

Electrochemical and photocatalytic reduction of perchlorate ion

Thomas L. Theis, Amy K. Zander, Xiang Li, Jeosadaque Sene and Marc A. Anderson

ABSTRACT

The presence of perchlorate in water supplies may have deleterious human health effects. Electrochemical and electrophotocatalytic reduction of the perchlorate ion to the chloride ion were assessed at laboratory scale. Studies were carried out in two-chambered batch reactor systems in which the cathodic and anodic compartments were separated by an ion exchange membrane. Electrodes consisted of titanium coated with a thin film of small TiO₂ particles. Test water systems were buffered to an acid pH and a background electrolyte was added. Applied voltages ranged from –1.75 to –2.0 v. For photolytic systems, ultraviolet light was supplied. Initial perchlorate concentrations ranged from 5×10^{-2} M to 5×10^{-7} M. Reduction initially proceeded rapidly but slowed with time. The percentage of perchlorate electrochemically reduced after 2 h was found to range from less than 1% at the highest concentration to 30–35% at lower concentrations. The extent of photocatalytic reduction at high perchlorate concentrations was approximately five times greater than for electrochemical reduction at the same concentrations. An additional fourfold improvement in reduction percentage was noted when the electrode was doped with vanadium. A mathematical model suggested that the limiting factor in perchlorate reduction was competition among anions for active sites on the electrode surface. Application of this technology for decontamination of water supplies will require further advances in electrode technology and/or innovations in engineering design.

Key words | drinking water, electrolytic reduction, perchlorate, photocatalytic reduction

Thomas L. Theis
Center for Environmental Management,
Clarkson University,
Potsdam, NY 13699-5715,
USA
Present address:
Director, Institute for Environmental Science and
Policy,
University of Illinois at Chicago,
2121 West Taylor Street,
Chicago, IL 60612-7260,
USA

Amy K. Zander (corresponding author)
Xiang Li
Department of Civil and Environmental
Engineering,
Clarkson University,
Potsdam, NY 13699-5710,
USA
Tel: 315-268-6532
Fax: 315-268-7985
E-mail: zander@clarkson.edu

Jeosadaque Sene
Marc A. Anderson
Environmental Chemistry Program,
University of Wisconsin,
660 N. Park Street,
Madison, WI 53706,
USA

INTRODUCTION

The use of ammonium perchlorate in the manufacture of solid rocket propellants, explosives, and fireworks has resulted in the contamination of groundwater used as a source for drinking water in California (CDHS 2000). Subsequent identification at low levels in the Colorado River and in Lake Mead suggest that it may occur more commonly in both ground and surface waters throughout the United States than previously considered. At present perchlorate contamination of drinking water supplies affects more than 12 million consumers in the United States (USEPA 1999).

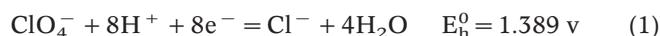
Perchlorate has the potential to adversely affect human health at low dose levels. A 'No Observable

Adverse Effects Level' (NOAEL) of 0.14 mg/kg/day was identified in a USEPA study, leading the California Department of Health Services Drinking Water Program to recommend 18 µg/l as the level that would be protective of human health (USEPA 1995; CDHS 2001). At the national level, perchlorate has been added to the contaminant candidate list required by the Safe Drinking Water Act Amendments of 1996 (Federal Register 1998).

It is important that treatment research for perchlorate in water be performed simultaneously with health effects and occurrence studies in the event these studies indicate that action is warranted. It is also important that

perchlorate treatment and destruction be studied at concentrations equal to and greater than the California action level. While most waters have concentrations in the low parts per billion range, higher concentrations have been observed and, as importantly, are generated by some removal technologies, such as ion exchange and reverse osmosis. The application of destructive technologies to such sources is advisable.

This study was undertaken in order to investigate the possibility of applying electrode technology to the destruction of perchlorate in water. Its objectives were twofold: first, to ascertain the operating limits for the use of electrodes in systems in which an electrical potential is applied to reduce perchlorate to chloride ion; and second, to determine the efficacy of catalysing the reaction through the use of ultraviolet/semiconductor surfaces. The perchlorate ion is thermodynamically unstable in water according to the half-cell reaction in Equation 1.



