogeneous or heterogeneous solutions, none of these studies has shown that perchlorate can be reduced at ultra-low concentrations, i.e., in the range of 250-1000 ppb to 1 - 10 ppm. The inability to reduce perchlorate at low to ultra-low perchlorate concentrations in heterogeneous system is attributed to the low surface concentration at the electrode surface. The Ti-TiO_2 developed in this SERDP project takes advantages of enhancing perchlorate adsorption on a polarized Ti-TiO_2 anode and the subsequent reduction of perchlorate with the Ti(II) and the Ti(III) species on the electrode surface. By combining these two unique steps, i.e., concentration and reaction, perchlorate is readily reduced in solutions of ultra-low concentrations.

- **Clean process:** There is no chemical addition needed in this process to promote perchlorate reduction. The reaction end products are non-toxic chloride and a small amount of particulate material, e.g., TiO_2(s), which is non-toxic and can be easily removed from the finished water stream.
- **Cost-effective:** As reported later, the major cost item of the technology is electricity. The total unit cost of the indirect-electrochemical Ti-TiO_2 process is estimated at \$10-15 per 1000 gallon. It is more expensive than the catalytic dual membrane process due to the higher current density required; however, the process is extremely competitive against any other current perchlorate treatment technologies.

6.2 Technical difficulties

Although preliminary laboratory results show the great potential of both processes, the following technical issues must still be addressed.

6.2.1 Scalability

The scalability of a system deals with transferring the laboratory results to large-scale applications. Once the detailed reaction kinetic equation is established, it is possible to establish the scale-up scheme. As reported above, the kinetics of the perchlorate reduction can be limited by the mass-transfer step. Speeding up the mass transfer of perchlorate toward the catalytic membrane remains challenging and definitely worthy of further study beyond the level of laboratory reactor.

For the Ti-TiO_2 system, there is also a mass transport issue during process scale-up. However, we believe that this can be readily dealt with by modifying the configuration of the Ti electrode, e.g., porosity and geometry. In large-scale operation, rod-shape material has a low specific surface area. This problem can be dealt with by using a membrane coated with titanium nanoparticles or thin film to increase the specific surface area. In summary, we believe that the scalability issue can be readily solved.

6.2.2 Competing ions effect

Results show that when present at ultra-low concentrations, e.g., in the ppb to the low ppm range, perchlorate reduction can be affected by competing anions such as sulfate, and nitrate. This is not avoidable regardless of treatment processes including ion exchange. Nonetheless, the competing ion effect can be eliminated or minimized in the catalytic dual-membrane system with great ease. One option is to use a perchlorate-ion-specific ion-exchange membrane instead of a general anion exchange membrane. It is known that a perchlorate-specific membrane available commercially. The other alternative is to concentrate the perchlorate to the same level as that of the major anions before feeding to the catalytic dual membrane reactor. Once the perchlorate concentration is at the same level as the competing anions, the competing effect is minimized. A third alternative is to modify the configuration of the Ti electrode to increase the concentration of the perchlorate. For example, the use of a porous Ti electrode or the use of nano-size Ti particles can drastically increase the specific surface area of the Ti electrode. Furthermore, the use of a nitrate- or sulfate-specific membrane to remove these competing ions before treatment with the indirect electrochemical Ti-TiO_2 system is another option, although additional treatment cost is expected. In conclusion, it is absolutely possible to minimize of eliminate the competing effect without necessary increase the total treatment cost.

6.3 System improvements (Focus for Year III)

To perfect the above two systems developed under this SERDP project, the following tasks are proposed for Year III aiming at the issues of scalability and competing ion effect.

The following experiments are proposed for further investigation using the catalytic dual membrane system:

- **The transport of perchlorate across the anion exchange membrane**. This information is needed to describe the surface concentration of perchlorate at the catalytic membrane surface. The kinetics of perchlorate accumulation in the Stern space will be quantified as a function of current density and temperature, among other pertinent chemical properties of the solutions such as pH and ionic strength.
- **The surface concentration of perchlorate on the catalytic membrane surface**. The adsorption capacity of perchlorate ions onto the surface of various catalytic membranes will be characterized and the adsorption isotherms established.
- **The selectivity and permeability of perchlorate ions of various commercial membranes.** Various anion exchange membranes will be characterized for ion selectivity and permeability toward perchlorate in relation to several competing anions including sulfate, nitrate, and chloride.
- **Characteristics of chlorine species at the catalytic membrane surface.** XPS analysis of the catalytic membrane will be conducted on various catalytic membranes to reveal the mechanisms of the surface reaction. For example, an attempt will be made to determine why chlorite (ClO_2) was the end product at the Co-membrane, while chloride was the major end product on the Pt- and the Ti-membrane.
- **Establish the rate equation**. The rate equation as described in terms of various relevant operational parameters as discussed in Chapter 3 will be established.
- **Overall performance of the bench-scale reacto**r. The overall performance of the bench-scale reactor will be tested for system scalability.

The following experiments are proposed for further investigation of the indirect electrochemical (Ti-TiO_2) system:

- **Configuration of the Ti-TiO_2 electrode**. A porous Ti electrode made by coating of nano-sized Ti particles will be tested. This is done by laser sputtering technique. We have the capability of preparing nano-TiO_2 particles on a titanium sheet. This Ti electrode will have excellent specific surface area.
- **Perchlorate ion specific membrane**. We will configure the Ti-TiO_2 electrode with a perchlorate-specific membrane to partition the competing anions.
- Incorporation of perchlorate pre-concentration step to the Ti-TiO_2 or the catalytic dual membrane system.

