Perchlorate Chemistry: Implications for Analysis and Remediation

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Abstract: Since the discovery of perchlorate in the ground and surface waters of several western states, there has been increasing interest in the health effects resulting from chronic exposure to low (parts per billion [ppb]) levels. With this concern has come a need to investigate technologies that might be used to remediate contaminated sites or to treat contaminated water to make it safe for drinking. Possible technologies include physical separation (precipitation, anion exchange, reverse osmosis, and electrodialysis), chemical and electrochemical reduction, and biological or biochemical reduction. A fairly unique combination of chemical and physical properties of perchlorate poses challenges to its analysis and reduction in the environment or in drinking water. The implications of these properties are discussed in terms of remediative or treatment strategies. Recent developments are also covered.

Keywords: perchlorate, bioremediation, reductase, thyroid, anion exchange, electrochemical reduction, kinetic barrier, oxidant, reverse osmosis, electrodialysis, ion chromatography, capillary electrophoresis, analysis.

Introduction

Several factors have brought about the current interest in perchlorate (ClO_4^-), which, because of its chemical and physical nature, presents challenges for analysis and remediation. Perchlorate has been found in groundwater and in surface waters in several western states, including the Colorado River. Concentrations ranging from 8 ng mL^{-1} to 3.7 mg mL^{-1} have been measured. The extensive use of Colorado River water in this region and the proximity of some of these sites to the river have heightened the concern. Other local water supplies also are affected. Perchlorate targets the thyroid, bone marrow, and muscle tissue at sufficiently high concentrations; however, it is unknown what effects, if any, occur at the levels currently encountered in the contaminated water sources. Although additional toxicological studies are ongoing (Table 1), an action level of 18 ng mL^{-1} has been adopted by California and informally by other affected states.

The fundamental physical and chemical nature of perchlorate make it difficult to uniquely analyze for and to remediate, especially at the low concentrations typically encountered (i.e., <500 μg mL^{-1}). Although ion chromatography is capable of determining very low levels (e.g., 5 ng mL^{-1}), retention time is not considered a unique identifier, and known confirmatory tests have much higher detection limits. Perchlorate ion is unreactive as a ligand and its salts are extremely soluble, even in organic solvents. Despite its strength as an oxidizing agent, perchlorate is nonlabile, that is, very slow to react. This kinetic barrier is well known and widely made use of in chemical studies. Common reducing agents do not reduce perchlorate, and common cations do not precipitate it. Consequently, standard practices of water treatment

Table 1. Perchlorate facts at a glance.

Date of discovery	Discovered in 1997 in Western U.S. ground and surface waters
Physiological implications	Known to target the thyroid, bone marrow, and muscle at high concentrations
Medical use	Once used medicinally to treat Graves' disease (hyperthyroidism)
Remediation implications	Difficult to quantitate and remediate because of its high solubility and low kinetic lability towards reduction

will neither remove it physically nor destroy it chemically.

Sources and Nature of the Contamination

Ammonium perchlorate (NH_4ClO_4) has been used as an energetics booster in rocket fuels, and it appears most perchlorate contamination is the result of discharge from rocket fuel manufacturing plants or from the demilitarization of weaponry (missiles). It is important to emphasize that ammonium perchlorate is *not* rocket fuel; it is an additive. Potassium perchlorate ($KClO_4$) can be used as a solid oxidant for rocket propulsion, and it was the original source for a fraction of the contamination. However, most of the contamination appears to have come from the legal discharge decades ago of then unregulated waste effluents containing high levels of ammonium perchlorate. Although ammonium perchlorate was released initially, the salt is highly soluble and dissociates completely to ammonium and perchlorate ions upon dissolving in water (equation 1):

$$NH_4ClO_4(s) \xrightarrow{\text{water}} NH_4^+(aq) + ClO_4^-(aq) \qquad (1)$$

It is likely that most of the ammonium has been biodegraded and the cation is now best viewed as mostly sodium (Na^+) or possibly hydrogen (H^+), especially where levels are below 100 $\mu g\ mL^{-1}$; nevertheless, those regions with high concentrations of perchlorate ion probably retain at least some ammonium ion. At those sites where contamination dates back decades, very little (if any) ammonium ion has been found. To date, there has been no quantitative determination of the cations responsible for the charge balance.

Three states are known to be substantially affected: Utah, California, and Nevada. Arizona also may be affected since it too draws water from the Colorado River. Perchlorate concentrations in Utah range from 4 to 200 ng mL^{-1} in groundwater wells on the property of rocket motor manufacturer Alliant Techsystems. A level of 13 ng mL^{-1} at the Kennecott Utah Copper mines in Magna, Utah has led the company to supply its miners with bottled water for drinking.

In Henderson, Nevada, water samples taken 1000 ft (300 m) from the site of the former Pacific Engineering & Production Company of Nevada (PEPCON) rocket fuel plant, which exploded in 1988, contain as much as 630 $\mu g\ mL^{-1}$. Wells near the site show concentrations ranging from 51.4 to 630 $\mu g\ mL^{-1}$. Samples drawn from 50 wells near ammonium perchlorate manufacturer Kerr-McGee Chemical Corporation, located about 1 mile (1.6 km) from the abandoned PEPCON site, also showed significant perchlorate contamination. The Kerr-McGee samples showed perchlorate levels as high as 3.7 mg mL^{-1} in the groundwater. Surface water samples taken in August 1997 from the Las Vegas Wash, which feeds into Lake Mead, had perchlorate concentrations between 1.50 and 1.68 $\mu g\ mL^{-1}$.

Lake Mead is formed by the Hoover Dam on the Colorado River and thus affects the water supply of southern California, including Los Angeles. Testing by the Los Angeles Metropolitan Water District found 8 ng mL^{-1} perchlorate at its intake anc$∞⁄ Lake Mead at the Hoover Dam. Lake Mead lies at the southern tip of Nevada, straddling the Arizona border. This prompted the Southern Nevada Water Authority (SNWA) to begin testing its water; the SNWA found 11 ng mL^{-1} perchlorate in tap water.