Its explosive reactivity with organic matter in concentrated acidic solutions is well known (Smith *et al.* 1955; Smith 1965; Schilt 1979). Unfortunately, from the point of view of treatment and residuals management, it is kinetically rather inert in dilute systems, with aqueous solutions of perchlorate salts stable indefinitely, even in the presence of reducing agents such as elemental and ferrous iron, reduced sulphur, and many organic compounds. Because of its high energy of activation, any practical methods to effect its destruction through chemical reduction must of necessity involve the use of suitable catalysts. In this work, the source of such catalytic effects are titanium dioxide-coated electrodes across which an electrical potential is applied, and ultraviolet light in combination with titanium dioxide used as a semiconductor photocatalyst.

Previous investigators have observed the reduction of the perchlorate ion at metal and metal-compound surfaces, both in the presence of a chemical reducing agent and through the application of a potential. Horányi and co-workers successfully reduced perchlorate at several material surfaces, including tungsten carbide, rhenium, technetium, platinum, and rhodium (Horányi &

Vértes 1974; Horányi *et al.* 1992; Bakos & Horányi 1993; Wasberg & Horányi 1995). In the case of tungsten carbide the chemical reducing agent was hydrogen, which was oxidized electrolytically and coupled to the perchlorate reduction half-cell (Equation 1). The other electrode reactions involved direct electrolytic reduction. Colom & Gonzalez-Tejera (1985) successfully reduced perchlorate at ruthenium, Cruz *et al.* (1985) at iridium, Almeida *et al.* (1997) at tin, Bet-Pera & Jaselskis (1985) at mercury, Painot & Augustynski (1975) at aluminum, and Brown (1986) at titanium. In all cases the end product of the reaction was chloride ion. Wasberg & Horányi (1995) provided evidence of a stepwise reduction sequence in which two electrons at a time are transferred. At titanium surfaces Brown (1986) hypothesized the cyclic formation of Ti(II) and Ti(III) hydroxyl-surface complexes as electron transfer catalysts.

The potentials used in these experiments varied, but were generally more negative than 1 v indicating the need for a substantial input of energy in comparison with the positive potential shown in Equation 1. Several of the researchers above report that the electrode reduction is acid-catalysed, with increasingly negative voltages required as pH is increased, and in the presence of other ions, such as sulphate and halide ions (Painot & Augustynski 1975; Brown 1986; Wasberg & Horányi 1995).

The photoreduction of perchlorate at semiconductor surfaces has not yet been reported. General characteristics of photochemical reactions are available in detail elsewhere (e.g. Ollis & Al-Ekabi 1993). The following steps summarize the process:

1. illumination of the semiconductor with light of greater energy than the semiconductor band gap yielding charge-carrying electron-hole pairs;
2. trapping of electrons and holes by adsorbed species;
3. occurrence of redox reactions between sorbates and trapped charge carriers; and
4. desorption of reaction products and regeneration of the surface to its original state.

It should be noted that for every oxidation reaction, a concurrent reduction must occur.

The characteristic times for these reaction steps vary from extremely fast (10^{-15} sec) for charge carrier trapping

to relatively slow for interfacial charge transfer, which can take place in the order of milliseconds or slower and so tend to be rate limiting. The overall efficiency of the photocatalytic process reduces to the relative rates of charge carrier recombination versus interfacial charge transfer to the reduced and oxidized species, thus much research into semiconductor photocatalysis has centred on ways to slow charge carrier recombination or accelerate interfacial electron transfer. One way of slowing recombination is to electrically bias the system through application of an external field. Interfacial charge transfer rates can sometimes be increased by doping the semiconductor with small amounts of metals such as platinum, chromium and vanadium, producing 'islands' of improved conductivity.

Although many semiconductors can be used as photocatalysts, to date the most common has been anatase (TiO_2), which has several advantages. It is highly absorptive of UV radiation, the potential of its valence band is suitable for catalysing the reaction of interest, it is highly resistant to corrosion and dissolution over a wide pH range, and it is inexpensive. In addition, promising results have been observed with TiO_2 that has been doped with small amount of metals such as vanadium, chromium, and platinum, which impart improved conductivity to the surface.

METHODS

The main electrodes, both cathode and anode, used in this research were made of titanium, a conductor, coated with a layer of small ($0.2 \mu\text{m}$), semiconducting TiO_2 particles. Coatings were prepared through a series of dipping, drying, and firing steps with the resulting coating quite resilient over time (Candal *et al.* 1998). For some experiments not involving UV-photocatalysis a reticulated carbon anode was employed during periods when the Ti/TiO_2 electrodes were unavailable. No significant differences in the reductive characteristics of systems with and without Ti anodes were observed.

