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Preparing for managing the risks associated with perchlorate in drinking water†

Edward T. Urbansky* and Michael R. Schock
United States Environmental Protection Agency (EPA)
Office of Research and Development
National Risk Management Research Laboratory
Water Supply and Water Resources Division
Treatment Technology Evaluation Branch
Cincinnati, Ohio 45268 USA

Perchlorate (ClO_4^-) contamination of ground and surfaces waters has placed drinking water supplies at risk in communities throughout the US, especially in the West. Several major assessment studies of that risk in terms of health and environmental impact are expected to be released by the EPA no later than early 1999, and preparations for how best to manage and minimize that risk are underway. Perchlorate salts are used in rocket and missile propulsion; therefore, it is believed that the pollution is derived primarily from defense and supporting industry. Because of the perchlorate anion's fundamental physical and chemical nature, the contamination is difficult to treat or remediate. The current work describes the evolution of the unique team-based governmental response to the problem and the rapidity of its development. Technologies under consideration that may prove feasible for treating contaminated water supplies are discussed and evaluated. The impact of these treatment technologies on other regulatory compliance matters and limitations of space, cost, and other resources are considered. Practical guidelines for approaching the problem are outlined, and current research needs are identified.

Keywords: perchlorate; risk management; risk assessment; drinking water; potable water; biodegradation; electroreduction; anion exchange; electrodialysis; membrane filtration; water treatment; regulatory impact; infrastructure; water utility.

Introduction

At least 11 American states have sites where perchlorate-contaminated effluents have been discharged into sewage streams or natural waters and where aquifers or waterways may be contaminated with this species. The perchlorate ion (ClO_4^-) is likely to be found in locations where perchlorate salts have ever been manufactured or used. Perchlorate salts are used as energetics boosters or solid oxidants in rockets and missiles; consequently, the source of the pollution is tied largely to the military, space program, and supporting industries. The US Air Force (USAF), National Aeronautics and Space Administration (NASA), and a host of defense contractors and perchlorate

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*Corresponding author.

salt manufacturers[1] are potentially responsible for the release and site clean-up (Fields, 1998). It is undeniable that an important way of dealing with such water pollution is to prevent it in the first place by keeping the water from contacting polluted soil or industrial waste, as might be accomplished with impermeable barriers, for instance. While such efforts must be part of overall risk management, this paper will focus only on treating water that has already been contaminated with perchlorate and making that water safe for consumption.

Much of the recent federally funded research has focused on the toxicological and ecological impact of perchlorate contamination and therefore is directed towards assessing risk, rather than managing it. The primary target organ appears to be the thyroid gland, although other effects are known (Urbansky, 1998; Von Burg, 1995, and references therein). Until a final reference dose (RfD) or a no observable adverse effects level (NOAEL) is established by the EPA National Center for Environmental Assessment (NCEA), risk management must aim for a moving target. Risk management has focused on technologies that can lower perchlorate concentrations to those levels which are undetectable by ion chromatography, *i.e.*, below 5 ng mL^{-1}. Regardless of what NOAEL is set and whether perchlorate is ever regulated,[2] water utilities in California and Nevada have expressed interest in lowering perchlorate to undetectable levels. In addition, a number of consumer interest, conservationist, and environmentalist organizations advocate setting a level of zero as the goal for treated potable water. This combined effort is driving the development of technologies that will lower perchlorate concentrations to < 5 ng mL^{-1} while ensuring that total water quality is not compromised.

Evolution of governmental response

When the analytical capabilities of ion chromatography (IC) methods had improved sufficiently that aqueous solution concentrations as low as 5 ng mL^{-1} could be measured reliably, studies by the industry and California agencies showed a number

[1]The industrial potentially responsible parties include Aerojet, Alliant Techsystems, American Pacific/Western Electrochemical Company, Atlantic Research Corporation, Kerr-McGee Chemical Corporation, Lockheed Martin, Thiokol Propulsion Group, and United Technologies Chemical Systems (Fields, 1998).

[2]The EPA Office of Water added perchlorate to the Contaminant Candidate List (CCL) as of March 2, 1998; however, it is unknown whether this will lead to the promulgation of a maximum contaminant level (MCL) for potable water (EPA, 1998a).

of contaminated aquifers, wells, and surface waterways. The EPA Region 9 office[3] was already aware of some of these sites on account of other contaminants, such as volatile organic compounds. Shortly thereafter, the EPA National Exposure Research Laboratory became involved in a search for confirmatory techniques and methods of chemical analysis. At the same time, the USAF and Air Force Research Laboratories were refining IC work and considering what studies might be necessary.

In the meantime, a perchlorate issue group was assembled by local utilities[4] to examine the problem. It issued a report proposing certain strategies and identifying several areas of research need, based on information available at the time. Subsequently, Congress appropriated $2 million to one of these utilities (EVWD) to begin to carry out appropriate studies. Because the health effects and ecotoxicology of perchlorate had been only minimally explored, a group of scientists was convened to propose and rank the studies necessary to accurately assess the risks associated with perchlorate in the environment. At present, eight separate investigations have been conducted (funded by the USAF and guided by NCEA), and results are anticipated to be released in late 1998 or early 1999 after completion of the external peer review (EPA, 1998a; Fields, 1998). Since fall 1997, there has been a sense of urgency associated with this process, and the timeframe for the risk assessment has been unprecedented for the EPA (Farland, 1998).

A case study in cooperation

There are two particularly unique qualities to the process that has followed the discovery of this pollutant. First and foremost has been the team approach. There has been a strongly interactive, cooperative spirit among the agencies and employees involved. The formation of the Interagency Perchlorate Steering Committee (IPSC) with representatives from throughout the federal government (see Table 1) is an unprecedented development in the history of dealing with water pollution. Although statutory obligations require that agencies maintain budgetary and adminstrative control over their respective domains, the interaction has proved invaluable in ensuring the rapid dissemination of information and the up-front consideration of alternate (and sometimes conflicting) requirements. By involving interested parties from the start, it has ensured that all concerns and obligations have been met, and it

[3]Region 9 includes the states of California, Nevada, Arizona, and Hawaii and the protectorates of American Samoa and Guam.

[4]The utilities were the East Valley Water District, Main San Gabriel Watermaster, Metropolitan Water District of Southern California, San Bernardino Valley Municipal Water District, and Southern Nevada Water Authority.

has minimized last minute objections to recommendations and conclusions. It is worth pointing out that the formalization of the IPSC was a gradual evolution as more agencies became involved and roles took shape; it was not a directive from senior management. Initially, it began as a combined effort among the staffs of various agencies to find out how much was known, who was doing what, and what should be done next. By early 1998, it had become clear that there was in fact a fairly well-defined team with similar goals and a commitment to accomplishing them.