The California Department of Health Services (DHS) began testing wells in early 1997, and has closed more than 20 wells for exceeding the action level of 18 ng mL^{-1}. Some wells could not be closed because of the high water demand of the regions served by the utility companies. Because the utilities often blend water from several sources, it is possible to dilute water from some of these wells. The DHS certifies commercial testing laboratories to perform perchlorate determinations, and has therefore stopped its own testing program (Cal DHS, 1997a). DHS reports that some regions of Lake Mead showed levels up to 165 ng mL^{-1}.

Physiological and Health Effects

In 1992, the U.S. Environmental Protection Agency (EPA) reviewed and assessed the health effects of perchlorate administered chemotherapeutically to patients with hyperthyroidism (Dollarhide, 1992, 1995; Stanbury, 1952). This study showed a no observable adverse effects level (NOAEL) of 0.14 mg kg^{-1} day^{-1}. Doses of 6 mg kg^{-1} day^{-1} or more for periods of at least 2 months led to fatal bone marrow changes. The EPA study recommended the following safety/error factors: 10 (nonchronic study), 10 (sensitive persons), 10 or 3 (database error margin) and allowed for two possible uncertainty factors, 1000 and 300.

Using the somewhat arbitrary, but relatively accepted, uncertainty factor of 300, the California DHS established 18 ng mL^{-1} as the action level for initiating remediation and stopping water usage (Cal DHS, 1997b). This cut-off assumes a 70-kg person consuming 0.5 μg perchlorate for each kilogram body mass who drinks 2 L of water daily (18 ng $mL^{-1} \approx 0.016$ mg $mL^{-1} = 0.14$ mg kg^{-1} $day^{-1} \times 70$ kg $\times$ 1 day/2 L $\div$ 300). The 0.5 μg number introduces a rounding error that was carried through (Cal DHS, 1997b). This 18 ng mL^{-1} action level has been adopted informally by other governmental agencies in the region as well. Using the same assumptions, we would calculate that harmful thyroid effects begin to occur at 49 μg mL^{-1}, and fatalities occur at 210 to 490 μg mL^{-1}. Meanwhile, the European Communities (1982) set a maximum admissible guide level of 20 μg $NaClO_4$ mL^{-1} for drinking water. This corresponds to 16 μg ClO_4^- mL^{-1}.

Perchlorate exerts its most commonly observed physiological effects on or through the thyroid gland. The primary effect is a decrease in thyroid hormone output. The thyroid gland takes up iodide ion from the bloodstream and converts it to organic iodide in the form of hormones that regulate metabolism. The mechanism responsible for this process, the cellular iodide pump, preferentially selects for anions on the basis of ionic volume: $I^- \approx SCN^- < ClO_4^-, TcO_4^-$ (Chiovato et al., 1997; Cooper, 1991; Foye, 1989; Orgiassi, 1990). Consequently, the presence of any large anion in the serum reduces thyroid hormone production.

This phenomenon was once used pharmaceutically to treat hyperthyroidism, which is known as Graves' disease (Foye, 1989; Chiovato et al., 1997; Cooper, 1991; Orgiassi, 1990). Chemotherapeutic use of perchlorate was reduced substantially in the United States after several instances of aplastic anemia and renal damage were observed (Foye, 1989; Hobson, 1961). Domestic perchlorate use now is restricted almost exclusively to use as a diagnostic tool for the evaluation of thyroid hormone production. As a diagnostic tool, perchlorate is still the standard for evaluating thyroid activity; the protocol at the University of California, Los Angeles (UCLA) requires a dose of 0.6 g (pediatric) or 1 g (adult) (UCLA, 1997). Following the administration of radiolabeled iodide, perchlorate is used to displace iodide anion in the iodide pump. When thyroid function is low, most of the radioiodine remains as inorganic iodide (rather than being converted to an organic iodide) and is lost; therefore, very little intrathyroid iodine shows the radiolabel.

Although perchlorate has been used as a treatment for hyperthyroidism, under the right circumstances it also can act as goitrogen in rodents and prevent thyroid hormone formation by interfering with iodide uptake (Capen and Martin, 1989). The low level of hormones is recognized by the pituitary gland which then stimulates the thyroid gland to work harder, eventually leading to goiter. A recent study of thyroid hormone levels in the Sprague-Dawley rat supported the EPA reference dose of 0.14 mg kg^{-1} day^{-1}. Male rats exhibited a thyroid NOAEL of 0.44 mg kg^{-1} day^{-1}, but females exhibited a thyroid NOAEL of only 0.124 mg kg^{-1} day^{-1} (King, 1995). Potassium perchlorate has been used to treat thyrotoxicosis without toxicity at doses ranging from 40 to 120 mg day^{-1} (Cooper, 1996). If we assume a daily intake of 3 L of water, this would correspond to 13 to 40 μg $KClO_4$ mL^{-1}, or about 9 to 12 μg ClO_4^- mL^{-1}. This is a factor of about 1000 times the California DHS action level, but close in line with the European Communities level. It is unknown whether secondary effects resulting from decreased thyroid function, indirectly caused by perchlorate, will be consequential. No studies link perchlorate to any secondary adverse health effects at this time.

Perchlorate can directly affect organs and tissues in addition to the thyroid gland. The mouse mammary gland has a mechanism similar to the thyroid iodide pump that is inhibited by perchlorate (Rillema and Rowady, 1997); however, it is unclear whether this has any significance for human health. At high (millimolar) concentrations, perchlorate is known to potentiate excitation-contraction (E-C) coupling and charge movement in muscle cells (Bruton et al., 1995; Gonzalez and Rios, 1993; Jong et al., 1997; Khammari et al., 1996; Ma et al., 1993; Pereon et al., 1996). At this level, part of the E-C effect is due to activation of calcium ion release from the sarcoplasmic reticulum (Fruen et al., 1994; Percival et al., 1994; Yano et al., 1995). In fact, this property of perchlorate often is exploited to study muscle physiology in animals. Much of what is known about perchlorate's effects on living organisms is derived from studies of acute toxicity over relatively short periods of time rather than chronic exposure to very low concentrations over a lifetime.

The U.S. Air Force Research Laboratories (AFRL) are conducting animal toxicology studies under the guidance of the EPA's National Center for Environmental Assessment (NCEA) and in consultation with state agencies. These studies are intended to refine the NOAEL and to set a standard to replace the current action level; preliminary results are scheduled for release in September 1998. EPA's Office of Water has added perchlorate to the candidate contaminant list (CCL), but it is unclear whether this will eventually culminate in the establishment of a maximum contaminant level (MCL) for perchlorate in drinking water.