Experiments were conducted in a 1-litre electrochemical cell in which anodic and cathodic chambers were separated with a Nafion 117 cation exchange

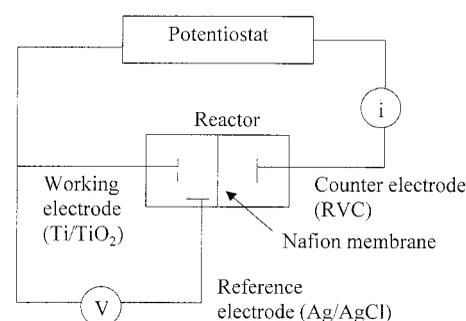


Figure 1 | Schematic of electrochemical cell.

membrane (DuPont, Fayetteville, NC). The purpose of the membrane was to prevent the migration of anions, in particular chloride, to the anode where it might be re-oxidized. As shown in Figure 1, a standard three electrode array was used: cathode (working), anode (counter), and a double junction reference cell (Ag/AgCl) which used KNO_3 as the outer chamber filling solution. The reference cell was located as close as possible to the cathode. An electrical potential was applied to the cathode using a bipotentiostat at constant values relative to the reference electrode. The potential of the anode was not controlled and thus changed with the concentration of the electrolyte. Cyclic voltammetry revealed that the potential range of interest ranged from -1.0 to -2.0 v.

Ultraviolet light for photocatalytic experiments was supplied by two 15-W fluorescent bulbs (General Electric Model F15T8), placed 10 cm from the cell. The illuminated area of the electrode was 40 cm^2 . Light intensity at the position of the photocathode was 1.35 mW/cm^2 as measured with a photometer (International Light Model IL 1400A). The entire reactor assembly was enclosed in a light-tight box during experiments.

Experimental solutions consisted of various initial concentrations of sodium perchlorate (0.05 M to 10^{-7} M), a background electrolyte of sodium sulphate ($5 \times 10^{-3} \text{ M}$) in order to provide relatively constant conductivity of the solution, and in most cases a formic acid buffer to control pH variations. All solutions were made using deionized distilled water. Prior to and during experiments, de-oxygenation was performed using high purity nitrogen, which was sparged through the solution for

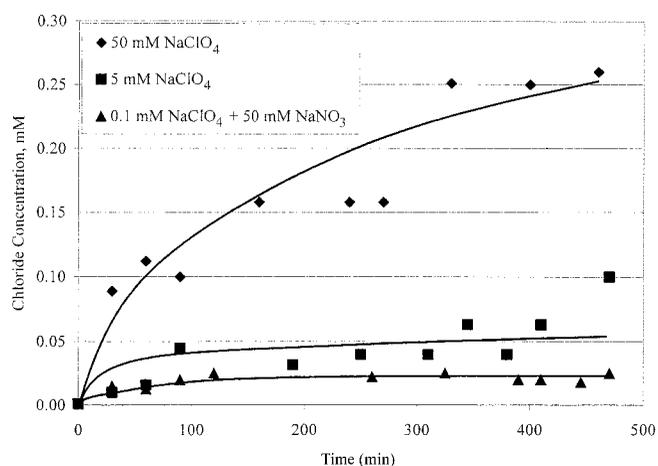


Figure 2 | Perchlorate reduction, as measured by chloride production, as a function of time ($E = -2.0$ V).

several minutes in order to lower the dissolved oxygen concentration to a level at or below most perchlorate concentrations, a condition assumed to exist in most contaminated aquifers. Experiments took place over a period of 2–3 h during which samples were taken at regular intervals. Checks for chloride ion in the anodic compartment during and after experimentation were negative, demonstrating the efficiency of the Nafion membrane.

Analysis for perchlorate was conducted by ion chromatography using a modified version of the method recommended by the California Department of Health Services (1997). This included using standard gradient elution with 45 mM sodium hydroxide and 40% methanol, yielding a detection limit of $4 \mu\text{g/l}$ of perchlorate (4×10^{-8} M). pH was measured using the standardized electrometric method (APHA 1995). In cases where chloride ion was determined, the chloride-ion electrode or argentometric methods were used (APHA 1992).