The IPSC has thus far proven itself to be a model for attacking future pollution problems. IPSC meetings have remained open; PRPs, government and university researchers, private organizations, industry and corporate representatives, and state and local agencies have all been free to address the full committee or to inquire about the status of projects or action items. Professionals from a wide variety of backgrounds and expertise were brought in at the beginning, including risk management (water treatment and remediation) and exposure (chemical analysis and occurrence) among others. This has helped to balance the vision as opposed to the more traditional linear approach in terms of completing detailed risk assessment (health effects), then developing analytical methods and determining occurrence, and finally managing risks.

The second unique quality has been the extremely rapid progression of events. This has been made possible only through concurrent work in several fields. Of course, this could not have been done without the integrated approach and inclusion of so many people up front. Since the discovery of the expanding low-level perchlorate plumes in late 1996, a network of perchlorate manufacturers, consumers, researchers, and regulators has been established. The risk assessment is nearly complete. There is a large body of analytical chemistry data to draw on, and interlaboratory method validation is well on its way. Sites likely to be contaminated have been identified, and there is a fairly comprehensive body of data on occurrence throughout the nation. Initial strategies for risk management have been identified, and pilot scale tests are underway for some technologies. Because information has been shared from the start, the regulatory community is prepared to receive the risk assessment and is familiar with technologies available for risk management. Of course, refinement and eventual implementation of risk management technologies for water treatment and site remediation will require the risk assessment results expected in early 1999.

Physical and chemical properties of perchlorate

The chemistry of perchlorate was reviewed in-depth in a previous paper (Urbansky, 1998). Nevertheless, several key points necessary for understanding risk management strategies bear repeating here. The perchlorate ion (ClO_4^-) is the most oxidized form of chlorine that can exist in water. It is a strong oxidizing agent (oxidation state +7).

When reduced to chloride in acidic solution it has a standard reduction potential of 1.29 V (Emsley, 1989), making it a stronger oxidant than oxygen, but not so strong as dichromate.

$$ClO_4^- + 8e^- + 8H^+ \rightarrow Cl^- + 4H_2O \qquad E^\circ = 1.29\ V \qquad (1)$$

When dilute (< 10% w/w) or in weakly acidic to basic (pH > 1) aqueous solution, perchlorate is so nonlabile as an oxidizing agent—*i.e.*, it reacts so slowly—with most reducing agents that no reaction is observable (Schilt, 1979). Only extremely reactive air-sensitive transition metal species show any observable redox reaction, making perchlorate famous for its lack of lability (Urbansky, 1998). This behavior results from the high strength of the chlorine-oxygen bonds and the requirement that reduction must proceed initially by oxygen atom abstraction rather than a direct involvement of the central chlorine atom. This kinetic behavior is illustrated in Figure 1. The abscissa marks the progression of a reaction between a perchlorate ion and a general reducing agent R, capable of accepting an oxygen atom. The conversion to chlorate shown in equation 2 is generally regarded as the first step in perchlorate reduction.

$$ClO_4^- + R \rightarrow ClO_3^- + RO \qquad (2)$$

The reaction is thermodynamically favored as shown by $\Delta E < 0$, *i.e.*, the products have lower internal energy than the reactants. Nonetheless, the reaction rate is controlled by the kinetic barrier of the high activation energy E_a of the transition state, the location of which is marked by the diesis (‡). Subsequent steps in the process are much less kinetically hindered.

Available treatment technologies

Ideally, a technology should be able to handle concentrations ranging from ≤ 5 ng mL^{-1} (μg L^{-1}) all the way to ~10 mg mL^{-1} (g L^{-1}). Most of the affected regions have perchlorate concentrations below 0.5 mg mL^{-1}; however, concentrations as high as 3.7 mg mL^{-1} have been encountered. The Colorado River and several California wells show concentrations in the range of 8-30 ng mL^{-1} (μg L^{-1}). Current technologies can be divided into two primary categories: destruction and removal. Destruction is generally regarded as a preferable process because it eliminates the need for subsequent disposal of removed material, which is regarded as a hazard in this case. Each of the techniques is described briefly, and the strengths and weaknesses of these technologies are summarized in Table 2. Regulatory and other impacts some of these techniques will be addressed or expanded upon in a later section.

Chemically destructive processes

Because perchlorate does not exhibit its oxidizing properties under the conditions found in contaminated raw and treated waters, it cannot be reduced with common agents, such as thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}), or elemental metals (*e.g.*, Fe, Zn, Cu). To be a candidate for consideration in drinking water treatment, a technique must demonstrate that it can overcome the high activation energy associated with perchlorate reduction. The speed of the rate limiting step (such as that shown in equation 2) must be increased.

Biological reduction

At the present time, biological reduction appears to hold the most promise for large scale treatment of perchlorate-laden waters. Several genera of microorganisms are capable of using perchlorate as an oxidant (electron acceptor) for metabolism (Logan, 1998; Urbansky, 1998). It is generally accepted that these microbes possess a reductase (an enzyme) that allows them to lower the activation energy of perchlorate reduction and thereby make use of the energy for cellular respiration. In addition, they appear to make use of a chlorite (ClO_2^-) dismutase, which allows direct conversion of chlorite to chloride and water, without formation of cytotoxic hypochlorous acid (HOCl).

Unfortunately, some of these organisms cause disease and/or prefer oxygen. When incoming water contains a significant concentration of dissolved oxygen, a large amount of reductant (food) may be consumed by the organisms without any reduction of perchlorate. Pathogenic organisms are likely to be excluded for obvious reasons; even if the water is subsequently subjected to disinfection, it seems ill-advised to intentionally introduce a pathogenic organism. The USAF and an engineering firm operating in Region 9, Harding Lawson Associates, have developed bioreactors based on organisms found in sludges; only the Air Force has isolated and identified the microbe (Urbansky, 1998). The fluidized bed biological reactor (FBBR) is a popular apparatus for biodegradative treatment. Shown in Figure 2, the usually funnel-shaped FBBR makes use of an inert support medium (*e.g.*, granular carbon) on which microbiota are grown. The FBBR's shape results in high influent water velocity, so that the water suspends the medium. As the FBBR widens towards the top, the water velocity is insufficient to suspend the medium, which settles out. This eliminates the need for a filter to retain the bioactive medium. Smith and Stewart (1998) constructed an FBBR using Celite® as the support; they inoculated their reactor with sludge from an anerobic municipal waste digester and fed the microbes cheese whey. Their FBBR reduced perchlorate concentrations from 1.3 $\mu g\ mL^{-1}$ in the influent to $\leq 5\ ng\ mL^{-1}$ in the effluent.

