Assessment of the Electrochemical Reduction of the Perchlorate Ion

Subject Area: Water Treatment
Assessment of the Electrochemical Reduction of the Perchlorate Ion
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The Awwa Research Foundation is a nonprofit corporation dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the industry. The research agenda is developed through a process of consultation with subscribers and drinking water professionals. Under the umbrella of a Strategic Research Plan, the Research Advisory Council prioritizes the suggested projects based upon current and future needs, applicability, and past work; the recommendations are forwarded to the Board of Trustees for final selection. The foundation also sponsors research projects through the unsolicited proposal process; the Collaborative Research, Research Applications, and Tailored Collaboration programs; and various joint research efforts with organizations such as the U.S. Environmental Protection Agency, the U.S. Bureau of Reclamation, and the Association of California Water Agencies.

This publication is a result of one of these sponsored studies, and it is hoped that its findings will be applied in communities throughout the world. The following report serves not only as a means of communicating the results of the water industry’s centralized research program but also as a tool to enlist further support of the nonmember utilities and individuals.

Projects are managed closely from their inception to the final report by the foundation’s staff and large cadre of volunteers who willingly contribute their time and expertise. The foundation serves a planning and management function and awards contracts to other institutions such as water utilities, universities, and engineering firms. The funding for this research effort comes primarily from the Subscription Program, through which water utilities subscribe to the research program and make an annual payment proportionate to the volume of water they deliver and consultants and manufacturers subscribe based on their annual billings. This program offers a cost-effective and fair method for funding research in the public interest.

A broad spectrum of water supply issues is addressed by the foundation’s research agenda: resources, treatment and operations, distribution and storage, water quality and analysis, toxicology, economics, and management. The ultimate purpose of the coordinated effort is to assist water suppliers to provide the highest possible quality of water economically and reliably. The true benefits are realized when the results are implemented at the utility level. The foundation’s trustees are pleased to offer this publication as a contribution toward that end.
This publication presents the results of a study to determine the technical feasibility of destroying perchlorate ion in drinking water by electrochemical reduction with a titanium electrode coated with titanium dioxide. Destruction, rather than removal, of perchlorate ion would provide a great advantage to water utilities in the treatment of perchlorate contaminated water supplies. Reduction was studied with simple electrochemical processes and with electrochemical processes catalyzed with ultraviolet light and titanium dioxide. Water utility personnel will be able to use the information contained within to assess the feasibility of electrochemical reduction of perchlorate ion in water for their particular facility.

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EXECUTIVE SUMMARY

The presence of perchlorate in water supplies may have deleterious human health effects, resulting in a recommended water quality standard of 18 μg/L (USEPA 1995; CDHS 2001). Methods to remove perchlorate from water have focused on phase transfer technologies such as ion exchange or carbon adsorption, and destructive technologies such as biological treatment. This research reports on different destructive technologies, those of electrochemical and photochemical reduction to the chloride ion, which attempt to catalyze the reduction of perchlorate using electrically biased electrodes and photochemically active semiconductor surfaces.

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. Systems were typically buffered using formate ion (pH = 3.2), and a background electrolyte, usually sodium sulfate, was added. Applied voltages ranged from −1.75 to −2.0 v. For photolytic systems, ultraviolet light was supplied via two 15-watt blacklight bulbs. Samples were taken over time up to a maximum of two to three hours. Initial perchlorate concentrations ranged from 0.05 M to 5x10⁻⁷ M (5000 mg/L to 50 μg/L as ClO₄⁻).

Results from electrolytic experiments indicated that reduction proceeded rapidly initially but slowed at later times. The percentage of perchlorate reduced after two hours was found to range from less than one percent at the highest concentration to 30 - 35% at lower concentrations. Photocatalytic experiments showed that at high perchlorate concentrations reduction was approximately five times greater than for electrochemical reduction under similar conditions. When the electrode was doped with vanadium, increasing conductivity, an additional fourfold improvement over simple electrochemical reduction was noted.