RESULTS AND DISCUSSION

Initial electrolytic reduction experiments were conducted at several potentials and with varying background electrolytes in order to determine the appropriate conditions for replicate studies. Figure 2 shows typical response data at an applied potential of -2.0 V over an extended period

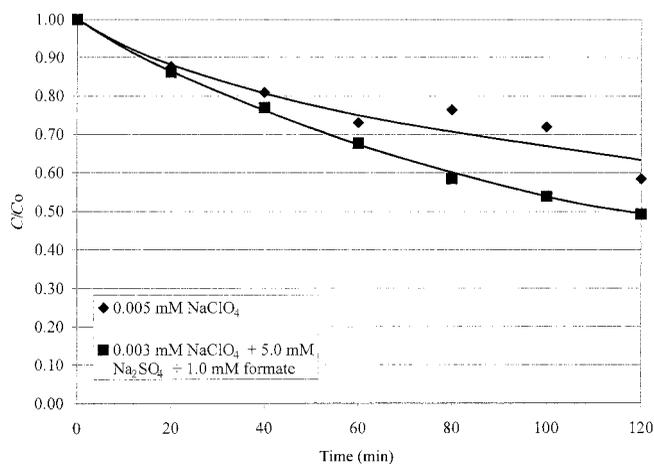


Figure 3 | Electrolytic reduction of perchlorate, 5×10^{-6} M, and 3×10^{-6} M ($E = -2.0$ V, sulphate = 5×10^{-3} M, formate = 10^{-3} M).

of time. Observations in these experiments generally revealed a relatively rapid initial reduction followed by a slower phase, and an associated rise in pH in the anodic compartment consistent with the stoichiometry of Equation 1. Chloride was the end product throughout all experiments. These results suggested that potentials between -1.75 and -2.0 V were the most effective in achieving reduction, and that the addition of a buffer was advisable in order to prevent wide pH variations during experiments. Experiments conducted at several buffered pH ranges showed that as pH increased, the amount of perchlorate reduced within a given amount of time decreased, as suggested in the literature.

Figure 3 shows two perchlorate reduction experiments. The presence of pH and ionic buffers appears to result in slightly more rapid reduction, probably due to lower pH and higher solution conductivity. The most interesting feature of the experiments, however, was the observation that as the initial perchlorate concentration in the systems decreased, the percent reduced within 2 h increased, down to an initial concentration of 10^{-6} M, beyond which no further improvement was noted as shown in Figure 4. This is suggestive of the influence of limited access of perchlorate ions to the electrode surface, which is treated more thoroughly below.

Experiments of a preliminary nature were performed in irradiated systems using TiO_2 photoelectrodes as

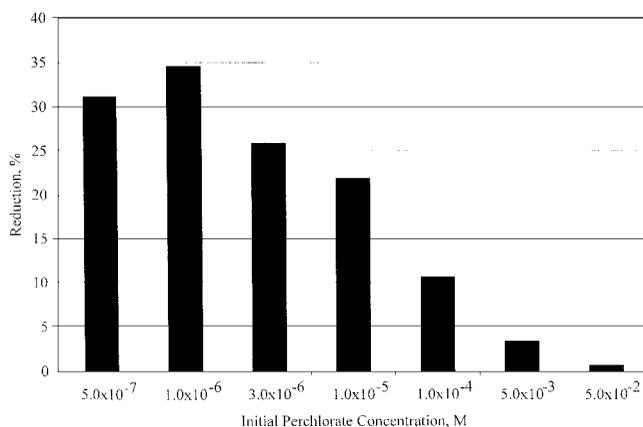


Figure 4 | Average percent electrolytic reduction of perchlorate at various initial concentrations over a 2 h reduction period ($E = -2.0$ v, sulphate = 5×10^{-3} M, formate = 10^{-3} M).

described previously. Samples of 0.05 M sodium perchlorate were electrolysed at -1.75 v (versus the saturated calomel electrode (SCE)) and pH 5.0 and compared to control samples. In addition, identical experiments were conducted with vanadium-doped titanium electrodes (1% molar ratio V/TiO₂), which results in larger conductivities of the catalyst. Results are summarized in Figure 5 in which the percentage of perchlorate reduced over a 3-h period is compared for the different electrode systems. As shown, the TiO₂ system yielded reduction percentages of 4–11% over the reaction