- **Establishment of the rate equation**. The rate equation as described in terms of various relevant operational parameters as discussed in Chapter 5 will be established. Additionally the optimal operational parameters for system scale up will be established.

6.4 Preliminary economic analyses

6.4.1 Introduction

Water will be one of the most important national strategic materials in the 21st century. The demand for quality potable water will become severe due to the world population increase and shortage of quality water in sufficient quantity to meet the needs of various industrial and human activities. In California, almost 43% of the drinking water comes from groundwater sources where perchlorate contamination has been found in many locations. The removal of perchlorate from contaminated water is an urgent and critical issue in these areas.

There is an R&D program at DoD to replace ammonium perchlorate as rocket fuel. However, until recently, it was not possible to produce the substitute chemicals in large quantity. Further, the cost of the new chemical is around $1000 per pound, which is at least three orders of magnitude more expensive than ammonium perchlorate, which costs only about $1 per pound. Therefore, the use of ammonium perchlorate will probably continue for a while; therefore, further release of perchlorate into the environment is expected.

Water treatment cost consists of two main components: (1) capital and (2) maintenance and operation (M&O). The total cost is a function of treatment capacity, Q. As a rule of thumb, the capital cost increases with an increase in treatment capacity (Q), whereas the O&M cost decreases with the treatment capacity. An optimal cost is found at a specific treatment capacity (Figure 6.1). In light of the high degree of technological capability, we have chosen to estimate the treatment costs of two systems: (1) catalytic dual membrane and (2) indirect electrochemical ($Ti-TiO_2$) based on the preliminary results and experimental conditions used in this study.

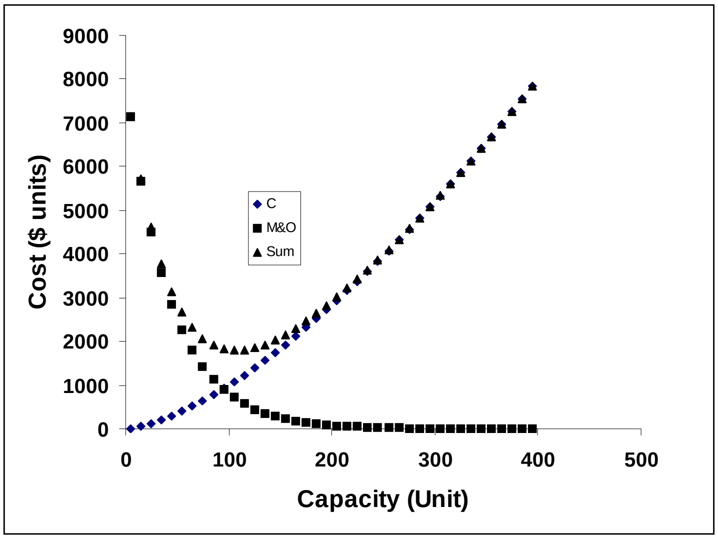


Figure 6.1. Water Treatment Cost as a Function pf Treatment Plant Capacity.

6.4.2 Catalytic dual membrane system

The cost estimate was made based on a semi-batch reactor with a treatment capacity of 1,000 gallons. The system consists of five heavy-duty plastic tanks, each with a volume of 200 gallons. Based on our preliminary results, we can achieve a greater than 90-95% removal of perchlorate in the initial concentration range of greater than 2 ppm in 6-8 hours. For the purpose of comparison, we use two time periods, i.e., 6 and 8 hours. In between each batch run, there is a period of two hours for emptying and refilling the tank. That is, each treatment cycle will take 8 and 10 hours, respectively. If the plant is operated for 360 days a year, it will process 1,080,000 and 864,000 gallons of water per year at treatment times of 6 and 8 hours, respectively.

The catalytic membrane is made of stainless steel mesh, which costs \$0.25/m^2. The unit cost for the anionic membrane is estimated at \$500 per m^2. The cost of electrodes is estimated at \$50 per piece, and the cost of the reactor tank is estimated at \$250 per 200-gallon tank made of heavy duty plastic. The capital cost is amortized against the service life of each component, five years for the catalytic membrane, anion exchange membrane, and electrode and 15 years for the reaction tank. With an interest rate of 4%, the annual capital costs are \$0.19, \$378.90, \$63.15 and \$105.00 for the catalytic membrane, the anion exchange membrane, the electrode and the rector tank, respectively. The total annual capital cost is \$547.28. Table 6.1 shows the breakdown of capital cost estimation.

Table 6.1 Summary of Capital Cost Estimated for the Catalytic Dual Membrane System.

Cost item	Unit	Unit Cost ($)	Subtotal ($)	Service life (year)	Total Annual Cost ($)
Catalytic membrane (m^2)	3	0.25	0.75	5	0.19
Anionic exchange membrane (m^2)	3	500	1500	5	378.90
Electrode	5	50	250	5	63.15
Reactor (200 gallon)	5	250	1250	15	105.00
Total			3000.75		547.28

The M&O cost of the system consists of mainly electricity, membrane maintenance, and catalyst. The electricity is calculated based on two constant current values of 5 and 10 mA. The resistance of the water is about 1000 ohm. The plant is operated for 360 days a year, and the electricity is estimated at a rate of \$0.04 per kW-h. It is assumed that there is monthly replacement of the catalyst and monthly membrane maintenance, each at a cost of \$50, which is a very conservative estimate. Table 6.2 summarizes the M&O cost estimate at constant currents of 5 and 10 mA, respectively.