Chemical and Physical Properties

Perchlorate as a Noncomplexing Anion

Perchlorate is widely known to be a very poor complexing agent (Cotton et al., 1987) and is used extensively as a counter ion in studies of metal cation chemistry, especially in nonaqueous solution. In this use, it is comparable with other noncomplexing or weakly ligating anions, e.g., trifluoromethanesulfonate (triflate, $CF_3SO_3^-$), tetrafluoroborate (BF_4^-), and to a lesser extent nitrate (NO_3^-). Some exceptions are known, but these are rare. All of these anions have a highly delocalized (NO_3^-, ClO_4^-, $CF_3SO_3^-$) or sterically blocked (BF_4^-) monovalent anionic charge and large volume; the low charge density reduces their affinity for cations and their extent of aquation (see Table 2). This low association with cations is responsible for the extremely high solubilities of perchlorate salts in aqueous and nonaqueous media. It is important to point out that the solubility is not due to association with the solvent. While perchlorate is often described as strongly retained on anion exchange resins, the truth is that the ion in the starting form of the resin (e.g., chloride or hydroxide) is much more hydrophilic than perchlorate (Table 2).

Table 2. Gibbs free energies of formation for selected anions in aqueous solution.[a]

Anion	ΔG_f°, kJ mol^{-1}
BF_4^-	–1490[b]
PO_4^{3-}	–1019
SO_4^{2-}	–744
HCO_3^-	–587
OH^-	–157
Cl^-	–131
NO_3^-	–109
Br^-	–104
ClO_4^-	–8.5
ClO_3^-	–8.0

[a] From Barrow (1988), except BF_4^-.
[b] From Dean (1985).

Perchlorate Salts as Supporting Electrolytes or Ionic Strength Adjustors

In addition to its use in synthesizing transition metal compounds where competition for coordination is undesirable, sodium perchlorate is used extensively as a means of adjusting ionic strength for equilibrium, kinetics, and electrochemical studies where potassium nitrate cannot be used. For example, many halogen species undergo multiple simultaneous equilibria in which a central halogen atom expands its octet and forms a hypervalent species; perchlorate does not act as a ligand in these situations (Urbansky et al., 1997). Inorganic perchlorate salts are generally extremely soluble, with potassium perchlorate the notable exception (~17 g L^{-1} = 0.12 M). The solubility of sodium perchlorate in water is extremely high, just under 8 M; only the mineral acids and the alkali metal hydroxides surpass it in solubility.

Kinetics and Thermodynamics of Perchlorate Reduction

Besides its weak ligating ability, perchlorate often is used to adjust ionic strength because of its low reactivity as an oxidant. At first glance, this seems surprising given that it contains a highly oxidized central halogen atom, chlorine(VII). However, the low reactivity is a matter of kinetic lability rather than thermodynamic stability. The standard reduction potentials (Emsley, 1989) for the half-reactions (equations 2 and 3) clearly indicate that reductions to chloride or chlorate are very favorable processes from a thermodynamic standpoint:

$$ClO_4^- + 8\,H^+ + 8\,e \rightleftharpoons Cl^- + 4\,H_2O \qquad E^\circ = 1.287\ \text{V} \tag{2}$$

$$ClO_4^- + 2\,H^+ + 2\,e \rightleftharpoons ClO_3^- + H_2O \qquad E^\circ = 1.201\ \text{V} \tag{3}$$

Given thermodynamics alone, we would expect perchloric acid to oxidize water to oxygen because the water-oxygen couple has an oxidation potential of –1.229 V (Emsley, 1989).

$$2\,H_2O \rightleftharpoons 4\,H^+ + O_2 \qquad -E^\circ = -1.229\ \text{V} \tag{4}$$

Consequently, we can confidently state that the observed behavior of perchlorate is dominated largely by its kinetics. In fact, perchloric acid is quite unreactive toward most reducing agents when cold and dilute. For example, digestion of organic material (wet ashing) with perchloric acid requires heating the material with the concentrated acid (Harris, 1991; Schilt, 1979). The kinetic barrier to perchlorate reduction is very useful in many oxidation-reduction investigations because it allows control of the ionic strength with a non-complexing anion, even at moderately acidic conditions (e.g., 1 M) where nitrate would be reduced.

It is fortunate, for the sake of remediation, that the behavior of perchlorate is due to a kinetic activation barrier rather than a thermodynamic barrier, because all kinetic problems can be reduced. It comes down to the matter of "where there's a will, there's a way." Also fortunate for us, the way is fairly well defined for perchlorate. Depending on the reductant, perchlorate may be reduced to either chlorate or chloride (Cotton and Wilkinson, 1988). Ruthenium(II) reduces perchlorate to chlorate, whereas vanadium(II), vanadium(III), molybdenum(III), dimolybdenum(III), chromium(II), and titanium(III) all reduce perchlorate to chloride.

The first work to show reduction of perchlorate by a metal cation was done by Rothmund (1909). He showed that Ti(III), V(II), and Cr(II) all reduce perchlorate to chloride in acidic aqueous solution at ambient temperature. Bredig and Michel (1922) refined Rothmund's Ti(III) work, and they showed that Mo(III) also reduces perchlorate to chloride.

With the right catalyst, other reductants will react with perchlorate. In the presence of ruthenium(III,IV) (Crowell et al., 1929) or osmium(IV) (Crowell et al., 1940), bromide will reduce perchlorate. Tin(II) will reduce perchlorate in the presence of molybdate (Haight and Sager, 1952). While these studies were significant and substantial at the time of publication, the treatment of the data was insufficiently rigorous to apply it here directly. Nevertheless, these papers laid the groundwork for many of the later investigations and still supply directions for future study.