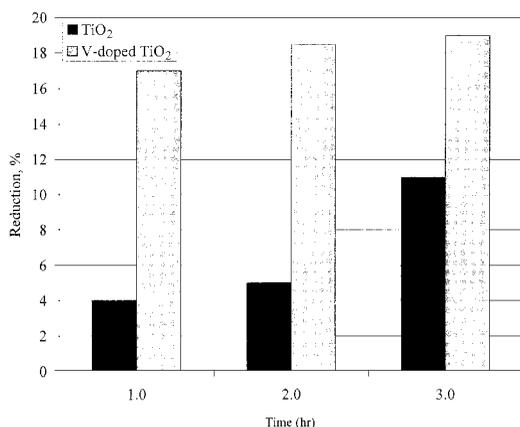


Figure 5 | Photolytic reduction of perchlorate with TiO₂ and V-doped TiO₂ ($E = -1.75$ v, pH = 5.0, formate = 10^{-5} M).

period, a low amount, but substantially in excess of systems with the same initial perchlorate concentration without irradiation (Figure 4). When the V/TiO₂ electrode is used, the percent reduced rose to 19% after 3 h, and was much greater during the first 2 h than the TiO₂ electrode alone. The observed improvement with the V-doped electrode occurs because the presence of the metal injects new conduction levels into the band gap of titanium dioxide, resulting in greater conductivities of the catalysts. The combined irradiation and V-doping of the electrode holds promise not only of increasing the rate of perchlorate reduction, but also lowering the effective potential (and hence cost) that must be applied. Indeed, Almeida *et al.* (1997) observed significant perchlorate reduction at a tin electrode surface at an applied potential of -1.1 v.

MATHEMATICAL MODEL

The reduction of perchlorate can be approximated by a system of equations that relates electrode surface sites, adsorption mass action expressions, and reduction kinetics. In systems buffered by formic acid (pH = 3.2), the majority of titanium surface sites can be considered to be in the protonated state since the zero point of charge of TiO₂ is 6.4 (Schindler & Gamsjager 1972). Assuming adsorption of formic acid to be negligible, since it is uncharged at experimental pHs, and following accepted notation for surface complexation modeling (Papelis *et al.* 1988), the sorption of perchlorate, chloride, and sulphate (assuming one to one stoichiometry) at the positively charged titanium surface is given by, respectively:

$$K_{ClO_4}^s = \frac{[TiOH_2^+ - ClO_4^-]}{[TiOH_2^+][ClO_4^-]_b} \quad (2)$$

$$K_{Cl^-}^s = \frac{[TiOH_2^+ - Cl^-]}{[TiOH_2^+][Cl^-]_b} \quad (3)$$

$$K_{SO_4^{2-}}^s = \frac{[TiOH_2^+ - SO_4^{2-}]}{[TiOH_2^+][SO_4^{2-}]_b} \quad (4)$$

where K^s refers to the respective surface adsorption constant (M^{-1}) and the 'b' subscript refers to bulk solution

concentrations (M). Mass balances on total chlorine, total sulphate, and total electrode sites, respectively, are:

$$[Cl]_T = [TiOH_2^+ - Cl^-] + [TiOH_2^+ - ClO_4^-] + [Cl^-]_b + [ClO_4]_b \quad (5)$$

$$[SO_4]_T = [TiOH_2^+ - SO_4^{-2}] + [SO_4^{-2}]_b \quad (6)$$

$$[S]_T = [TiOH_2^+] + [TiOH_2^+ - Cl^-] + [TiOH_2^+ - ClO_4^-] + [TiOH_2^+ - SO_4^{-2}] \quad (7)$$

The rate of perchlorate reduction at the electrode surface is given by:

$$\frac{-d[TiOH_2^+ - ClO_4^-]}{dt} = k[TiOH_2^+ - ClO_4^-] \quad (8)$$

The initial condition for this system corresponds to the initial distribution of perchlorate and sulfate between electrode surface and bulk solution.