Electrochemical reduction

It is possible to reduce perchlorate to chloride using an electric current applied directly to the water by a cathode at high potential. A number of different materials have been used as cathodes, including platinum, tungsten carbide, ruthenium, titanium, aluminum, and carbon doped with chromium(III) oxide or aluminum oxide (Urbansky, 1998). There are several problems with electroreduction, most notably, the time required to get ions to the electrode surface from the bulk water as well as the time required for them to associate with the surface. Electrode corrosion, surface passivation, and natural organic matter (NOM) adsorption to the surface present technological difficulties. Skillful design could likely overcome at least some these, however. While this technology is well-established for such industrial processes as metal electroplating or brine electrolysis, it has not yet been implemented in the potable water industry, probably because there has never been any real need. Figure 3 shows the expected oxidation and reduction half-reactions for a simple electrolytic cell. An actual electrolytic cell used for this process would more reasonably be modeled on a diaphragm cell used for brine electrolysis.

Physical removal

Physical removal processes work exactly as the name suggests; they physically separate the perchlorate ion from the drinking water. Because these techniques do not destroy the perchlorate, they create a subsequent need for disposal of both the perchlorate and any waste products of the process. In addition, all of these techniques currently suffer from a lack of selectivity. Along with the perchlorate, they tend to remove or replace unacceptably large quantities of beneficial dissolved salts or their component parts. Deionized water presents a corrosion and disinfection problem for distribution systems, resulting in aesthetic degradation of the water, and potentially detrimental health effects by increased mobilization of toxic trace metals (*e.g.*, lead). Although these technologies are all well-established, they will be difficult to use in large systems, and their use is limited even in small water systems by pre-treatment and post-treatment factors.

Anion exchange

With this technique, perchlorate is replaced by an innocuous anion, usually chloride. Water flows through a resin that contains a high concentration of this replacement ion. Because of the relative concentration difference of the two ions in the resin, the perchlorate switches places with the other ion, which is now released into the water (see Figure 4). Eventually, the resin reaches an equilibrium concentration where no more perchlorate can be extracted from the water; at that point, the resin must be regenerated. The used regenerant solution contains a high concentration of perchlorate

and must be disposed of properly. While some highly selective resins have been developed, these are expensive and not commercially available. Those resins which are commercially available at this time are not sufficiently selective for perchlorate. On account of their relative concentrations, harmless and even desirable anions[5] can be preferentially replaced over perchlorate. Consequently, the resin's chloride supply is rapidly depleted, and the water may be transformed into one having highly undesirable chemical characteristics (particularly corrosiveness), as well as unpleasant taste. The US Department of Energy has developed an anion exchange resin and concommitant process for rapid removal of pertechnetate ($^{99m}TcO_4^-$), a poorly aquated ion (a category into which perchlorate also fits), with minimal retention of strongly aquated ones[5] (Brown, 1998).

Membrane filtration

This includes such techniques as reverse osmosis (RO) and nanofiltration. Water is forced through a semiporous polymer membrane; meanwhile, dissolved salts are unable to penetrate the membrane (Figure 5). Membrane permeability towards different anions and cations can be adjusted in manufacture to some degree; however, the filtrate (or permeate) is nearly always a relatively deionized water. The concentrate contains all rejected dissolved matter, including the perchlorate. Membrane fouling by alkaline earth and transition metal compounds can present a problem, depending on their concentrations in the water. Additionally, high concentrations of NOM and certain microbiota can irreversibly foul or damage the membrane material, necessitating complete replacement. Work at the Metropolitan Water District of Southern California (Liang *et al.*, 1998) showed that nanofiltration and RO membranes were capable of removing 80% or more of the perchlorate, but it did not measure the rejection of other dissolved salts.

Electrodialysis

In electrodialysis, water is passed through channels of alternating membranes permeable to either anions or cations, all the while being exposed to an electric field (see Figure 6). This produces alternate channels of nearly deionized water (the diluate or dialyzate) and salty water (the concentrate). The diluate is used, and the concentrate is discarded.

[5]The list of harmless or beneficial anions that are found in natural in water sources includes, but is not limited to, the following: monohydrogen carbonate (bicarbonate), HCO_3^-; carbonate, CO_3^{2-}; dihydrogen *ortho*-phosphate, $H_2PO_4^-$; hydrogen *ortho*-phosphate, HPO_4^{2-}; and sulfate, SO_4^{2-}. All of these are highly aquated, *i.e.*, strongly associated with water molecules.

Regulatory and engineering constraints

The regulatory balancing act

The drinking water quality regulatory structure in the United States is organized around specifying either a permissible level maximum as an MCL or a treatment technique (EPA, 1994). This approach is similar to that practiced by many other countries or international organizations. If the decision is made to regulate perchlorate in the United States by the promulgation of an MCL, the identification of *best available technologies* (BATs) may be undertaken, consistent with the approach of other regulations governing some specific contaminants (EPA, 1980). Historically, these determinations have focused only on individual contaminants of interest. While some determination of treatment cost was included, the costs rarely adequately reflected pre- and post-treatment costs to adjust to needs of other regulations in force, and the specific construction or adaptation needed for each treatment plant. The new Safe Drinking Water Act Amendments of 1996 (P.L. 104-82) sought to balance the burden of high cost and sophistication of treatments for smaller water systems (serving under 10,000 persons) with allowances for the use of *variance* technologies under special different approval conditions. These result when no affordable technology can be found that will meet an MCL, but a technology or treatment system can be employed which will achieve the maximum affordable reduction given the size of the system and quality of the source water (EPA, 1997). The terms of the variance agreement by the primacy agent (*i.e.*, state or federal government) must assure adequate protection of human health. This new approach could be applicable to the problem with regulating perchlorate.

The treatment technique approach has been followed in the notable cases of the US regulations for lead and copper (EPA, 1991a, 1991b, 1992, 1994b, 1998b, 1998c), and newer or upcoming regulations covering DBPs and microbes such as *Cryptosporidium*. This approach has generally been selected either when the reduction of the contaminant to the human health effects goal may not be achievable with conscientious application of the best known process technologies available to water utilities (*e.g.*, the case with lead from household plumbing), or when the direct quantitative measurement of the contaminant is not possible at a level assuring adequate safety (*e.g.*, *Cryptosporidium* and some other pathogenic microbes). This could become a viable approach for perchlorate regulation, and the pros and cons of treatment technique versus the MCL approach must be seriously debated.