King and Garner (1954) published the results of the first thorough kinetic investigation of the reaction of vanadium(II) and vanadium(III) with perchlorate. Reactions 5 through 7 summarize the behavior they observed. The oxidation-reduction reactions of perchlorate with V(II) or V(III) occur on comparable time scales (equations 5 and 6). The comproportionation in equation 7 is much faster, essentially instantaneous.

$$8\ \mathrm{V}^{2+} + \mathrm{ClO}_4^- + 8\ \mathrm{H}^+ \rightarrow 8\ \mathrm{V}^{3+} + \mathrm{Cl}^- + 4\ \mathrm{H_2O} \quad (5)$$

$$8\ \mathrm{V}^{3+} + \mathrm{ClO}_4^- + 4\ \mathrm{H_2O} \rightarrow 8\ \mathrm{VO}^{2+} + \mathrm{Cl}^- + 8\ \mathrm{H}^+ \quad (6)$$

$$\mathrm{VO}^{2+} + \mathrm{V}^{2+} + 2\ \mathrm{H}^+ \rightarrow 2\ \mathrm{V}^{3+} + \mathrm{H_2O} \quad (7)$$

Kallen and Earley (1971) published a detailed investigation on the reaction between hexaaquoruthenium(II) and perchlorate (equation 8). They also discussed the factors that control reaction rates of perchlorate reduction by metal cations.

$$2\ \mathrm{Ru} + \mathrm{ClO}_4^- + 2\ \mathrm{H}^+ \rightarrow 2\ \mathrm{Ru}^{3+} + \mathrm{ClO}_3^- + \mathrm{H_2O} \quad (8)$$

Duke and Quinney (1954) published the first rigorous study on the reaction of titanium(III) and perchlorate (equation 9). They found that the reaction proceeds through an initial complexation, after which Ti(III) is oxidized to a titanyl ion, TiO^{2+} (equation 10).

$$8\ \mathrm{Ti}^{3+} + \mathrm{ClO}_4^- + 8\ \mathrm{H}^+ \rightarrow 8\ \mathrm{Ti(IV)} + \mathrm{Cl}^- + 4\ \mathrm{H_2O} \quad (9)$$

$$\mathrm{Ti}^{3+} + \mathrm{ClO}_4^- \rightleftharpoons \mathrm{TiO}^{2+} + \mathrm{ClO}_3^{\circ} \quad (10)$$

Their postulation of the radical chlorine trioxide as the first product is still accepted today.

Cope et al. (1967) studied the $\mathrm{Ti^{III}}$-$\mathrm{ClO_4^-}$ reaction in the absence of chloride. They obtained the differential rate expression given by equation 11:

$$\mathrm{rate} = -\mathrm{d}\left[\mathrm{Ti^{III}}\right]\Big/\mathrm{d}t = \left(k + k'\left[\mathrm{H}^+\right]^2\right)\left[\mathrm{Ti^{III}}\right]\left[\mathrm{ClO}_4^-\right] \quad (11)$$

where $k = 1.9 \times 10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$ and $k' = 1.25 \times 10^{-4}\ \mathrm{M^{-2}\ s^{-1}}$.

Possibly the most significant paper with regard to chemical reduction deals with the redox reaction of perchlorate with *N*-(hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetatopentaaquotitanium(III) ion (Liu et al., 1984). The net reaction is shown in equation 12.

$$8\ \mathrm{Ti(Hedta)} + \mathrm{ClO}_4^- + 8\ \mathrm{H}^+ \rightarrow 8\ \mathrm{Ti(IV)} + \mathrm{Cl}^- + \mathrm{Hedta}^{3-} + 4\ \mathrm{H_2O} \quad (12)$$

This Ti(III) chelate is reasonably stable in air. The Ti(IV) produced begins to form hydrous oxides over a matter of an hour or so. Over the course of hours to days, fine suspended crystallites of $\mathrm{TiO_2}$ develop. They found the rate expressible as

$$\mathrm{rate} = -\mathrm{d}\left[\mathrm{Ti^{III}}\right]\Big/\mathrm{d}t = \left(k\left[\mathrm{ClO}_4^-\right]\left[\mathrm{H}^+\right]^2 + k'\right)\left[\mathrm{Ti(Hedta)}\right] \quad (13)$$

where $k = 2 \times 10^{-3}\ \mathrm{M^{-2}\ s^{-1}}$ and $k' = 2 \times 10^{-8}\ \mathrm{s^{-1}}$.

Based on this study by Liu et al. (1984), we might propose to treat perchlorate-contaminated waters with Ti(III) chelates under anaerobic conditions. The chloride produced is harmless, and the TiO_2 may be removed by agglutination and sedimentation or by filtration. TiO_2 is very insoluble and quite nontoxic. A number of stable titanium(III) chelates and complexes have been prepared; however, in general, precautions have been taken to exclude oxygen (Chaudhuri and Diebler, 1986). It is unclear if any fairly air-stable titanium(III) chelate may be synthesized that will still react quickly with perchlorate. Even if other factors can be overcome, this reaction is still too slow to be useful. If we could lower the pH to 4, for 1 mM ClO_4^- and 800 mM Ti(Hedta), the rate of the perchlorate oxidation of Ti(III) would be 1.6×10^{-10} M s^{-1}, while the rate of the decomposition would be 1.6×10^{-8} M s^{-1}, i.e., 100 times faster! Even if we stopped the decomposition, the half-life for this reaction would be 50 days, far too long to be practicable in a water treatment plant.

Hills et al. (1986) demonstrated that molybdenum(III) and dimolybdenum(III) are capable of reducing perchlorate in acidic solution. This is noteworthy in light of the fact that molybdenum is not known to have any stable "-yl" ions in aqueous solution, the significance of which is described below.

Taube (1982) has speculated that the relative stability of the resulting "-yl," i.e., $M{=}O^{n+}$, ions is largely responsible for the behavior observed for titanium, vanadium, and other metals, whereas others (Kallen and Earley, 1971; Liu et al., 1984) have put forth an alternative explanation that they feel is superior relating to the polarizability of the metal *d*-orbitals and the interaction of these orbitals with the lowest unoccupied molecular orbital (LUMO) of the perchlorate. Although Taube's explanation is more well known, the Kallen-Earley postulate is reasonable and fits better with some of the experimental evidence.