Table 6.2 Breakdown of M&O Estimated for the Catalytic Dual Membrane System.

Cost Item	Unit	Unit Cost ($)	Subtotal ($)
Electricity (kW-h) @5 mA	43,200	0.04	1728
Electricity (kW-h) @10 mA	86,400	0.04	3456
Membrane maintenance	12	50	600
Supplement of catalyst	12	50	600

The total unit cost for the catalytic dual membrane system is summarized in Table 6.3. It is noted that the electricity cost is estimated based on continuous operation of the plant 24 hours a day for 360 days a year. It is noted that that there is a 2-hour break for tank emptying and refilling, during which there is no electricity use. If this time is subtracted from the estimate, the electricity cost will be reduced even further. However, we purposely included this 2-hour period in the electricity calculation as a safety factor.

Overall, the cost ranges from $2.66 to $5.33 per 1000 gallons. This is very affordable and very competitive against other water purification processes. Hackney and Weisner (Cost Assessment of Various Produced Water Treatment and Disposal Scenarios, **http://www.ruf.rice.edu/~weisner/hackney.html**) reported that minimum treatment cost of groundwater for drinking purpose is from $0.63 to $3.15 per cubic meter, or $3.00 to $12.00 per 1000 gallons. The M&O cost alone for the ion exchange process was in the range of $7.55 to 12.48 per 1000 gallons (Boodoo, F. Perchlorate Facts for Technology Vendors, **http://www.Purolite.biz/Perchlorate_Facts_for_Vendors_090203.pdf**).

Table 6.3 Summary of Total Unit Cost of the Catalytic Dual Membrane System.

Constant current (mA)	5	5	10	10
Treatment time (h)	6	8	6	8
Total water production (gallons/year)	1,080,000	864,000	1,080,000	864,000
Total Annual Capital Cost ($/year)	547.28	547.28	547.28	547.28
Total M&O cost ($/year)	2328	2328	4056	4056
Unit Annual Capital Cost ($/1000 gallons)	0.51	0.63	0.51	0.63
Unit M&O cost ($/1000 gallons)	2.16	2.69	3.76	4.69
Total Unit cost ($/1000 gallons)	2.66	3.32	4.26	5.33

6.4.3 Ti-TiO_2 system

The capital cost items for the indirect electrochemical (Ti-TiO_2) systems are titanium metal, cation exchange membrane, counter electrodes, and reactor. We will assume that the system is to be operated for 24 hours a day, 360 days a year in semi-batch mode. Between each batch treatment, there is a two-hour layoff for emptying and refilling the tank. The treatment capacity is 1000 gallons. This will require 0.5 m^2 of titanium electrode, and 0.2 m^2 of cation exchange membrane, five pieces of counter electrode (graphite or steel), and five 200-gallon heavy-duty plastic tanks. Table 6.4 lists the capital costs. Based on our preliminary results, we can achieve a greater than 90-95% removal of perchlorate in the initial concentration range of 100 ppb to ~2 ppm in 6-8 hours. For comparison, we use two treatment periods of 6 and 8 hours. In between each batch, a period of two hours is allowed for tank emptying and refilling. That is, the total cycle time will be 8 and 10 hours per batch. The plant is operated for 24 hours a day, 360 days a year. The plant will produce 1,080,000 and 864,000 gallons of water per year at treatment times of 6 and 8 hours, respectively.

Table 6.4 Breakdowns of M&O Cost Estimate for the Ti-TiO_2 System.

Cost item	Unit	Unit Cost ($)	Subtotal ($)	Service Life (year)	Total Annual Cost ($/year)
Ti metal (m^2)	0.5	2000	1000	5	25.2
Cation exchange membrane (m^2)	0.2	500	100	5	2.52
Counter electrode	5	50	250	5	6.3
Reactor (@200 gallons)	5	250	1250	15	105
Sum			2600		139.02

Based on our preliminary results, we use the constant current of 20 and 50 mA. Again assuming that the water to be treated has a resistance of 1000 ohm, the system will require 172,800 and 422,000 kW-h of electricity. At an assumed cost of $0.04 per kW-h, the annual electricity costs will be $6,912 and $17,280, respectively, when the system is operated at 20 and 50 mA constant current, individually. It is noted that electricity dominates the M&O cost. As a result, the Ti-TiO_2 system has a higher M&O cost compared to the catalytic dual membrane system as expected. Table 6.5 summarizes the annual M&O cost of the Ti-TiO_2 system.

Table 6.5 Breakdown of M&O Estimate for the Ti-TiO_2 System.

Cost Item	Unit	Unit Cost ($)	Subtotal ($)
Electricity (kW-h) @20 mA	172,800	0.04	6,912
Electricity (kW-h) @50 mA	432,000	0.04	17,280
Membrane maintenance	12	50	600
Supplement of catalyst	12	25	300

The total unit cost for the Ti-TiO_2 system is summarized in Table 6.6. The unit cost of the Ti-TiO_2 system is estimated to be between $7 and $21 per 1000 gallons versus $3 to $5 per 1000 gallons for the catalytic dual membrane system. This reflects the cost of electricity between the two systems. Although the unit treatment cost of the indirect electrochemical Ti-TiO_2 system is about 2 to 3 times that of the catalytic dual membrane system, it is still very competitive with other current commercial processes such as membrane and electrodialysis such as EDR or EDI.