Whatever the regulatory target for perchlorate becomes, the challenge to the drinking water system will be to develop an integrated treatment process that will result in successfully meeting all existing state or federal drinking water quality regulations. Because many other regulations of serious health consequences will

already be in place [*e.g.*, lead, copper, disinfection byproducts (DBPs), microbial contaminants, other inorganics, or synthetic organics], much discretion is lost in optimizing treatment purely for perchlorate reduction or removal.

The current schedule for new regulations in the US is as follows: (1) disinfectants and disinfection byproducts (D/DBP) rule—stage 1, November 1998; stage 2, May 2002; (2) enhanced surface water treatment rule (ESWTR)—final interim rule, November 1998; final long-term ESWTR, November 2000; (3) groundwater disinfection rule (GWDR)—final rule, January 2001; (4) arsenic—final rule, January 2001; (5) radionuclides other than radon—reproposed rules for uranium and radium by December 2000.

Producing acceptable drinking water full-scale

The lead and copper rule poses some of the most severe constraints to practical full-scale removal of perchlorate. Two of the most readily usable technologies, anion exchange and membrane filtration, can be expected to produce water that is corrosive towards plumbing materials. Solubilization of pipe metals can adversely affect both health and major distribution system materials such as unlined cast or ductile iron, and cement-based materials (AWWARF, 1990, 1996). Membrane permeates are frequently low in pH relative to that essential for protection against the release of lead and copper. The aggressive nature of high concentrations of chloride ion towards iron and copper, for instance, has been well-documented by corrosion studies going back 40 or more years (AWWARF, 1996). The excessive removal of bicarbonate would result in the loss of buffering ability to control the pH to non-corrosive levels, and would remove an essential component of many passivating films on metallic and cementitious piping materials (AWWARF, 1996), as would excessive loss of calcium hardness. Attack on unlined iron pipe, a ubiquitous material in many American water distribution systems, can result in the premature loss of disinfectant residual, dislodging of existing pipe scales that might have microorganisms entrained within or adsorbed upon them, and increases in pH from cement leaching. Thus, water quality can be degraded by iron corrosion, increased turbidity, poor taste, and reduction in disinfection effectiveness. Corrosion control treatment provides many benefits to distribution system water quality beyond reduced lead and copper levels (Schock, 1998). When a water system has conducted monitoring for lead and copper, and has optimized treatment based on historical or recently-improved corrosion control, major changes in water chemistry brought about by the installation of perchlorate treatment could have serious adverse health or distribution system water quality impacts.

Not all regulatory interactions are necessarily negative. Water systems that have problems with current and future regulated contaminants such as DBP formation, arsenic, nitrate, or with the potential for microbial contamination, may find it necessary to employ enhanced membrane filtration or other processes that could also reduce perchlorate levels. In these cases, re-optimization of corrosion control for lead and

copper would be necessary in the regulatory framework anyway, and the perchlorate removal would not be the only factor driving up the cost and complexity of treatment.

It must be emphasized that the output capacity of a water purification plant is one of the most important factors in determining which techniques are suited for perchlorate treatment. In addition, physical space and other resources play an important role in making this decision. Likewise, influent water quality also bears on this choice. If the raw water has an extremely high level of alkaline earth metal cations (*e.g.*, Ca^{2+} or Mg^{2+}), membrane filtration will not be directly applicable since fouling will occur. Other obvious considerations include downtime for systems requiring regeneration, operational maintenance, operational staffing, staff certification, operational cost, electricity consumption, selectivity, and speed. We have attempted to rank these techniques in terms of applicability to different size systems in Table 3, which provides a starting point for evaluating the reasonableness of using any one technique or combination of techniques in a given size system.

Caution must also be exercised in the selection of perchlorate removal technologies, lest the problem merely be shifted from one environmental "compartment" to another. Waste products from removal or destruction processes may be covered by a variety of regulations that do not relate to drinking water quality, and which may not necessarily be under the economic control or regulatory attention of the drinking water production utility. Additional complexity is introduced when different private companies or public governmental agencies are responsible for source water management and production, drinking water treatment, wastewater treatment and discharge, and the disposal of process solids materials (such as waste treatment sludges).

In particular, the key drawback of physical removal is that something must be done with the removed perchlorate. When these techniques are applied in a home or point-of-use (POU) membrane filtration or electrodialysis system, there is little concern as long as the raw influent water does not exceed the permitted perchlorate discharge limits. The filtrate/dialysate and concentrate are essentially recombined in the sewage stream since nearly all the water that goes into a house goes down the drain. Accordingly, there is no net increase in perchlorate concentration in the sewage over the raw water. However, in large or intermediate systems, the local discharge of concentrate into a sewage system could have a disastrous impact on the local ecology. In rural areas served by a central water utility, there may not be a central sewage treatment system, but individual septic tanks or cesspools instead; consequently, there would be no recombining of the concentrate and filtrate streams.

Combining technologies

It is important to point out that the technologies described above are not necessarily mutually exclusive in application. It is possible to physically separate perchlorate by

membrane filtration and to subject the concentrate to subsequent biodegradation. Or it is possible to remove perchlorate by anion exchange and then subject the spent regenerant to electrochemical reduction. The decision to combine techniques must be made after careful consideration of total water quality management, including the fundamental characteristics of the influent water. In many cases, the best approach may be a combination. This can especially benefit a facility that has sufficient space to install ion exchange columns, and who may, for example, hire a contractor to regenerate them offsite. Development of an inexpensive, highly selective anion exchange resin could substantially alter the applicability and attractiveness of this technique.

Areas requiring research

While a number of investigators are currently working on bioreduction, studies are needed to identify and characterize more of the microorganisms that reduce perchlorate so as to optimize conditions for maximal destruction while minimizing byproduct formation, wasteful side-reactions, and nutrient consumption. Presumably, several transition metal complexes act in key roles in the reduction process as active sites in reductases or dismutases. Nevertheless, it is impossible to know if the raw water provides a sufficient supply of essential minerals and trace metals since neither the waters nor the organisms are well-characterized at this time. Similarly, it is impossible to gauge the ongoing health and reliability of a bioreactor without well-defined, measurable properties of the active microbe populations. Ideally, some studies should be directed towards genetically engineering and selecting for bacteria that preferentially consume perchlorate over oxygen as a terminal oxidant (electron acceptor).

Biological degradation is already in use by the USAF for wastewater treatment. Before it can move to the arena of drinking water, it will have to demonstrate itself as a safe and cost-effective tool. There are presently too many unanswered questions about the organisms involved in the process to meet the regulatory needs of safe drinking water.