Very recently, methylrhenium dioxide (CH_3ReO_2) has been shown to abstract oxygen atoms from halates and perhalates (Cl, Br, and I) (Abu-Omar and Espenson, 1995; Abu-Omar et al., 1996). The net reaction is given by equation 14:

$$4\ CH_3ReO_2 + ClO_4^- \rightarrow 4\ CH_3ReO_3 + Cl^- \qquad (14)$$

The first step in the process is a reduction to chlorate:

$$CH_3ReO_2 + ClO_4^- \rightarrow CH_3ReO_3 + ClO_3^- \qquad (15)$$

with a reaction rate given by

$$\text{rate} = -d\left[CH_3ReO_2\right]/dt = 4k\left[CH_3ReO_2\right]\left[ClO_4^-\right] \qquad (16)$$

where $4\ k = 29\ M^{-1}\ s^{-1}$; the subsequent chlorate reduction is about 1000 times faster. The reaction rate for equation 15 is not dependent on acid concentration, which is unusual. The rate is unusually fast, several orders of magnitude faster than for any other transition metal compound. Abu-Omar and Espenson (1995) provide a very convenient and useful table of rate constants for the reduction of perchlorate and chlorate by transition metal complexes.

There are two serious problems with chemical reductants: (1) they tend to suffer from oxidation by atmospheric oxygen, and (2) they are too slow under normal conditions (i.e., pH and concentration). Consequently, anaerobic conditions would be required for their delivery as well as for the duration of their reaction time.

The electrochemical reduction of perchlorate ion has been reported for a wide variety of cathodes, including platinum (Horányi and Vértes, 1975b; Vasina and Petrii, 1969), tungsten carbide (Horányi and Vértes, 1974, 1975a; Vértes and Horányi, 1974), ruthenium (Gonzales Tejera and Colom Polo, 1984), carbon doped with chromium(III) oxide or aluminum oxide (Mouhandess et al., 1980), aluminum (Kiss et al., 1973), and titanium (Mathieu and Landolt, 1978; Mathieu et al., 1978; Tsinman et al., 1975). Brown (1986) showed that chlorate and perchlorate may be reduced successfully to chloride by active titanium, and he discusses the possibility of passivation of the titanium electrode as titanium(IV) forms, presumably from the deposition of titanium dioxide.

Given the exceptionally fast reaction between methylrhenium dioxide and perchlorate, it seems possible that alkyl rhenium oxides might be used catalytically if not chemically. Moreover, this suggests an entire area of research into the use of organometallic compounds as chemical reductants for perchlorate. Besides the possible application to remediation, this also suggests possibilities for use in kinetic methods of analysis since anyone with an ultraviolet-visible spectrophotometer could follow this reaction in as low as submillimolar levels of perchlorate based on the molar absorptivity of CH_3ReO_3.

Quantitative Analytical Chemistry

Gravimetry

The strongly dissociative property of perchlorate, which makes it so highly desirable in the uses described, makes it correspondingly difficult to quantitate by gravimetry or to remove by precipitation. However, some insoluble or sparingly soluble perchlorate compounds are known. The first methods reported for quantitation of perchlorate were based on gravimetry with nitron (DOC, 1996; Harris, 1991; Welcher, 1947), $C_{20}H_{16}N_4$, $M_r = 312.36$ g mol^{-1}. Other names for nitron include 4,5-dihydro-2,4-diphenyl-5-(phenyl-imino)-1*H*-1,2,4-triazolium hydroxide, inner salt; 1,4-diphenyl-3-(phenylimino)-1,2,4-triazolidine, mesoionic didehydroderivative; 1,4-diphenyl-3,5-endanilodihydrotriazol; and 3,5,6-triphenyl-2,3,5,6-tetraazabicyclo[2.2.1]hex-1-ene.

As might be expected, nitron also quantitatively precipitates BF_4^-, WO_4^{2-}, ReO_4^-, and NO_3^- as well as a few other anions. In fact, nitron takes its name from its ability to precipitate *nitr*ate ani*on*. It is important to note that the precipitates contain the acidic hydrogen ion, which protonates the positive nitrogen of the inner ring; however, there is no significant association between the proton and the inorganic anion. The anion is simply a large counterion to balance the charge. Table 3 gives the solubilities reported for some nitron salts. In addition to the anions in Table 3, other large anions should be expected to interfere; interference is documented for ferrocyanide, ferricyanide, picrate, and oxalate (Welcher, 1947).

Perchlorate may be assayed gravimetrically using tetraphenylarsonium chloride, $AsPh_4Cl$ ($Ph = C_6H_5$) (Harris, 1991). While this material may be very useful in the analysis of perchlorate, it is doubtful that it will establish itself in any way for remediation because of the arsenic.

The low solubilities of Nit · $HClO_4$ (Nit = nitron) and $AsPh_4ClO_4$ immediately suggest several opportunities for both analysis and remediation. Besides traditional gravimetric analyses, this property may be exploited for electrochemical analyses. As might be expected, potentiometric titrimetry with nitron has been used for perchlorate and other anions (Selig, 1988). An indirect method has been used to determine as little perchlorate as 0.05 to 0.15 nmol using nitron followed by an iodimetric back-titration (Shahine and Ismael, 1976).

Table 3. Solubilities of some nitron · HX species.[a]

HX	Solubility, g L^{-1}
$HClO_4$	0.08
HNO_3	0.099
HI	0.17
HSCN	0.4
$HCrO_4H$	0.6
$HClO_3$	1.2
HONO	1.9
HBr	6.1

[a] From Welcher, 1947.

Potentiometry and Ion-Selective Electrodes (ISEs)

One technique that holds excellent promise as a routine monitoring device is potentiometric measurement via an ion-selective electrode. The perchlorate ion-selective electrode (ISE) has an extensive history and has been under development for about 20 years. Many designs and components abound, some with outstanding response. A liquid-membrane ISE has been shown to have nearly Nernstian response to perchlorate in the range of 10^{-5} to 10^{-2} M with a lower limit of detection of ~10^{-6} M (Hassan and Elsaied, 1986). A polyvinyl chloride (PVC) membrane impregnated with HNitSCN has been used to determine perchlorate down to 2.5×10^{-5} M, and one impregnated with $As(C_6H_5)_4SCN$ has been constructed, but it was not tested for response to ClO_4^- (Elmosalamy et al., 1987). Perchlorate, along with several other anions, has been determined using flow injection analysis with a carbon electrode and *bis*(diphenylphosphino)propane-copper complex as an ion exchanger (Wang and Kamata, 1992). Making use of the low solubility of potassium perchlorate, a potassium cation ISE was used to study the migration of perchlorate into a PVC membrane (Verpoorte and Harrison, 1992). Perchlorate ISEs based on a barium complex with a macrocyclic Schiff base have been developed (Masuda et al., 1991). The newer perchlorate ISEs are based on large, inert, metal-ligand complexes that do not undergo complexation with small, hard Lewis bases and have no open coordination sites.