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 sulfate 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 practical 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, depending on the initial concentration of perchlorate and the desired treatment efficiency. It is suggested that one approach is through the fabrication and design of reactors in which flexible plastic guides, coated with a conductor and TiO₂, are arranged in a closely packed cathode/anode array. If materials capable of transmitting light are used, such a “waveguide” array might also be used in a photocatalytic system.
CHAPTER 1
INTRODUCTION

STATEMENT OF THE PROBLEM

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 greater than twelve 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 to 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 is performed simultaneously with health effects and occurrence studies in the event these studies indicate that action is called for. 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.
RESEARCH OBJECTIVES

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 catalyzing the reaction through the use of ultraviolet/semi-conductor surfaces.
CHAPTER 2
LITERATURE REVIEW

PERCHLORATE IN WATER

The perchlorate ion is thermodynamically unstable in water according to the half-cell reaction

\[ \text{ClO}_4^- + 8\text{H}^+ + 8e^- = \text{Cl}^- + 4\text{H}_2\text{O} \quad E_h^0 = 1.389 \text{ v} \quad (2.1) \]

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 sulfur, and many organic compounds, although its explosive reactivity with organic matter in concentrated acidic solutions is well known (Schilt 1979, Smith 1965, Smith et al. 1955). 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 semi-conductor photocatalyst.

PREVIOUS RESEARCH

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. Horanyi and co-workers successfully reduced perchlorate at several material surfaces, including tungsten carbide, rhenium, technetium, platinum, and rhodium (Horanyi and Vertes 1974, Horanyi et al. 1992, Bakos and Horanyi 1993, Wasberg and Horanyi 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 (reaction (1)). The other electrode reactions involved direct electrolytic reduction. Colom and Gonzalez-Tejera (1985) successfully reduced perchlorate at ruthenium, Cruz et al. (1985) at iridium, Almeida et al. (1997) at tin, Bet-Pera and Jaselskis (1985) at mercury, Painot and Augustynski (1975) at aluminum, and Brown (1986) at titanium. In all cases the end product of the reaction was
chloride ion. Wasberg and Horanyi (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 one volt indicating the need for a substantial input of energy in comparison with the positive potential of reaction (1). Several researchers report that the electrode reduction is acid catalyzed, with increasingly negative voltages required as pH is increased, and in the presence of other ions, such as sulfate and halide ions.

PHOTOCATALYTIC SURFACE REACTIONS

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 and El-Ekabi 1993). The following steps summarize the process:

a) illumination of the semiconductor with light of greater energy than the semiconductor band gap yielding charge-carrying electron-hole pairs,

b) trapping of electrons and holes by adsorbed species,

c) occurrence of redox reactions between sorbates and trapped charge carriers, and
d) 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 ($10^{-15}$ seconds) for charge carrier trapping to relatively slow for interfacial charge transfer, which can take place on 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 centered 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 Pt, Cr, and V, producing "islands" of improved conductivity.
Although many semiconductors can be used as photocatalysts, to date the most common has been anatase (TiO₂), which has several advantages. It is highly absorptive of UV radiation, the potential of its valence band is suitable for catalyzing 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 TiO₂ that has been doped with small amount of metals such as vanadium, chromium, and platinum, which impart improved conductivity to the surface.
CHAPTER 3
MATERIALS AND METHODS

ELECTRODES

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 μm), semi-conducting TiO₂ 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/TiO₂ electrodes were unavailable.

POTENTIOSTATIC EXPERIMENTS

Experiments were conducted in a 1-liter electrochemical cell in which anodic and cathodic chambers were separated with a Nafion 117 cation exchange membrane. 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 3.1, a standard three electrode array was used: cathode (working), anode (counter), and a double junction reference cell (Ag/AgCl) which

![Figure 3.1 Schematic of electrochemical cell](image-url)
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 bi-potentiosstat 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 $-2.0$ volts.

Ultraviolet light for photocatalytic experiments was supplied by two 15-watt fluorescent ultraviolet bulbs (General Electric Model F15T8) placed 10 cm from the cell. The illuminated area of the photocathode 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 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, 5000 mg/L to 50 µg/L as ClO$_4^-$), a background electrolyte of sodium sulfate ($5\times10^{-3}$ M, 480 mg/L as SO$_4^-$) in order to provide relatively constant conductivity of the solution, and either a formic acid or acetic acid buffer to control pH variations. All solutions were made using deionized distilled water.

Prior to and during the electrochemical reduction experiments, de-oxygenation was performed using high purity nitrogen, which was sparged through the solution for several minutes. Prior to and during the photoelectrochemical experiments, oxygen was bubbled through the solution, resulting in a dissolved oxygen concentration of roughly 40 mg/L for these experiments.

Experiments took place over a period of two to three hours 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.