Parameterization of Equations 2 through 8 requires that the surface adsorption constants be supplied. No studies of perchlorate, chloride, or sulphate adsorption to anatase have been reported, however reasonable approximations can be obtained from similar systems in the literature. For perchlorate, nitrate ion is a reasonable surrogate for which James (1981) reports an adsorption constant onto anatase of 10^2 l/mole. Chloride adsorption to anatase is less clear, however complexes of chloride with most metal cations in aqueous solution are one to two orders of magnitude greater than the corresponding complexes with perchlorate and nitrate (NIST 1997). As Hingston (1981) has shown, surface complexation constants tend to follow rather closely the order of solution phase complex formation constants, thus in this study a value of 10^4 l/mole is used. Similarly a surrogate for sulphate is the selenate ion; Papelis *et al.* (1988) report a value of $10^{6.8}$ l/mole for selenate adsorbing to goethite. Total cathode surface area corresponds to the surface area of the coated TiO_2 on the surface of the titanium electrode. Schindler (1981) suggests a molecular site occupancy for large anions adsorbing to anatase no greater than about $2/nm^2$. Given an exposed electrode surface area of approximately 50 cm^2 , reactor volume of 1 litre, and assuming a uniform coating of anatase on the electrode, this yields a site concentration of about 10^{-8} M.

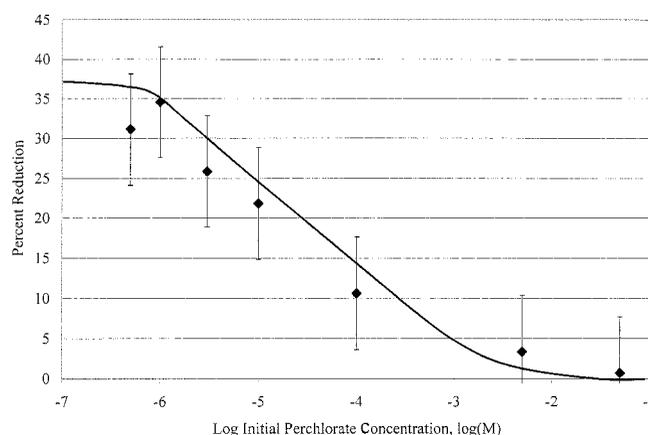


Figure 6 | Fit of model equations 2 through 8 with perchlorate reduction data of Figure 4.

The rate constant, k , of Equation 8 was estimated through comparison of solutions of Equations 2 through 8 with the data of Figure 4. The best visual fit is shown in Figure 6 for a rate constant $6 \times 10^{-5} \text{ s}^{-1}$, a value within the range reported by Brown (1986) and Earley & Kallen (1971) for the reduction of perchlorate in aqueous solution. In addition, the governing equations successfully capture the inverse relationship between initial perchlorate concentration and percent reduced after 2 h of reaction time.

Given the uncertainty of the constants used in Equations 2 through 8, the results must be considered approximate. They are, however, in accord with expectations and can provide a basis for understanding the electroreduction of perchlorate. In particular, Figure 7 shows projections for the percentage of perchlorate reduced in 2 h as electrode site concentration varies. Clearly the concentration of surface sites available in experiments was inadequate to achieve reduction of high concentrations of perchlorate; indeed site concentration would have to be increased by several orders of magnitude to bring about acceptable results. Analysis of modeling results reveals that the limiting factor is related to competition for sites at the surface of the electrode. Sulphate ion, which is necessary in order to provide solution conductivity, is more strongly adsorbed than perchlorate and, except at the highest perchlorate concentration studied, is present at much higher concentrations. In addition chloride ion, the end product of the reaction, is also adsorbed more strongly, thus as the reduction reaction proceeds less perchlorate is

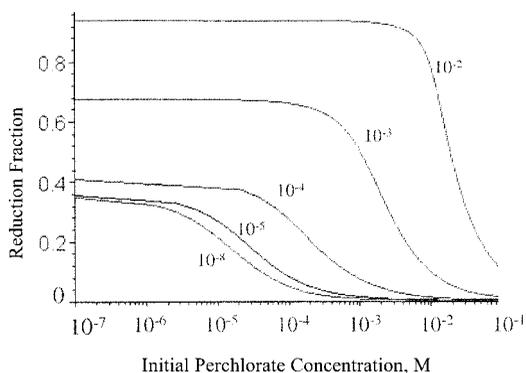


Figure 7 | Model results for calculated electrolytic perchlorate reduction after 2 h at different electrode areas.

able to adsorb at the surface. This offers an explanation for the observed lowering of the reaction rate at later times as noted in Figure 2. Such competition exists at all electrode areas, but is less pronounced as the total area increases since sulphate ion concentration remains constant.