The perchlorate ISE has already established itself as a research tool, and it has been used to monitor perchlorate concentration in a variety of investigations (Alegret et al., 1986; Baczuk and Dubois, 1968; Cakrt et al., 1976; Ciavatta et al., 1989; Efstathiou and Hadjiioannou, 1977a, 1977b; Fogg et al., 1977; Hiiro et al., 1979; Hopirtean and Stefaniga, 1978; Hopirtean et al., 1976, 1977; Hseu and Rechnitz, 1968; Imato et al., 1980; Ishibashi and Kohara, 1971; Ishibashi et al., 1973; Jain et al., 1987; James et al., 1972; Jasim, 1979; Jyo et al., 1977, 1983; Kataoka and Kambara, 1976; Manahan et al., 1970; Matei et al., 1986; Nikolskii et al., 1977; Pathan and Fogg, 1974; Rohn and Guilbault, 1974; Sharp, 1972; Silber and Zhang, 1991; Sykut et al., 1979; Tateda et al., 1970; Vosta and Havel, 1973a, 1973b; Wilson, 1979; Wilson and Pool, 1976). Based on the significant advances in perchlorate ISEs, the time is ripe for exploration of perchlorate ISEs as a technique both for first-line assay in the field and for continuous monitoring within a treatment facility, especially in regions with known contamination.

Ion Chromatography and Capillary Electrophoresis

Perchlorate ion is commonly described as strongly retained on anion exchange resins. What this really means is that other ions are more strongly attracted to the aqueous mobile phase. It does *not* mean that the resin has a high affinity for perchlorate. Chloride and hydroxide have much higher charge densities than perchlorate and therefore associate more strongly with water than they do with a fairly diffuse quaternary ammonium site. If eluent components are not chosen wisely, perchlorate elution times can run over an hour, allowing substantial diffusion and thus peak broadening.

The California Department of Health Services has established an ion chromatography (IC) method that uses *p*-cyanophenoxide to displace the perchlorate from the resin (Cal DHS, 1997b). Recently, Maurino and Minero (1997) showed that hydrogen cyanurate ions, H_2A^- and HA^{2-} (cyanuric acid = H_3A), can be used to effect excellent separation and peak shape for perchlorate. Biesaga et al. (1997) showed that phthalate can be used, but retention times are long (40 min) and some degradation of peak shape is observed. Jandik et al. (1990) used acetonitrile to modify the eluent dielectric constant and a solid-phase reagent to obtain retention times under 20 min. In a study of retention time and polarizability, Daignault et al. (1990) used 1.7 mM $NaHCO_3$-1.8 mM Na_2CO_3 eluent for perchlorate; however, they used analyte concentrations of 2 mg mL^{-1}. Buchberger and Haider (1997) used IC with particle beam mass spectrometry to detect perchlorate, providing a definitive identification of the ion. An earlier study used micropacked alumina columns to separate anions and cations simultaneously, making use of the amphoteric nature of aluminum oxide (Takeuchi et al., 1988). Wirt et al. (1998) reported a new IC method using only NaOH as the eluent with a retention time of <10 min.

One of the advantages of capillary electrophoresis (CE) over IC is readily apparent when considering strongly retained ions, such as perchlorate. In CE separation, the electrophoretic (ionic) mobility is the most important factor, unlike IC where interactions with the stationary and mobile phase are important. In CE, associations with the wall or a modifier are generally unintended, undesirable, and, most importantly, avoidable. Furthermore, a slow eluter when using IC may be a very fast one when using CE. Avdalovic et al. (1993) showed that perchlorate can be eluted by CE at 10 min; meanwhile, bromide, chloride, and iodide all take more than 15 min by their method. Hauser et al. (1995) used CE with a micro-ISE to quantitate as little as 10 μM perchlorate. Corr and Anacleto (1996) used CE coupled with mass spectrometry with ion spray introduction on a wide variety of cations and anions. Although it is common practice to use quaternary ammonium salts, such as cetyltrimethylammonium chloride, to reverse the electroosmotic flow, Krokhin et al. (1997) used water-soluble polymers with quaternary ammonium moieties to promote the elution of perchlorate by CE.

AFRL and EPA's National Exposure Research Laboratory (NERL) have begun the process of interlaboratory validation for the California DHS IC method (Tsui and Pia, 1998). There currently is no EPA-approved method for the quantitation of perchlorate in drinking water; however, Cal DHS has established its own approval process for laboratories that seek to analyze for perchlorate. AFRL continues to work on methods for determining perchlorate in other media, e.g., soils and plant tissues.

Other Techniques

In addition to gravimetry and electrochemistry, other techniques also offer promise when coupled with these reagents, particularly spectrophotometry. Methylene blue forms an insoluble complex with perchlorate; the loss of methylene blue from the supernatant is determined spectrophotometrically (Nabar and Ramachandran, 1959). The neocuproine-cuprous ion complex also has been used to extract perchlorate into ethyl acetate; the *bis*(neocuproine)cuprous perchlorate species has a visible absorption spectrum (λ_{max} = 456 nm) or, alternatively, the copper content may be determined by atomic absorption photometry (λ = 324.7 nm) (Collinson and Boltz, 1968). A similar method designed for biological fluid samples makes use of an anion exchange resin (Amberlite IR-45) to preconcentrate the perchlorate and thereby lower (improve) the quantitation limit (Weiss and Stanbury, 1972).

Both tetraphenylarsonium chloride and nitron can be used to determine perchlorate concentration spectrophotometrically by difference in samples containing nitrate (Shahine and Khamis, 1979). An aliquot of nitron solution is added to the sample, and the excess nitron is determined photometrically as $(HNit)_2[Co(NCS)_4]$ at 625 nm; perchlorate alone is determined by precipitation with $AsPh_4^+$, and the excess is determined as $(AsPh_4)_2[Co(NCS)_4]$ at 620 nm. Although not reported, it seems reasonable that laserinduced fluorescence would be be a sound technique, especially if the $HNitClO_4$ or $AsPh_4ClO_4$ were extracted into an organic solvent.