**MEASUREMENTS**

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 (1800 mg/L as NaOH) and 40 percent methanol, yielding a detection limit of 4 μg/L of perchlorate (4x10⁻⁸ 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 1995).
ELECTROLYTIC REDUCTION EXPERIMENTS

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 4.1 shows typical response data at an applied potential of -2.0 v over an extended period 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 reaction (1). Chloride was the end product throughout all experiments. These results suggested that potentials between -1.75 and -2.0 volts 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 4.2 shows two perchlorate reduction experiments conducted under typical conditions of potential (-2.0 v), pH buffering (10^{-3} M formic acid (46 mg/L H_{2}CO_{2}), yielding a pH of approximately 3.2), and ionic buffering (10^{-3} M sodium sulfate, (142 mg/L Na_{2}SO_{4})). An interesting feature of the experimental results was the observation that as the initial perchlorate concentration in the systems decreased, the percent reduced within two hours increased down to a concentration of 10^{-6} M, beyond which no further improvement was noted as shown in Figure 4.3. This is suggestive of the influence of limited access of perchlorate ions to the electrode surface, which is treated more thoroughly below.
Figure 4.1 Perchlorate reduction, as measured by chloride production, as a function of time ($E = -2.0 \, \text{v}$).
Figure 4.2 Electrolytic reduction of perchlorate, $\bullet$ $5 \times 10^{-6}$ M (500 µg/L ClO$_4^-$), $\blacksquare$ $3 \times 10^{-6}$ M (300 µg/L ClO$_4^-$) ($E = -2.0$ v, sulfate = $5 \times 10^{-3}$ M (480 mg/L SO$_4^{2-}$), formate = $10^{-3}$ M (46 mg/L H$_2$CO$_2$))
PHOTOREDUCTION EXPERIMENTS

Experiments of a preliminary nature were performed in irradiated systems using TiO₂ photoelectrodes as described previously. Samples of 0.05 M sodium perchlorate (5000 mg/L ClO₄⁻) were electrolyzed at -1.75 V (versus the SCE) and pH 5.0 and compared to control samples. In addition, identical experiments were conducted with vanadium-doped titania electrodes (1 % molar ratio V/TiO₂), which results in larger conductivities of the catalyst. Results are summarized in Figure 4.4 in which the percentage of perchlorate reduced over a three-hour period is compared for the different electrode systems. As shown, the TiO₂ system yielded reduction percentages of 5-10% over the reaction period, a low amount, but substantially
in excess of systems with the same initial perchlorate concentration without irradiation. When the V/TiO₂ electrode is used, the percent reduced rose to 18% after 3 hours, and was much greater during the first two hours 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.

![Graph showing photolytic reduction of perchlorate with TiO₂ and V-doped TiO₂](image)

Figure 4.4 Photolytic reduction of perchlorate with TiO₂ and V-doped TiO₂ (E = -1.75 v, pH = 5.0)
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 titania surface sites can be considered to be in the protonated state since the zero point of charge of TiO$_2$ is 6.4 (Schindler and Gamsjager 1972). Following accepted notation for surface complexation modeling, the sorption of perchlorate, chloride, and sulfate (assuming one to one stoichiometry) at the positively charged titania surface is given by, respectively

\[ K_{\text{ClO}_4}^s = \frac{[\text{TiOH}_2^+ - \text{ClO}_4^-]}{[\text{TiOH}_2^+][\text{ClO}_4^-]} \]

(4.1)

\[ K_{\text{Cl}^-}^s = \frac{[\text{TiOH}_2^+ - \text{Cl}^-]}{[\text{TiOH}_2^+][\text{Cl}^-]} \]

(4.2)

\[ K_{\text{SO}_4}^s = \frac{[\text{TiOH}_2^+ - \text{SO}_4^{2-}]}{[\text{TiOH}_2^+][\text{SO}_4^{2-}]} \]

(4.3)

where $K^s$ refers to the respective surface adsorption constant and the "b" subscript refers to bulk solution concentrations. Mass balances on total chlorine, total sulfate, and total electrode sites are

\[ [\text{Cl}]_r = [\text{TiOH}_2^+ - \text{Cl}^-] + [\text{TiOH}_2^+ - \text{ClO}_4^-] + [\text{Cl}^-] + [\text{ClO}_4^-] \]

(4.4)

\[ [\text{SO}_4]_r = [\text{TiOH}_2^+ - \text{SO}_4^{2-}] + [\text{SO}_4^{2-}] \]

(4.5)

\[ [S]_r = [\text{TiOH}_2^+] + [\text{TiOH}_2^+ - \text{Cl}^-] + [\text{TiOH}_2^+ - \text{ClO}_4^-] + [\text{TiOH}_2^+ - \text{SO}_4^{2-}] \]

(4.6)

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

\[ -\frac{d[\text{TiOH}_2^+ - \text{ClO}_4^-]}{dt} = k[\text{TiOH}_2^+ - \text{ClO}_4^-] \]

(4.7)
The initial condition for this system corresponds to the initial distribution of perchlorate and sulfate between electrode surface and bulk solution.