CONCLUSIONS

The goal of this study was to assess the possibility of using electrochemical and photochemical electrode technologies for reducing perchlorate ion in aqueous solution. The study found that the electrochemical reaction using Ti/TiO₂ electrodes proceeded faster at lower pH conditions, and required applied potentials of -1.75 to -2.0 v and the presence of a background electrolyte (sodium sulphate was used in this study). Limited studies using UV-catalysed photochemical reduction revealed positive effects, an approximate fivefold increase at 0.05 M perchlorate, and an additional fourfold improvement when electrodes were doped with small quantities of vanadium.

The fraction of perchlorate reduced during electrochemical experiments ranged from less than 1 to approximately 34% over a 2-h reaction period, and was observed to be inversely proportional to the initial perchlorate concentration in solution. Further, the reaction exhibited self-arresting features, i.e. the rate decreased with time. Additional analysis, aided by the development of a mathematical model of the system, showed that the limiting factor in perchlorate reduction was competition among anions for active sites on the electrode surface, with perchlorate being less strongly adsorbed than sulphate

and chloride. In addition, the stronger sorptive tendency of chloride, the end product of the reaction, offers an explanation for the slowing of the reaction with time.

The application of these technologies would require that the number of reactive sites on the electrode surface relative to the solution volume be increased by several orders of magnitude, to concentrations above the background electrolyte concentration in solution. Practical use of this technology for the decontamination of water supplies will require further advances in electrode technology and/or engineering design.

ACKNOWLEDGEMENTS

This work was funded in part by Grant number 2578 from the American Water Works Association Research Foundation. Albert Ilges was the project officer. Additional financial support from FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) (99/10250-5) São Paulo, Brazil is also gratefully acknowledged.

NOMENCLATURE

Ag/AgCl	silver/silver chloride
CDHS	California Department of Health Services
e ⁻	electron
<i>E</i>	electrical potential (volts)
<i>E</i> _H ⁰	standard oxidation potential (volts)
l	litre
µg/l	microgram per litre
µm	micrometre
mg/l	milligram per litre
mg/kg/day	milligram per kilogram per day
mM	millimolar
M	Molar (moles/litre)
NOAEL	No Observable Adverse Effects Level
RVC	reticulated vitreous carbon
SCE	saturated calomel electrode
Ti	titanium
TiO ₂	titanium dioxide
USEPA	United States Environmental Protection Agency
UV	ultraviolet
v	volts
V	vanadium