6.4.4 Summary

Based on the preliminary results obtained in this project, it is possible to estimate the cost of the two processes that are most technically feasible for perchlorate removal from surface or groundwater. The cost estimated falls at the conservative end as conditions and parameters have not yet been optimized. Depending on the scale of the treatment plant, the distribution between the capital and the M&O costs can be quite different. Generally, the capital cost is higher and the M&O cost is lower for larger plants. The above estimate is not optimized with respect to plant capacity. Results also indicate that based on the experimental conditions of this study, the total unit cost for the catalytic dual membrane system will be between $3 and $5 per 1000 gallons for treatment times of 6 and 8 hours, respectively in a semi-batch operation. The unit cost of the Ti-TiO_2 system is between $7 and $21 per 1000 gallons. The catalytic dual membrane system is so inexpensive that it is possible for the process to be integrated with the pre-perchlorate concentration process. Pre-chlorate concentration using methods such as ion exchange can minimize the competing anion effect without increasing the total treatment cost.

Table 6.6 Summary of Total Unit Cost of the Ti-TiO_2 System.

Constant current (mA)	20	20	50	50
Treatment time (h)	6	8	6	8
Total water production (gallons/year)	1,080,000	864,000	1,080,000	864,000
Total Annual Capital Cost ($/year)	139.02	139.02	139.02	139.02
Total M&O cost ($/year)	7,812	7,812	18,180	18,180
Unit Annual Capital Cost ($/1000 gallons)	0.13	0.16	0.13	0.16
Unit M&O cost ($/1000 gallon)	7.00	9.04	16.83	21.04
Total Unit cost ($/1000 gallon)	7.36	9.20	16.96	21.20

Overall, the unit costs of the catalytic dual membrane and the indirect electrochemical (Ti-TiO_2) systems are extremely competitive with current commercial processes. Boodoo (2003) reported that the total resins and disposal cost was $7.55 and $12.48 per 1000 gallons for the A-530E and A-600E ion exchange resin systems. This same author also reported the unit cost for various perchlorate treatment systems including the activated carbon adsorption and ion exchange processes. The total M&O costs for typical household units (e.g., 15 to 30 gpm/ft3) were $15-30, $48-96, $2.0-5.25, $1.8-4.25 and $1.5 - $3.5, for the activated carbon, the Acrylic SBA Type I, Styrenic SBA Type I, Nitrate selective (TEA), and BiQuat perchlorate selective resin systems, respectively (Appendix E). The Office of Pollution Prevention and Technology Development, California Environmental Protection Agency conducted a survey of various perchlorate treatment technologies currently in practice and reported that the unit cost of a full-scale ion exchange system by the Calgon ISEP process was $3.83 to $4.45 per 1000 gallon. (Office of Pollution Prevention and Technology Development, California Environmental Protection Agency, Perchlorate Contamination Treatment Alternatives, 2004. (**http://www.dtsc.ca.gov/TechnologyDevelopment/wpload/TD_REP_Perchlorate_Alternatives.pdf**)

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Appendix A: Summary of Catalysts and Catalytic Systems Studied