More effort must be expended in elucidating the mechanism by which microbes reduce perchlorate, including the isolation, purification, and characterization of the active enzyme(s). It may be possible to exploit the mechanism whereby the bacteria are capable of overcoming the activation barrier, but only if we have a better understanding of that mechanism. Along these lines, chemical reduction may become an option if suitable—that is, labile, nontoxic, convenient, inexpensive—reductants are found.

Electrochemical reduction experiments reported in the literature have remained at the bench scale. Additional bench (beaker) scale, intermediate (bucket) scale, and pilot (barrel and tank) scale experiments are needed to determine what electrodes can be practically constructed with cost constraints and how thoughtful designs to maximize surface area might be effectively used to obviate problems such as slow ion diffusion to the cathode surface and poor association with the surface. It will be necessary to explore means of minimizing corrosion, surface deactivation, and undesirable competing redox reactions (*e.g.*, the electrolysis of water and sodium chloride) under drinking water conditions. If electrolysis of sodium chloride cannot be prevented, it will be necessary to recombine the NaOH with the Cl_2; this could ultimately have some use in disinfection. Since pipe corrosion will be substantially influenced by other water components (*i.e.*, pH; alkalinity; NOM, metal, and salt content), a thorough characterization of influent water will also be essential, and the effects of influent water quality on the electroreduction process must be considered.

The development of inexpensive and highly selective resins for anion exchange should be pursued. While there are some nitrate-selective resins, this technology will require further refinement before it can be applied to perchlorate because of the much higher concentration permissible and the much lower concentration of perchlorate in the raw water in most cases. Similarly, since the semipermeable membranes of electrodialysis are based on ion exchange technology, they too will benefit from projects in this area. Integrating these or other systems into existing treatment schemes for utilities processing large volumes of water daily needs extensive pilot-scale or demonstration work, with careful attention paid to the net benefits relative to the total costs.

Because some techniques, such as electrodialysis or reverse osmosis, can be expected to dominate the home or POU system market, the development of standards for perchlorate removal by commercially available units will be essential. This could logically be done as an extension of the voluntary performance-based standards for POU devices that already exist under American National Standards Institute/National Sanitation Foundation (ANSI/NSF) standards for drinking water treatment units and related products.[6]

Little is known about the natural occurrence of perchlorate. It is not a significant component of seawater, but deposits are found in Chilean potassium nitrate (Chile saltpeter) (Schilt, 1979). Given the celerity with which perchlorate-reducing microbes

[6]Relevant voluntary standards for certification of unit performance developed by NSF International, Ann Arbor, Michigan, include ANSI/NSF Standard 53 (Drinking Water Treatment Units, Health Effects), ANSI/NSF Standard 58 (Reverse Osmosis Drinking Water Treatment Systems) and ANSI/NS F Standard 62 (Drinking Water Distillation Systems).

seem to appear in FBBRs inoculated with sludge, one can only conclude that these organisms evolved naturally from exposure or have a serendipitous advantage in their ability to metabolize this ion. Since the former seems more reasonable than the latter, natural sources of perchlorate must be in the environment. Additional investigation into naturally occurring mechanisms for the generation of perchlorate would be helpful in ascertaining whether only anthropogenic sources are significant contributors to pollution. Moreover, further knowledge of natural background occurrence levels is required. If it can be shown that perchlorate is produced naturally in the environment and yet levels are very low, we must conclude that natural attenuation is responsible for the apparent dichotomy. At present, little is known about the ability of normal flora and fauna (macro- or microscopic) to consume perchlorate, regardless of the source. However, the confirmed existence of several genera of perchlorate-reducing monera in the laboratory suggests that some organisms are already present in the environment. Because of its aridity, the western US is not a choice place for discovering these organisms; however, they may play a significant role in moister regions of the country. This remains largely unknown.

Although ammonium perchlorate appears to have been the original source for most of the perchlorate in the environment, we do not know what cation is presently responsible for the charge balance. Because ammonium is readily biodegraded and has not been identified at many sites, there is speculation that it has been replaced primarily by sodium. While this is not an unreasonable assertion *per se*, one can view ammonium perchlorate as ammonia and perchloric acid. If the ammonia alone is biodegraded naturally, then remaining cation is a proton (hydrogen ion). Since perchloric acid is a strong acid, whatever basic anhydrides (of alkaline earth, transition, or other metals in low oxidation states) are present in the soil will react to form the respective metal perchlorate salts. Thus, the composition of the surrounding soil and rock will determine what cations are present

Managing risk: other issues for researchers, utilities, policy makers, and regulators

As of the writing of this paper, the EPA had not established a formal policy for the risk management of perchlorate-tainted water, and we do not intend to propose one here. Nevertheless, we shall raise a number of questions that apply to risk management decisions and that will have to be considered in formulating policy or regulations at any level—federal, state, or local. In addition, it will be up to regulators and policy makers to address these issues (and probably others) when facing the public that consumes the water, the utilities that treat and produce the water, and anyone else with an interest.

Among some consumer groups and even some water purveyors, there is a growing desire to reduce perchlorate concentrations to undetectable levels (< 4 ng mL^{-1}) with public health as the concern. Suppose the established safe level[7] is higher than the detection limit (the provisional action level is 18 ng mL^{-1}). Is there then any benefit in treating water to reach perchlorate concentrations below the safe level? Corrosion of the distribution system or other similar engineering matters do not appear to apply, so seemingly there are no secondary benefits to reducing the perchlorate concentration below the safe level. If there is no public health benefit, is there any other reason to do it? If the benefit is peace of mind, what cost is appropriate? Depending on the answers to these questions, many water supplies may require no treatment at all.

How does the risk from perchlorate compare with other public health risks in drinking water? Are financial resources better devoted to other problems in potable water production systems? Whatever treatment technologies are eventually employed must be based on sound scientific reasoning, bearing in mind that there will always be multiple viewpoints of varying intensity. In terms of economic resources, how can the opportunity cost of treatment be justified?

Besides the treatment technologies described here, which involve directly modifying contaminated water, other options may be available at a particular location. For example, can a contaminated water be blended with a "clean" water? For those utilities that have the luxury of drawing from multiple water sources, diluting a water that exceeds the safe level with a water containing less perchlorate is a conceivable option.

[7]Rather than choose a particular legal definition of what is a safe level for drinking water, *e.g.*, NOAEL or MCL, we shall use the generic term *safe level* without further elaboration, realizing that various public health, regulatory, and environmental authorities view this differently. When we use this term, we mean a level that has been established by government authority and that ensures the protection of public health.