Parameterization of equations 4.1 - 4.7 requires that the surface adsorption constants be supplied. No studies of perchlorate, chloride, or sulfate 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 sulfate is 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 titanium electrode. Schindler (1981) suggests a molecular site occupancy for large anions adsorbing to anatase of no greater than about 2/nm$^2$. Given an exposed electrode surface area of approximately 50 cm$^2$, reactor volume of 1 liter, and assuming a uniform coating of anatase on the electrode, this yields a site concentration of about $10^{-8}$ M.

The rate constant of equation 4.7 was estimated through comparison of solutions of equations 4.1-4.7 with the data of Figure 4.3. The best visual fit is shown in Figure 4.5 for a rate constant $6 \times 10^{-5}$ s$^{-1}$, a value within the range reported by Brown (1986) and Earley and 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 two hours of reaction time.

Given the uncertainty of the constants used in equations 4.1 - 4.7, 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 4.6 shows projections for the percentage of perchlorate reduced 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. Sulfate 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 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 4.1. Such competition exists at all electrode areas, but is less pronounced as the total area increases since the sulfate ion concentration remains constant. A practical way to increase electrode area is presented in Chapter 6.

Figure 4.5 Fit of model equations 4.1 - 4.7 with perchlorate reduction data of Figure 4.3.
Figure 4.6 Model results for calculated electrolytic perchlorate reduction after two hours at different electrode areas.
CHAPTER 5

SUMMARY AND CONCLUSIONS

The objective 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 proceeds faster at lower pH conditions, at applied potentials of -1.0 to -2.0 v, and required the presence of a background electrolyte (sodium sulfate was used in this study). Limited studies using UV-catalyzed photochemical reduction revealed positive effects, an approximate fivefold increase over electrochemical reduction at 0.05 M perchlorate (5000 mg/L ClO₄⁻), 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 percent over a two-hour 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 sulfate 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 practical application of these technologies for treatment of drinking water would require that the number of reactive sites on the electrode surface relative to the solution volume be increased by several orders of magnitude, depending on the initial concentration of perchlorate and the desired treatment efficiency. It is suggested that one approach is through the fabrication and design of reactors in which flexible plastic guides, coated with a conductor and TiO₂, are arranged in a closely packed cathode/anode array. If materials capable of transmitting light are used, such a “waveguide” array might also be used in a photocatalytic system.
Application of photochemical reduction to the treatment of residuals from another water treatment process is possible. A membrane treatment process or ion exchange process will produce a concentrated residual stream that could be partially managed by reduction of the perchlorate concentration through this process. An advantage of this is the complete destruction of the perchlorate from the residual stream.
It is clear that if electrochemical and/or photo electrochemical technologies for the reduction of the perchlorate ion in water supplies are to be viable, a way must be found to increase the available electrode surface area. One approach to this is the fabrication and incorporation of planar waveguide electrodes into a reactor system in such a manner that the total electrode surface area is increased several-fold. The waveguides consist of flexible plastic films that have been metalized for conductance, and coated with TiO$_2$ or V-doped TiO$_2$. Because of their flexibility, these materials can be configured in a variety of ways to increase electrode surface area. And because they are opaque to light, the active UV wavelengths are optically transmitted to the active sites at the electrode surface. Such waveguides are quite thin (less than 0.5 μm), both for flexibility and to allow for operation in an Attenuated Total Reflectance (ATR) mode, which significantly enlarges the film area able to be illuminated.

Each of the TiO$_2$-metalized waveguides represents a single electrode in the reactor assembly. In order to attain the surface area required, several such waveguides are arranged in a cathode/anode/cathode/anode...array with insulators placed between. Such insulators prevent short-circuiting and serve as baffles to enhance mixing of fluid that flows through the reactor. All anodes and all cathodes are connected in series to a potentiometer, which furnishes the electrical bias to the system. Illumination, if desired, can occur from UV light sources located on the exterior of the reactor and surrounded by parabolic reflectors. Figure 6.1 shows a schematic of such a design.
Figure 6.1 Suggested waveguide UV reactor for perchlorate reduction.
REFERENCES


Federal Register, March 2, 1998, 63(40).


Schilt, A.A. 1979. Perchloric Acid and Perchlorates. The G. Frederick Smith Chemical Company, Columbus, Ohio.


<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
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<tr>
<td>AWWA</td>
<td>American Water Works Association</td>
</tr>
<tr>
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</tr>
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<tr>
<td>ClO₄⁻</td>
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<td>e⁻</td>
<td>electron</td>
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<td>KNO₃</td>
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<td>L</td>
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<tr>
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