REFERENCES

- Almeida, C. M. V. B., Giannetti, B. F. & Rabockai, T. 1997 Electrochemical study of perchlorate reduction at tin electrodes. *J. Electroanal. Chem.* **422**, 185–189.
- APHA 1992 *Standard Methods for the Examination of Water and Wastewater*, 18th edition. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, D.C.
- Bakos, I. & Horanyi, G. 1993 Study of the relationship between voltametric behaviour and electrocatalytic activity in the reduction of ions at platinized platinum electrodes. *J. Electroanal. Chem.* **347**, 383–391.
- Bet-Pera, F. & Jaselskis, B. 1985 Reduction of perchlorate at the dropping mercury electrode in the presence of molybdate. *Electrochim. Acta* **30**(2), 217–221.
- Brown, G. M. 1986 The reduction of chlorate and perchlorate ions at an active titanium electrode. *J. Electroanal. Chem.* **198**, 319–330.
- Candal, R. J., Zeltner, W. A. & Anderson, M. A. 1998 TiO₂-mediated photoelectrocatalytic purification of water. *J. Adv. Oxidation Technologies* **3**, 270–276.
- CDHS (California Department of Health Services) 1997 *Determination of Perchlorate by Ion Chromatography*. Rev. No. 0, May 7.
- CDHS (California Department of Health Services) 2000 Perchlorate: early findings. www.dhs.ca.gov/ddwem/chemicals/perchl/earlyfindings.htm (revised December 6).
- CDHS (California Department of Health Services) 2001 Perchlorate's Drinking Water Action Level. www.dhs.ca.gov/ps/ddwem/chemicals/perchl/actionlevel.htm (revised March 2).
- Colom, F. & Gonzalez-Tejera, M. J. 1985 Reduction of perchlorate ion on ruthenium electrodes in aqueous solutions. *J. Electroanal. Chem.* **190**, 243–255.
- Cruz, M. S., Gonzalez-Tejera, M. J. & Villamanan, M. C. 1985 Reduction electrochimique de l'ion ClO₄⁻ sur l'électrode d'iridium. *Electrochim. Acta* **30**(11), 1563–1569.
- Earley, J. E. & Kallen, T. W. 1971 The reduction of perchlorate ion by Aquoruthenium(II). *Inorganic Chem.* **10**(6), 1152–1155.
- Federal Register 1998 **63**(40) (March 2).
- Hingston, F. J. 1981 A review of anion adsorption. In: *Adsorption of Inorganics at Solid-Liquid Interfaces*, M. Anderson & A. Rubin (Eds). Ann Arbor Science, Ann Arbor, MI, pp. 51–90.
- Horányi, G. & Vértes, G. 1974 Reduction of perchlorate ions by molecular hydrogen in the presence of tungsten carbide. *Inorg. Nucl. Chem. Letters* **10**, 767–770.
- Horányi, G., Bakos, I., Szabó, S. & Rizmayer, E. M. 1992 Preliminary note—new observations in the field of the electrochemistry of technetium and rhenium: electrocatalytic reduction of ClO₄⁻ ions at electrosorbed and electrodeposited Tc and Re layers in acid medium. *J. Electroanal. Chem.* **337**, 365–369.
- James, R. O. 1981 Surface ionization and complexation at the colloid/aqueous electrolyte interface. In: *Adsorption of Inorganics at Solid-Liquid Interfaces*, M. Anderson & A. Rubin (Eds). Ann Arbor Science, Ann Arbor, MI, pp. 219–261.
- National Institute of Standards & Technology 1997 Critically selected stability constants of metal complexes database. *NIST Standard Reference Database 46*, Version 3.0, US Department of Commerce, Gaithersburg, MD.
- Ollis, D. F. & Al-Ekabi, H. (Eds) 1993 *Photocatalytic Purification and Treatment of Water and Air*. Elsevier, Amsterdam.
- Painot, J. & Augustynski, J. 1975 Etude potentiostatique et spectroscopique de l'aluminium recouvert par une couche d'oxyde: eddet de differents anions. *Electrochim. Acta* **20**, 747–752.
- Papelis, C., Hayes, K. F. & Leckie, J. O. 1988 *HYDRAQL: A program for the computation of chemical equilibrium composition of aqueous batch systems including surface-complexation modeling of ion adsorption at the oxide/solution interface*. Technical Report No. 306, Department of Civil Engineering, Stanford University, Stanford, CA.
- Schilt, A. A. 1979 *Perchloric Acid and Perchlorates*. The G. Frederick Smith Chemical Company, Columbus, Ohio.
- Schindler, P. W. 1981 Surface complexes at the oxide-water interface. In: *Adsorption of Inorganics at Solid-Liquid Interfaces*, M. Anderson & A. Rubin (Eds). Ann Arbor Science, Ann Arbor, MI, pp. 1–49.
- Schindler, P. W. & Gamsjager, H. 1972 Acid-base reactions of the TiO₂ (anatase)-water interface and the zero charge of TiO₂ suspensions. *Kolloid-Z. u. Z. Polymere* **250**, 759–763.
- Smith, G. F. 1965 *The Wet Chemical Oxidation of Organic Compositions Employing Perchloric Acid With—or Without Added HNO₃–H₅IO₆–H₂SO₄*. The G. Frederick Smith Chemical Company, Inc., Columbus, Ohio.
- Smith, G. F., McCurdy, W. H. & Diehl, H. 1955 *The Dualistic and Versatile Reaction Properties of Perchloric Acid—Illustrative Experimental Demonstration Procedures and The Colorimetric Determination of Iron in Raw and Treated Municipal Water Supplies*. The G. Frederick Smith Chemical Company, Columbus, Ohio.
- USEPA 1992 *Provisional Non-Cancer and Cancer Toxicity Values for Potassium Perchlorate* (CASRN 7778-74-7). Memorandum from Joan S. Dollarhide, Superfund Health Risk Technical Support Center, Environmental Criteria & Assessment Office, Office of Research & Development, to Dan Stralks, USEPA Region IX.
- USEPA 1995 *Review of Proposed RfD for Perchlorate*. Correspondence from Joan S. Dollarhide, National Center for Environmental Assessment, Office of Research & Development, to Mike Girrard, Chairman, Perchlorate Study Group.
- USEPA 1999 Perchlorate. www.epa.gov/OGWDW/ccl/perchlor/perclo.html. Office of Ground Water and Drinking Water, Washington (revised April 15).
- Wasberg, M. & Horányi, G. 1995 The reduction of ions on Rh electrodes. *J. Electroanal. Chem.* **385**, 63–70.