As long as blending would not substantially change the background constituent concentrations, no new corrosion control studies would be needed (EPA, 1991a, 1991b, 1992, 1994b, 1998b, 1998c).

If a health advisory is eventually issued by the EPA Office of Water, primacy agents will have to ask: What other factors besides the concentration of perchlorate in the drinking water determine what is safe?

Perchlorate exerts its effect not by reacting with something, but by impeding another process. Cells in the thyroid gland (as well as the salivary and gastric glands), possess an iodide pump which brings iodide ions into the cell for subsequent generation of iodinated hormones. The pump discriminates among anions on the basis of size; consequently, perchlorate (and other large anions) interfere with this process by competing for uptake (Capen, 1994; Chiovato *et al.*, 1997; Cooper, 1991; Foye, 1989; Orgiassi, 1990). Presumably, the only adverse effects of perchlorate in drinking water would be derived from its direct hindrance of the synthesis of thyroid hormones or secondary effects resulting from decreased output of those hormones. As a result of decreased thyroid hormone production, the pituitary gland releases more thyroid-stimulating hormone (TSH), causing the thyroid to grow. In rodents, continued exposure to chemicals that bring about this effect has been shown to lead to the development of neoplasias or adenomas (Capen, 1994). At present, we do not know whether the perchlorate concentrations in drinking water are capable of producing similar effects in humans.

The medical literature has anecdotal reports of toxicity (especially aplastic anemia) from chemotherapeutic use in treating thyroid problems (Hobson, 1961; Johnson and Moore, 1961). Despite these reports, potassium perchlorate ($KClO_4$) has been successfully and safely used to treat thyrotoxicosis induced by the cardiac drug amiodarone, which is used to treat arrhythmias; daily doses of 0.80-1.00 g $KClO_4$ have resulted in neither aplastic anemia nor nephrotoxicity as the earlier reports suggested (Connell, 1981; Martino, E. *et al.*, 1986; Martino, E. *et al.*, 1987; Harjai, K.J. *et al.*, 1997). A review of the toxicology literature by Von Burg (1995) found that there is *currently* no evidence to suggest that perchlorate, when ingested at daily doses of less than 1 mg, will have any non-thyroid impact. A recent study by Lamm *et al.* (1998) found that workers in an ammonium perchlorate manufacturing plant suffered no thyroid effects from inhalation of NH_4ClO_4 dust and that perchlorate was readily egested by glomerulonephrofiltration.

Although we do not want to disproportionately emphasize them, several questions remain: Are there likely to be any effects, especially with chronic low-level exposure over a lifetime (rather than acute exposure)? Does the water contain any other thyroid-interfering agents? Are there any potentiators or synergistic agents in a water supply that could make the effects worse? Even if the answer to all three questions is *not likely*

or *probably not*, should an additional safety net be built into a regulatory or risk management position?

Because of the competition between iodide and perchlorate, it is clear that the safe level must be influenced by the daily dietary intake of iodide salts. Increased use of iodine-containing compounds antiseptics, nonprescription drugs, and foodstuffs has raised the US daily intake to ~ 0.50-0.75 mg of iodide, and it may be as high as 1.0 mg, up from 0.2 mg 10-15 years ago (Wartofsky, 1998; Andreoli, *et al.*, 1997). Meanwhile, the US Department of Agriculture recommended dietary allowance (RDA) is 0.20 mg per day for a lactating woman and 0.15 mg for a 170 lb (77 kg) adult man; thus, the average American ingests ~ 2-5 times the RDA (USDA, 1998; Andreoli, *et al.*, 1997). The safe level set overall must assume some average iodide intake for this purpose, which may not be representative of the iodide consumption for a particular region. As the dietary consumption of iodide increases, the competition at the iodide pump is lessened. Accordingly, is it possible that some regional populations might be afforded a level of protection because of a diet naturally high in iodide?

We are familiar with the use of iodized salt when local soils are too deficient to produce crops that supply the daily iodide requirement. Iodide supplements are cheap and readily available. Therefore, is it possible to counter the effects of perchlorate simply by supplementing the diet with more iodide? Iodide supplementation of up to 0.50 mg/day has shown no effect on thyroid function; consumption of 40-150 mg/day for 1-3 weeks produced observable changes in hormone levels, but these nonetheless remained within normal physiological ranges (Roti and Vagenakis, 1996). Although initial dosing inhibits iodine organification (the Wolff-Chaikoff effect), continued administration of iodide results in escape from this inhibition (Nagataki and Yokoyama, 1996). Does managing the risk associated with perchlorate-contaminated drinking water necessarily imply treating the water or can other public health measures be viable solutions?[8]

There are no simple or straightforward answers to the questions posed, and each community, utility, or regulatory body will need to wrestle with these questions as they work towards specific solutions to meet specific needs. What works for Las Vegas, Nevada, might not work for Magna, Utah, and vice versa. As with most environmental problems, dealing with perchlorate contamination is complex; each medium (drinking water, wastewater, land, etc.) has its own subset of issues. There is unlikely to be any best solution for any set of circumstances, but rather a compromise of competing strategies for meeting competing needs. Maintaining a reasonable "big-picture"

[8]We want to stress that neither the EPA nor the authors advocate the administration or consumption of iodide supplements as a preventive or curative measure without medical supervision. Nevertheless, we do consider it to be an area worthy of investigation and exploration.

perspective is one of the most important things that researchers, policy makers, and regulators alike can do.

Authors' note: Perchloric acid and perchlorate salts have a rich history in industry, science, medicine, space exploration, and defense. They function as inert electrolytes in chemical studies, catalysts in industrial and synthetic processes, and boosters or solid oxidants in rockets and missiles. They are too valuable to give up, and so we must find safe ways to accommodate their use.