Reverse-phase high-performance liquid chromatography also could be used on such an extract to separate perchlorate from interferents such as nitrate or bromide with detection by ultraviolet (UV) absorbance. The use of a photodiode array detector may provide a UV absorption spectrum sufficiently distinct to ensure definitive identification of perchlorate, eliminating the retention time problem. It is known that $AsPh_4ClO_4$ has a unique infrared absorption spectrum that permits it to be distinguished from other tetraphenylarsonium salts. Numerous methods using wet chemical or instrumental techniques or a combination thereof are known, and these have been reviewed extensively for the literature prior to 1979 (Schilt, 1979). Although mulls in Nujol or perfluorosilicone grease may be safe, compressing $AsPh_4ClO_4$ in a KBr pellet seems to be flirting with disaster. Even if KBr pellets can be made safely, there is no guarantee that some decomposition of the perchlorate will not occur or that a reaction with bromide will not take place during pressurization.

Walter Selig at Lawrence Livermore Laboratory has investigated a number of potentiometric precipitation titrations to determine perchlorate using quaternary ammonium compounds as titrants (Selig, 1977, 1979, 1980a, 1980b).

A carbon paste electrode that uses thallium for catalysis has been used to voltammetrically quantitate perchlorate in drinking water samples down to 50 ng mL^{-1}; however, it suffers from a number of significant direct and indirect interferences (Neuhold et al., 1996). Of these, bromide, chlorate, and nitrate are most likely to be found in a drinking water matrix.

Remediation and Treatment

Overview

It is helpful to keep in mind the following criteria for any drinking water treatment technology. The treatment must not (1) adversely affect other treatment technologies for regulatory compliance, (2) produce water that corrodes the distribution system, (3) produce water that is unpalatable, (4) suffer from degradation by other components in the water, (5) fail to perform reliably, (6) produce excessive waste, or (7) fail to meet time and expense constraints. The best choice for any situation will require a careful evaluation of options and probably some combination of techniques. We must remember that the potential for success of any technology is dependent on two factors: the establishment of a safe level of perchlorate for drinking water and a quantitative chemical analysis that ensures this safe level is in fact achieved.

Remediation and Treatment by Physical Processes

Membrane-Based Techniques. Membrane-based techniques can be effective, but they suffer from several drawbacks. While reverse osmosis (RO) would effect sufficient remediation, it can be impractical for a municipal treatment system because of the fouling of membranes and the associated cost. RO-treated water has to be remineralized with sodium chloride, sodium bicarbonate, and other innocuous salts to prevent degradation of the distribution system and to make the water palatable, since deionized water generally is considered to have an unpleasant taste. Therefore, as long as sufficient salts are taken in from food and other sources, consumption of deionized water is not likely to pose a threat to the normal electrolyte balance. As with RO, electrodialysis also might be used in this fashion. These two techniques are probably best suited for point-of-use or small systems.

Anion Exchange. Although perchlorate ion is strongly retained by quaternary ammonium resins, the crux of the matter is its initially low concentration in most cases. For example, it might be necessary to reduce perchlorate concentration from 1 $\mu g\ mL^{-1}$ to 20 ng mL^{-1}. However, consider that bicarbonate, carbonate, chloride, and a host of other anions are all likely to be present at much higher concentrations. Assuming that a chloride-form resin is used, the presence of phosphates, carbonates, and sulfate remains an issue. Although it may be possible to produce a resin salt that matches the proportions of the major anions in the influent water, to do so would be extremely inconvenient. In addition, the low concentration of perchlorate in the raw water substantially reduces the driving force for its removal. In other words, to adequately remove the perchlorate may require essentially demineralizing and remineralizing the water, depending on its anion content.

It is possible to modify resins so as to improve their selectivity for particular anions. Kawasaki et al. (1993) have used Dowex 1X-8 to selectively preconcentrate perchlorate; the selectivity of the resin for perchlorate is about 100 times that for chloride and 10 times that for nitrate. In addition to selectivity in a thermodynamic sense, there is the matter of rapid equilibration and anion exchange. If the rate of exchange is too slow, a resin will not be usable no matter how high its selectivity. The U.S. Department of Energy has developed a mixed triethylammonium-trihexylammonium resin that is capable of removing pertechnetate down to the parts-per-trillion level (Brown, 1997).

Tethered triphenylarsonium or phosphonium moieties or a tethered (through a phenyl group) nitron might work in an anion-exchange resin to selectively preconcentrate perchlorate as a step in remediation. The disadvantage of the tethered triphenylarsonium group is that normal degradation of the resin would lead to the release of arsenic into the treated water. Although the health effects of nitron are unknown, it would be expected to undergo biodegradation; furthermore, it would be destroyed readily by UV irradiation ($\lambda \leq 185$ nm), whereas arsenic would remain as an inorganic oxyanion even if the organic portion of the species were destroyed.

Precipitation. The low solubility of the $HNitClO_4$ ion pair reveals a strong association between the protonated nitron cation and the perchlorate anion. All insoluble ion pairs and complexes exist at some level in solution. It may be possible to exploit this pairing for purposes of remediation. If the addition of nitron to perchlorate-containing waters results in formation of the soluble ion pair, it may be possible to subsequently induce an intramolecular reaction in which both the perchlorate and the nitron are destroyed. Photoactivation of the perchlorate by UV or laser irradiation may promote an intramolecular redox reaction (probably by oxygen atom transfer). The proximity of the $HNit^+$-ClO_4^- ion pair within a solvent (water) cage means that it is not necessary to form an encounter complex. In addition, the local concentration of the two species is very high within the solvent cage. This should help to reduce the effects of the perchlorate kinetic barrier (discussed below). Of course, irradiation with UV light also will promote destruction of the nitron by hydroxyl radical formation. Ideally, the largest possible wavelength (lowest frequency and energy) light would be used to reduce side reactions that would destroy the nitron.

Unfortunately, nitron has potential to remediate only those sites with very high perchlorate concentrations unless it can be synthesized more cheaply. At present, nitron is about 52 times more expensive than an equal mass of reagent-grade sodium chloride. However, should a method involving nitron prove effective, bulk synthesis of the material would likely drop the cost by 40 to 50%, and use of a less refined technical (rather than reagent) grade would probably reduce it by another 10 to 25%.