Table A.1. Summary of Catalysts and Catalytic Systems Studied

No.	Catalyst type	Catalyst	Reduction result		Rate** µM-L^{-1}-h^{-1}	Reducing agents	Reactor***	Condition				End product
			YES	Group*				pH	Temp	Pressure	other	
1	Catalytic membrane (stainless steel)	Sc	•	moderate	5.9	Atomic H	DM	5.6-7	21-25	1		Cl^-
2		Ti	•	Excellent	11.0	Atomic H	DM	5.6-7	21-25	1		Cl^-
3		V	•	Moderate	7.4	Atomic H	DM	5.6-7	21-25	1		Cl^-
4		Cr	•	Excellent	9.9	Atomic H	DM	5.6-7	21-25	1		Cl^-
5		Mn	•	Moderate	7.0	Atomic H	DM	5.6-7	21-25	1		Cl^-
6		Co	•	Excellent	10.4	Atomic H	DM	5.6-7	21-25	1		Cl^-
7		Ni	•	Moderate	6.8	Atomic H	DM	5.6-7	21-25	1		Cl^-
8		Cu	•	Good	8.6	Atomic H	DM	5.6-7	21-25	1		Cl^-
9		Zn	•	Moderate	6.6	Atomic H	DM	5.6-7	21-25	1		Cl^-
10		Zr	•	Moderate	5.5	Atomic H	DM	5.6-7	21-25	1		Cl^-
11		Mo	•	Good	9.3	Atomic H	DM	5.6-7	21-25	1		Cl^-
12		Ru	•	Good	9.2	Atomic H	DM	5.6-7	21-25	1		Cl^-
13		Rh	•	Moderate	7.3	Atomic H	DM	5.6-7	21-25	1		Cl^-
14		Pd	•	Good	7.6	Atomic H	DM	5.6-7	21-25	1		Cl^-
15		Cd	•	Good	8.9	Atomic H	DM	5.6-7	21-25	1		Cl^-
16		Sn	•	Excellent	9.8	Atomic H	DM	5.6-7	21-25	1		Cl^-
17		Pt	•	Moderate	6.0	Atomic H	DM	5.6-7	21-25	1		Cl^-
18		Pb	•	Good	8.8	Atomic H	DM	5.6-7	21-25	1		Cl^-
19		Co-Mo	•	Moderate	5.3	Atomic H	MM	5.6-7	21-25	1		Cl^-
20		Co-Cr	•	Good	8.3	Atomic H	MM	5.6-7	21-25	1		Cl^-, ClO_2^-
21		Co-Rh	•	Poor	3.4	Atomic H	MM	5.6-7	21-25	1		Cl^-, ClO_2^-
22	Catalytic membrane (Cupper mesh)	Raney-Ni	•	poor	1.7	Atomic H	DM	5.6-7	21-25	1		Cl^-
23		Cu	•	poor	1.3	Atomic H	DM	5.6-7	21-25	1		Cl^-
24		Sn	•	moderate	6.6	Atomic H	DM	5.6-7	21-25	1		Cl^-
25		Cd	•	poor	1.2	Atomic H	DM	5.6-7	21-25	1		Cl^-
26		Pb	•	poor	0.9	Atomic H	DM	5.6-7	21-25	1		Cl^-
27	Elemental metal particle	Ti	•	poor	2.6	Atomic H	TT	3	21-25	1		Cl^-
28		Fe	•	poor	0.16	Atomic H	TT	3	21-25	1		Cl^-, ClO_2^-
29		Co	•	poor	3.1	Atomic H	TT	3	21-25	1		Cl^-, ClO_2^-
30		Ni	•	poor	3.75	Atomic H	TT	3	21-25	1		Cl^-
31		Cu	•	poor	0.28	Atomic H	TT	3	21-25	1		Cl^-
32		Zn	•	poor	0.26	Atomic H	TT	3	21-25	1		Cl^-
33		Pd	•	poor	2.5	Atomic H	TT	3	21-25	1		Cl^-
34		Sn	•	poor	0.64	Atomic H	TT	3	21-25	1		Cl^-, ClO_2^-
35	Nano-metal particle prepared	Cu/SiO_2		N/A	ND	H_2	HP	4.5	22	5	Add isopropanol	
36		Fe		N/A	ND	H_2	HP	7	22	4		
37		Cu/Ni		N/A	ND	H_2	NP	7	22	1.2		

38	by Reverse micelle technology	Ni/SiO_2		N/A	ND	H_2	HP	5.5	22	3		
39		Co		N/A	ND	H_2	HP	7	22	3		
40		Co-Fe		N/A	ND	H_2	HP	7	22	3		
41	Commercial catalyst	5%Pd/C	●	poor	0.37	H_2	NP	7	22	1.2		Cl^-
42		5%Pd/C		N/A	ND	H_2	NP	8	22	1.2		
43		5%Pd/C		N/A	ND	H_2	NP	7.5	22	1.2		
44		5%Pd/C		N/A	ND	H_2	NP	8	22	1.3		
45		5%Pd/C		N/A	ND	H_2	NP	7	22	1.6		
46		5%Pd/C	●	poor	0.89	H_2	NP	7	22	1.6	Add Ag_2SO_4	Cl^-
47		5%Pd/C	●	poor	0.32	H_2	NP	7	35	1.7		Cl^-
48		5%Pd/C		N/A	ND	H_2	NP	5.3	22	1.2	Add Fe	
49		5%Ru/C		N/A	ND	H_2	NP	7	22	4		
50		10%Pd/C		N/A	ND	H_2	HP	7	22	2	Add acrolinitril	
51		10%Pd/C		N/A	ND	H_2	NP	8	22	1.2		
52		10%Pd+5%Ru/C		N/A	ND	H_2	NP	7	22	1.2		
53		5%Ru/C		N/A	ND	H_2	NP	4	22	1.2		
54		5%Pd/C		N/A	ND	H_2	NP	7	22	1.2	Add TCE	
55		10%Pd/C		N/A	ND	H_2	NP	7	22	2	Add ethanol	
56		10%Pd/C		N/A	ND	H_2	NP	7	22	2	Add DCE, ethanol, Ag2NO3	
57		10%Pd/C		N/A	ND	H_2	NP	7	22	1.2	Add Ag2NO3, ethanol	
58		10%Pd/C		N/A	ND	H_2	NP	5.5	22	1.2	Add ethanol	
59		5%Ru/C		N/A	ND	H_2	NP	7	22	1.2	Add FeS	
60		5%Ru/C		N/A	ND	H_2	NP	7	22	1.2	Add ethanol	
61		5%Pd+1%Fe/C		N/A	ND	H_2	NP	7	22	1.2	Add ethanol	
62		5%Pd+1%Fe/C		N/A	ND	H_2	NP	7	22	1.2	Add ethanol,acrolinitril	
63		10%Pd/C	●	Poor	0.96	H_2	US	7	25	1	Ultrasound	Cl^-
64		5%Pd+1%Fe/C		N/A	ND	H_2	US	4.9	25	1		
65		99%WC		N/A	ND	H_2	US	5.6	75	1		
66		10%Pd/C		N/A	ND	H_2	US	3.5	80	1		
67		99%WC		N/A	ND	H_2	US	6	83	1		
68		10%Pd/C		N/A	ND	H_2	US	4.2	50	1		
69		10%Pd/C		N/A	ND	H_2	US	5.6	50	1		
70		10%Pd/C		N/A	ND	H_2	US	5.6	50	1		
71		10%Pd/C		N/A	ND	H_2	US	5.0	50	1		
72		5%Ru/C		N/A	ND	H_2	US	5.0	50	1		
73		10%Pd/C		N/A	ND	H_2	US	5.0	50	1	Add NiS	
74		99%WC		N/A	ND	H_2	US	3.8	50	1		
75		5%Pd/C		N/A	ND	H_2	HP	5.6	20	3		