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Table 1. Principal agencies involved in cooperative planning and discussion over how to handle perchlorate pollution[a]

US military and space programs

- US Air Force (USAF) and Air Force Research Laboratories (AFRL)
- US Army
- US Navy
- National Aeronautics and Space Administration (NASA)

US Environmental Protection Agency

- Office of Research and Development (ORD)
  - National Center for Environmental Assessment (NCEA)
  - National Risk Management Research Laboratory (NRMRL)
  - National Exposure Research Laboratory (NERL)
  - National Health and Environmental Effects Research Laboratory (NHEERL)
- Region 6 office [b]
- Region 9 office [c]
- Office of Solid Waste and Emergency Response (OSWER)
  - Office of Emergency and Remedial Response (OERR)
- Office of Water (OW)
- Office of Science Policy (OSP)

Sundry US federal research agencies

- National Institute of Environmental and Health Sciences (NIEHS)
- Oak Ridge National Laboratory (ORNL)
- Lawrence Livermore National Laboratory (LLNL)
- Agency for Toxic Substances and Disease Registry (ATSDR)
- National Institute for Environmental and Health Sciences (NIEHS)
- US Geological Survey (USGS)

State agencies

- Utah Department of Environmental Quality
- Utah Department of Health Laboratories
- Nevada Division of Environmental Protection
- California Department of Health Services
- Arizona Department of Environmental Quality

Local authorities

- East Valley Water District
- Main San Gabriel Watermaster
- Metropolitan Water District of Southern California
- San Bernardino Valley Municipal Water District
- Southern Nevada Water Authority
- Las Vegas Valley Water District

[a]Many agencies have been involved along the way, including state and county health or environmental protection departments or public utilities; however, the agencies listed here have been responsible for and continue to guide this effort. Some of the agencies listed in this table have been involved primarily in technical or scientific consulting roles. Note that the IPSC is comprised only of US federal agencies. [b]Region 6 includes the states of Arkansas, Louisiana, New Mexico, Oklahoma, and Texas. [c]See footnote 3.

Table 2. Pros and cons of currently available drinking water treatment technologies

Technique	Pros	Cons
Biological reduction	Selective Fairly rugged Fairly fast Other contaminants also destroyed Low operating cost	Unknown pathogenesis Food source needed O_2 competition Unknown byproducts Moderate/high monitoring and maintenance Insufficiently developed at this time Difficult to implement in existing facilities with high output
Electro-reduction	No waste products Low maintenance	Electricity consumption/high operating cost Worker safety Difficult to implement in existing facilities with high output Insufficiently developed at this time
Anion exchange	Easily implemented Moderate maintenance Fairly inexpensive Existing technology	Regeneration/down time Hard to make selective Waste disposal (from regeneration)
Membrane filtration	Existing technology Highly effective Fast Ideal for point-of-use	Maintenance Membrane corruption Concentrate disposal Not selective
Electro-dialysis	Existing technology Highly effective Fast Ideal for point-of-use	Electricity consumption/moderate operating cost Membrane corruption Concentrate disposal Not very selective at this time

Table 3. Applicability of treatment technologies to different size systems

	Large[a]	Medium[b]	Small[c]	Home[d]
Biodegradation	✔	✔		
Electroreduction	✔	✔		
Anion exchange			✔	✔
Membrane filtration			✔	✔
Electrodialysis			✔	?
Combination[e]	✔	✔	✔	

[a]Large refers to systems serving >10,000 persons, for example, metropolitan municipal systems. [b]Medium refers to systems serving ~1000–10,000 persons, such as a rural township or county system. [c]Small refers to systems serving a population in the hundreds, such as a village, corporate facility, or residential subdivision. [d]Home refers to systems serving under 20 people, including all point-of-use devices. [e]Combination refers to two or more of the other techniques used together; see text for further explanation.

Figure Captions

1. Energy profile for the rate-limiting step in perchlorate reduction (equation 2), abstraction of the first oxygen atom. The kinetic barrier is the result of the high activation energy, E_a, despite the fact that the reaction is driven forwards by the release of energy, *i.e.*, $\Delta E < 0$.

2. Fluidized bed biological reactor (FBBR). Untreated water enters the bottom with high velocity, which allows it to support the bed of supporting medium (which the microbial population grows on). Due to the shape of the FBBR, the water loses velocity with altitude, and the medium settles out before the effluent is discharged. Although not shown in the diagram, FBBRs are often constructed with a recycle loop that increases the residence time of the water.

3. Simple electrolytic cell for the reduction of perchlorate. Electrons are applied directly to the perchlorate at the cathode, which is maintained at high electrical potential (voltage). The reduction half-reaction must be accompanied by an oxidation half-reaction, and the electrolysis of water is the most likely to occur.

4. Mechanism of anion exchange—chloride for perchlorate. A chloride ion is released from the quaternary ammonium moiety of a strong anion exchange resin, and perchlorate ion takes the place originally occupied by the chloride in the resin.

5. Membrane filtration. In reverse osmosis and nanofiltration, influent water is forced through a membrane that is impermeable to dissolved salts. Exclusion is the result of ionic size and charge. Effluent water is relatively deionized.

6. Electrodialysis. Water flows through alternate semipermeable membranes (anion-impermeable unshaded; cation-impermeable, shaded) while under the influence of an electric field. Cations migrate down; anions migrate up. Ions stop migrating when they reach their respective impermeable membranes. Alternate layers of salty and deionized water form as the water moves through the electrodialysis cell. The layers are drawn off separately, and the diluate is used.