76		Raney-Ni		N/A	ND	H_2	HP	7.8	22-55	4		
77		10%Pd		N/A	ND	H_2	HP	7.1	22-55	3.5	UV	
78		10%Pd/C		N/A	ND	H_2	HP	5.0	22	4		
79		Raney-Ni+Pd		N/A	ND	H_2	HP	8.3	22	4		
80		Pt/C+raney Ni		N/A	ND	H_2	HP	7.5	22	3		
81		10%Pd/C reduced		N/A	ND	H_2	HP	9.5	23	3		
82	Commercial catalysts with electricity (graphite)	10%Pd/C	●	poor	0.5	H_2	HP	9.5	25	3		Cl^-
83		PdAc	●	poor	0.4	H_2	HP	9.5	23	1.6		Cl^-
84		Raney-Ni, Zn	●	poor	0.2	H_2	HP	7.5	20	1.6		Cl^-
85		PdAc, Zn		N/A	ND	H_2	HP	5.2	23	1		
86		Raney-Ni, Cr^{3+}	●	moderate	7.0	H_2	HP	2.0	23	1		Cl^-
87		Ti_2O_3		N/A	ND	H_2	HP	2.7	23	1		

Appendix B: Literature Search

Table B.1. Literature Survey on Perchlorate Removal Processes

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Appendix C: Chemistry of Tap Water

Table C.1. Chemical Composition of Local Tap Water

Inorganic & Physical	MCL	Date (2006)			
		5-Dec	6-Jan	6-Feb	6-Mar
Alkalinity (mg/l as $CaCO_3$)		18	20	22	18
Carbon Dioxide (mg/l)		4	6	6	4
Chloride (mg/l)	250	35	42	40	44
Chlorine, free (mg/l)	4	1.51	1.48	1.53	1.89
Conductivity (μS/cm)		270	260	262	265
Fluoride (mg/l)	2	0.87	0.81	0.89	0.88
Hardness, TOTAL (mg/l)		88	80	84	100
Hardness, Ca (mg/l)	60	54	56	68	
Iron, Total (mg/l)	0.3	< 0.01	< 0.01	< 0.01	< 0.01
LSI (unit)		-1.46	-1.65	-1.54	-1.48
Manganese, (mg/l)	0.05	0.002	0.002	0.002	0.002
$N\text{-}NO_3^-$ (mg/l)	10	4.2	4.8	3.2	4.1
pH (units)	6.5 - 8.5	6.7	6.5	6.6	6.8
Sodium (mg/l)	250	18			
Solids, Total (mg/l)	500	180	170	184	190
Sulfate (mg/l)				28	
Temperature (^oC)		12	10	11	15
TOC (mg/l)					
Turbidity (NTU)	0.5	0.02	0.04	0.04	0.03

* Total hardness in grains / gallon = 4 - 5

Appendix D. Proposed Pathways for Indirect Electrochemical Reduction of Perchlorate

Table D.1. Proposed Reaction Pathways for Indirect Electrochemical Perchlorate Reduction.

Step or process	No	Reaction
Anode erosion	1	$Ti \rightarrow 2e + Ti^{2+}$
	2	$Ti \rightarrow 3e + Ti^{3+}$
	3	$Ti \rightarrow 4e + Ti^{4+}$
Side-reaction	4	$Ti^{4+} + 2\,H_2O \rightarrow TiO_2 + 4H^+$
	5	$2Ti^{3+} + 4\,H_2O \rightarrow 2TiO_2 + 6H^+ + H_2$
	6	$Ti^{2+} + 2\,H_2O \rightarrow TiO_2 + 2H^+ + H_2$
Perchlorate reduction	7	$2Ti^{3+} + 3H_2O + ClO_4^- \rightarrow 2TiO_2 + 6H^+ + ClO_3^-$
	8	$2Ti^{3+} + 3H_2O + ClO_3^- \rightarrow 2TiO_2 + 6H^+ + ClO_2^-$
	9	$Ti^{3+} + H_2O + ClO_3^- \rightarrow TiO_2 + 2H^+ + ClO_2$
	10	$2Ti^{3+} + 3H_2O + ClO_2^- \rightarrow 2TiO_2 + 6H^+ + ClO^-$
	11	$Ti^{3+} + H_2O + ClO_2^- \rightarrow TiO_2 + 2H^+ + ClO$
	12	$2Ti^{3+} + 3H_2O + ClO^- \rightarrow 2TiO_2 + 6H^+ + Cl^-$
	13	$2Ti^{3+} + 2x\,ClO_4^- + (3-x)\,H_2O \rightarrow Ti_2O_{3+7x}Cl_{2x} + (6-2x)\,H^+$
	14	$Ti^{2+} + H_2O + ClO_4^- \rightarrow TiO_2 + 2H^+ + ClO_3^-$
	15	$Ti^{2+} + H_2O + ClO_3^- \rightarrow TiO_2 + 2H^+ + ClO_2^-$
	16	$Ti^{2+} + 2ClO_3^- \rightarrow TiO_2 + 2ClO_2$
	17	$Ti^{2+} + H_2O + ClO_2^- \rightarrow TiO_2 + 2H^+ + ClO^-$
	18	$Ti^{2+} + 2ClO_2^- \rightarrow TiO_2 + 2ClO$
	19	$Ti^{2+} + H_2O + ClO^- \rightarrow TiO_2 + 2H^+ + Cl^-$
	20	$2Ti^{2+} + 2x\,ClO_4^- + (2-x)\,H_2O \rightarrow Ti_2O_{2+7x}Cl_{2x} + (4-2x)\,H^+$
	21	$2ClO^- \rightarrow ClO_2^- + Cl^-$
Nitrate reduction	22	$2Ti^{3+} + 3H_2O + NO_3^- \rightarrow 2TiO_2 + 6H^+ + NO_2^-$
	23	$Ti^{3+} + H_2O + NO_3^- \rightarrow TiO_2 + 2H^+ + NO_2$
	24	$Ti^{3+} + H_2O + NO_2^- \rightarrow TiO_2 + 2H^+ + NO$
	25	$6Ti^{3+} + 8H_2O + 2NO_2^- \rightarrow 6TiO_2 + 16H^+ + N_2$
	26	$2Ti^{3+} + 2x\,NO_3^- + (3-x)\,H_2O \rightarrow Ti_2O_{3+5x}N_{2x} + (6-2x)\,H^+$
	27	$Ti^{2+} + H_2O + NO_3^- \rightarrow TiO_2 + 2H^+ + NO_2^-$
	28	$Ti^{2+} + 2NO_3^- \rightarrow TiO_2 + 2NO_2$
	29	$Ti^{2+} + 2NO_2^- \rightarrow TiO_2 + 2NO$
	30	$3Ti^{2+} + 2H_2O + 2NO_2^- \rightarrow 3TiO_2 + 4H^+ + N_2$
	31	$2Ti^{2+} + 2x\,NO_3^- + (2-x)\,H_2O \rightarrow Ti_2O_{2+5x}N_{2x} + (4-2x)\,H^+$
	32	$2NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+$
Interaction of Cl, N species	33	$2NO_2^- + ClO_2^- \Rightarrow 2NO_3^- + Cl^-$
	34	$NO_2^- + ClO^- \Rightarrow 2NO_3^- + Cl^-.$
Tap water	35	$2Ti^{3+} + 2xClO_4^- + 2y\,NO_3^- + (3-x-y)\,H_2O \rightarrow Ti_2O_{3+7x+5y}Cl_{2x}N_{2y} + (6-2x-2y)\,H^+$
	36	$2Ti^{2+} + 2xClO_4^- + 2y\,NO_3^- + (2-x-y)\,H_2O \rightarrow Ti_2O_{2+7x+5y}Cl_{2x}N_{2y} + (4-2x-2y)\,H^+$

	37	$3TiO_2 + 4H^+ + 4Cl^- \rightarrow Ti + 4ClO + 2H_2O$
	38	$5TiO_2 + 4H^+ + 4Cl^- \rightarrow Ti + 4ClO_2 + 2H_2O$
	39	$TiO_2 + 4H^+ + 4Cl^- \rightarrow TiCl_4 + 2H_2O$
	40	$2TiO_2 + 2xH^+ + 2xCl^- \rightarrow Ti_2O_{4-x}Cl_{2x} + xH_2O$
	41	$Ti^{2+} + 2Cl^- \rightarrow TiCl_2$
	42	$Ti^{3+} + 4Cl^- \rightarrow TiCl_3$
	43	$Ti^{4+} + 4Cl^- \rightarrow TiCl_4$
	44	$2Ti^{4+} + (4-x) H_2O + 2xCl^- \rightarrow Ti_2O_{4-x}Cl_{2x} + (8-2x)H^+$
	45	$Ti^{4+} + H_2O + SO_4^{2-} \rightarrow TiOSO_4 + 2H^+$
	46	$2Ti^{3+} + 2H_2O + 2SO_4^{2-} \rightarrow 2TiOSO_4 + 2H^+ + H_2$
	47	$Ti^{2+} + H_2O + SO_4^{2-} \rightarrow TiOSO_4 + H_2$

Appendix E. Perchlorate Reduction by Hydrogen Gas

E1 Introduction

Hydrogen gas can also be served as the electron donor on perchlorate reduction. It can be used as the reducing agent in electrochemical approach with the aid of electrode as the catalyst [55, 56]. In biological system, it was also used as a clean electron donor to remove perchlorate[57-59]. Recently, it was found effective to remove perchlorate by homogeneous catalyst[1]. In the open system of Ti-TiO_2 surface, both dissolved oxygen and produced oxygen made contributions on the production TiO_2 particles. In close system, the dissolved oxygen gas can be diminished by purging and produced oxygen reacts with adsorbed hydrogen gas into water. Furthermore, the Ti-TiO_2 surface can be functioned as a catalytic wall by the formation of titanium hydride layer. The formation of titanium hydride layer and its catalytic nature been reported by different researchers previously[60-62]. In order to investigate the catalytic reduction of perchlorate at Ti-TiO_2 surface, hydrogen gas was introduced into the reactor as the reducing agent.