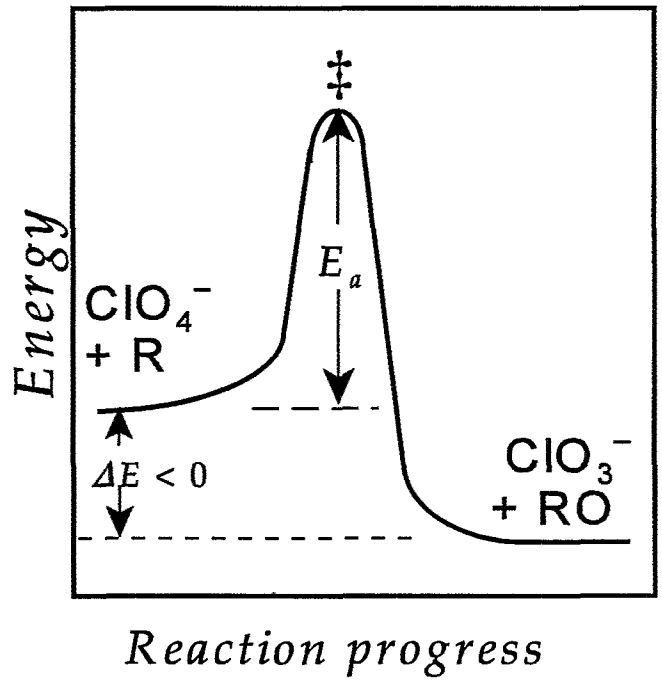

Figure 1

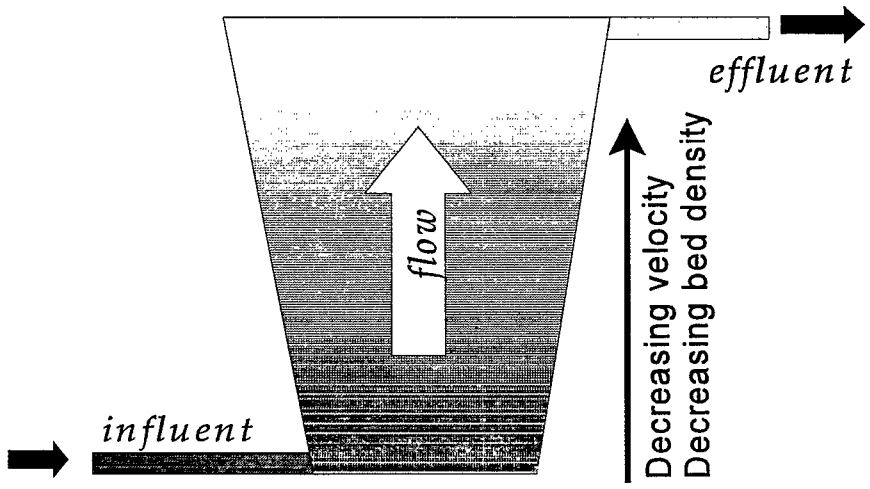
Decreasing velocity
Decreasing bed density
flow
influent
effluent

Figure 2

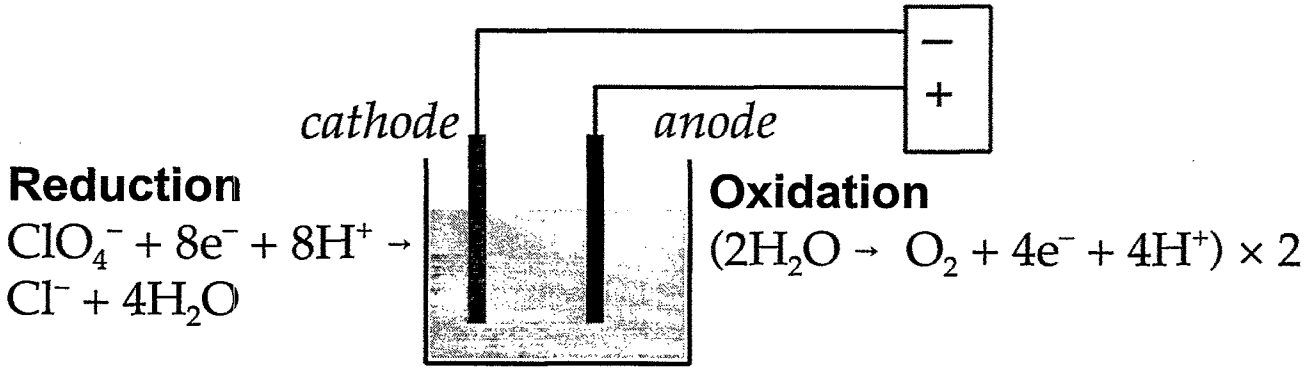
cathode
anode
−
+
Reduction
$ClO_4^- + 8e^- + 8H^+ \rightarrow Cl^- + 4H_2O$
Oxidation
$(2H_2O \rightarrow O_2 + 4e^- + 4H^+) \times 2$

Figure 3

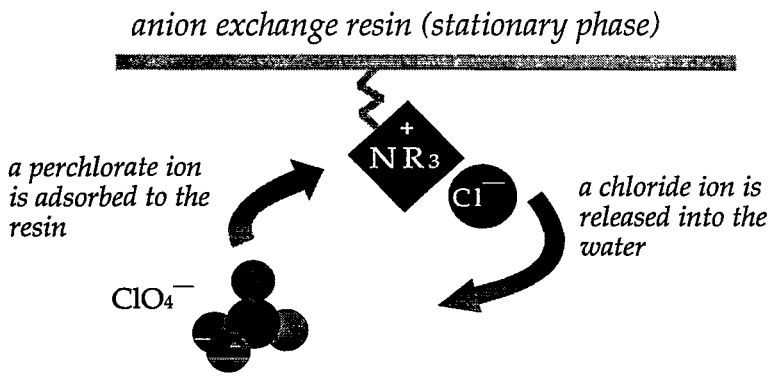
anion exchange resin (stationary phase)
+
NR3
Cl−
a perchlorate ion is adsorbed to the resin
a chloride ion is released into the water
ClO4−

Figure 4

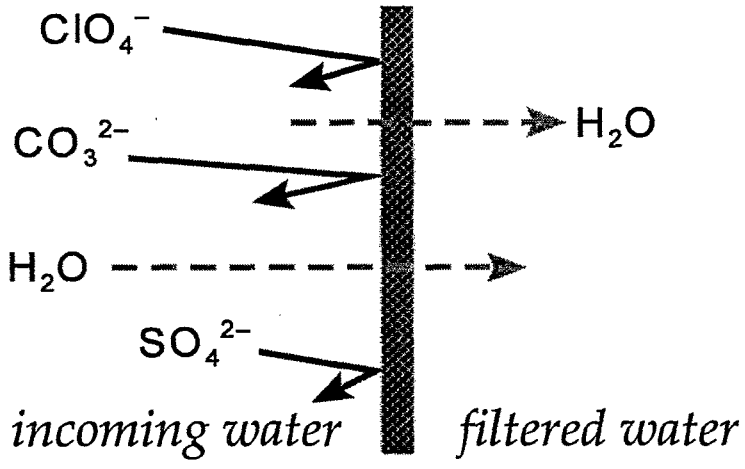

Figure 5

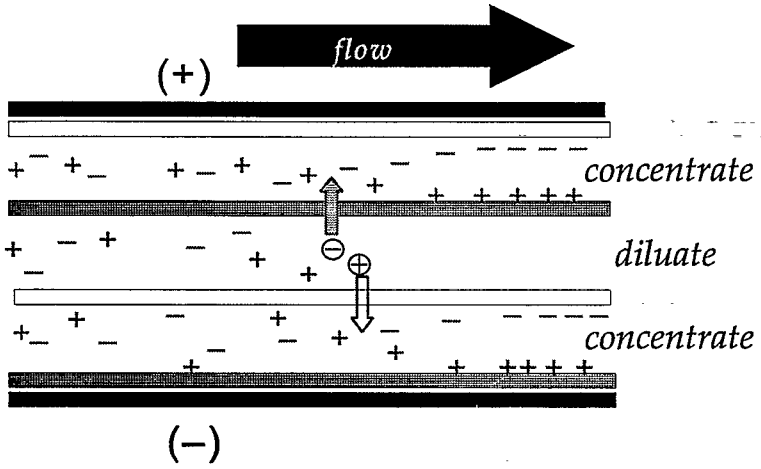

Figure 6