E2 Methods

Figure E1 shows the reactor used to investigate the effect of H_2 gas on perchlorate reduction. It system consists of an high-pressure-resistant cylinder, a reactor and pressure control and sampling valves. The pressure resistant cylinder was made of stainless steel and the rector was a pyres glass beaker. The reactor after being filled with 1.5 mL of perchlorate solution was placed inside of the stainless steel container and purged with hydrogen gas. After hydrogen gas purging for one hour, the system was closed completely while keeping the container under pressure from a hydrogen gas tank. Samples were taken hourly once a constant potential was applied on the Ti electrode.

E3 Results and discussions

Figure E2 shows the results of the reduction of perchlorate in the presence of hydrogen gas. Results indicated that the perchlorate reduction followed a 5-stage reaction sequence. Perchlorate concentration decreased immediately from 1000 to 900 ppb in 2 hours then increased to 1000 ppb again at 8 hours. The perchlorate concentration decreased from 1000 to 900 ppb when the reaction time increased from 8 to 52 hours. Then the perchlorate concentration decreased further from 900 to 250 ppb when the reaction time increased from 52 to 72 hours. After 72 hours, the perchlorate concentration decreased drastically to less than 100 ppb.

Results indicated that perchlorate reduction by hydrogen gas was slow. Nonetheless, it was observed that hydrogen gas could renew the Ti electrode effectively as the amount of solid precipitate on the Ti electrode decreased markedly.

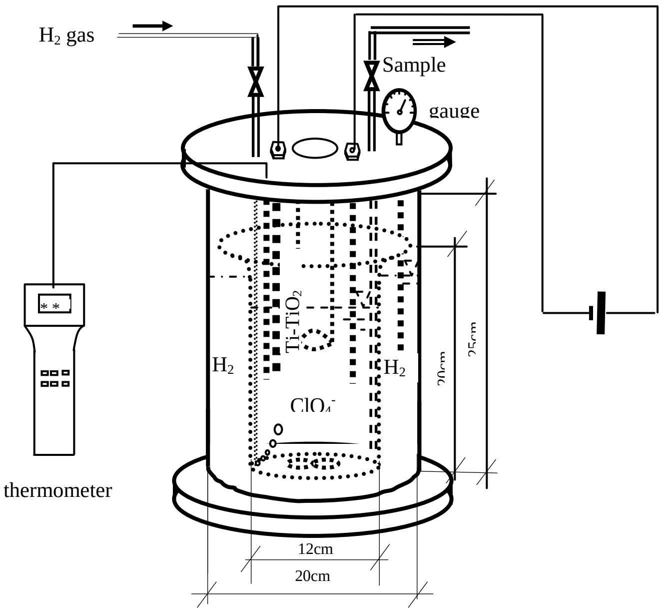

Figure E1 Closed Ti-TiO_2 system for kinetics on perchlorate reduction

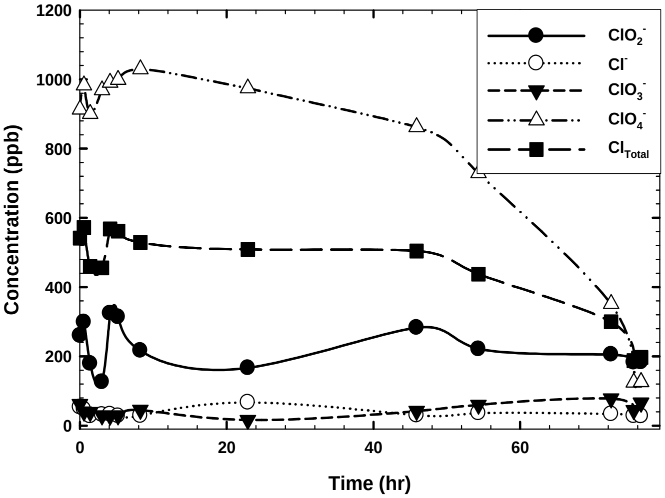

Figure E2 Reduction of ClO_4^- at Ti-TiO_2 surface with the presence of H_2 gas.

Experimental conditions: The perchlorate concentration was 1000 ppb and H2 pressure was 1.5 atm. All other experimental conditions were: temperature = 22 oC; pH = 5.6; anode = Ti; cathode = Fe; voltage applied = 10 V; current = ~10 mA (or current density = 1.9 mA/cm2).

Appendix F. Unit Treatment Cost for Various Chemical Processes

Table F1 POU Economics (Based on 1 Liter of media per device).

Disposable media	Average capacity (bv)	Average media life @1000 gallon per device per year	Media cost only- $ per 1000 gallons of water treated
Carbon	200	2.5 weeks	30,00
Acrylic SBA Type I	300	1 month	96.00
Styrenic SBA Type I	4,000	1 year	5.25
BiQuat perchlorate selective resin	28,000	7.4 years	3.50

Source: Francis Boodoo, POU/POE Removal of Perchlorate, Water Conditioning & Purification, August 2003.

Table F2 POE Economics (Based on 1 Liter of media per device).

Disposable media	Average capacity gallon per ft	Average media life @350 gallons per day usage	Media cost only- $ per 1000 gallons of water treated
Carbon	3,000	10 days	15.00
Acrylic SBA Type I	3,700	12 days	48.00
Styrenic SBA Type I	125,000	1 year	1.80
BiQuat perchlorate selective resin	500,000	3.9 years	1.50

Source: Francis Boodoo, POU/POE Removal of Perchlorate, Water Conditioning & Purification, August 2003.