At some of the sites where the perchorate concentration is 0.037 M, nitron could readily be used as a precipitant since the nitron-hydrogen perchlorate salt has a solubility of only 0.19 mM. Although the action level of 18 ng mL^{-1} corresponds to 0.18 M, a level of 0.19 mM is certainly preferable to 37 mM. Of course, one drawback is that a source of acid (usually 5% acetic acid) must be present. On the other hand, vinegar is probably preferable to 0.037 M ClO_4^-. Moreover, such post-remediation acetic acid and acetate would be biodegradable.

In addition to cost, all physical separation processes have one major problem: waste disposal. Presumably, the regenerant from ion exchange and the concentrate from RO or electrodialysis would contain perchlorate at concentrations too high to be released into a sewage system. This waste presents a problem in terms of cost and post-treatment needs. Although these techniques take the perchlorate out, they concentrate it somewhere else where it must be dealt with later.

Remediation and Treatment by Chemical Processes

Chemical and Electrochemical Reduction. Here we refer to reduction specifically in the redox sense of adding electrons. From the description of the oxidation-reduction reactions of perchlorate above, it is clear that chemical reduction will play no role in drinking water treatment in the near future. Chemical reduction is simply too slow. Unless safe new catalysts become available, this appears unlikely to change. Commonplace reductants (e.g., iron metal; thiosulfate, sulfite, iodide, and ferrous ions) do not react at any observable rate, and the more reactive species are too toxic (and still too sluggish). In addition, any reductant will necessarily have oxidized by-products. The toxicity of the by-products must be considered.

There is more hope for electrochemical reduction. A decided advantage of electrochemical reduction is the large amount of control over kinetics that results from control of the operating potential. Electrode reduction kinetics reasonably can be viewed as being limited by three factors: (1) diffusion of the ions to the electrode surface, (2) association with the electrode surface, and (3) activation past the overpotential required to reach the transition state. Although overpotential usually is the greatest barrier, it also is the one that can be dealt with best. Because we are not concerned with other reductions (including reducing water to hydrogen), the only barrier is the limit of a negative potential that is practical and safe to apply. Fortunately, most of the materials in raw water are reducing agents. Although some may be affected by electroreduction, this probably does not present a significant obstacle. To date, this option has not been explored for low-concentration treatment at anything approaching pilot scale. Although electrochemical technologies are well established for other industries (e.g., electroplating of metals, electrolysis of brine), they have not yet found a place in drinking water treatment.

In this category, it appears that the most successful strategies for remediating perchlorate contamination will utilize metal cation-catalyzed reduction by either chemical or electrochemical means. Several metal chelates have potential at this point, especially if embedded in an electrode for use in electrochemical reduction.

Biological and Biochemical Techniques. Bioremediation is another matter entirely, and it may prove to be the most practical approach. A number of bacteria that contain nitrate reductases (Payne, 1973) are capable of reducing perchlorate (Schilt, 1979). *Staphylococcus epidermidis* is capable of reducing perchlorate in the absence of nitrate. Cell-free extracts of nitrate-adapted *Bacillus cereus* also reduce perchlorate (and chlorate) (Hackenthal, 1965). As would be expected, sodium perchlorate, especially in higher concentrations, has been shown to be toxic to several species of bacteria. Unfortunately, *S. epidermidis* is also pathogenic; it increasingly is encountered as a source of nosocomial infections, especially opportunistic infection with in-dwelling intravenous or urinary catheters (Archer, 1995). It is encountered with other medical apparatus such as prosthetic joints, pacemakers, heart valves, and breast implants (Archer, 1995). Like *S. epidermidis*, *B. cereus* is pathogenic. *B. cereus* is known for food poisoning, ocular infections, and pneumonia with other sites sometimes affected (Tuazon, 1995).

Rikken et al. (1996) reported that perchlorate and chlorate are reduced to chloride by *Proteobacteria* with acetate as a nutrient (reductant) at near-neutral pH. While they did show loss of perchlorate and chlorate, their mechanisms failed to include contributions from uncatalyzed reactions. Specifically, they concluded that a dismutase is responsible for all elimination of toxic chlorite from the cell, catalyzing its disproportionation to dioxygen and chloride. However, the uncatalyzed disproportionation of chlorite to chloride and chlorate is not necessarily negligible. Korenkov et al. (1976) patented *Vibrio dechloraticans* Cuzensove B-1168 for perchlorate reduction; *V. dechloraticans* is nonsporulating, motile, and gram negative. Malmqvist et al. (1994) showed that *Ideonella dechloratans* can reduce chlorate, but they did not test for perchlorate reduction.

Over the past 8 years, work at AFRL has shown that perchlorate is metabolized by *Wolinella succinogenes*, strain HAP-1 (U.S. Air Force, 1994; Wallace and Attaway, 1994). *W. succinogenes* is capable of using either chlorate or perchlorate to oxidize Brewer's yeast. Pilot-scale systems at Tyndall AFB, Florida showed that perchlorate levels could be reduced from 3000 μg mL^{-1} to below 0.5 μg mL^{-1} (Hurley et al., 1997). HAP-1 was first isolated from a municipal anaerobic digestor. The bacterium is an antibiotic-resistant, nonsporulating, motile, Gram-negative, obligately anaerobic bacillus (Wallace et al., 1996). This sort of remediation may be effective at a site where perchlorate concentrations in water are high, but it very likely would be impractical for the treatment of drinking water unless it can be demonstrated to reach even lower perchlorate concentrations. AFRL's efforts have led to the implementation of a production-scale bioreactor in Utah for meeting perchlorate discharge requirements (Hurley, 1998).

Very little research has been done on perchlorate reductases. It may be possible to isolate these from bacteria and use them directly as reagents without the parent organisms. The mechanisms of these catalysts are not well understood, and the reductases themselves have not been well characterized. It may be possible to synthesize an analogous catalyst based on the reductase, but only if the fundamental bioinorganic chemistry is understood. Although nitrate reductases are based on molybdenum (Coughlan, 1980), it has not been verified whether this is also true for the perchlorate reductases.

Several projects are ongoing in the affected areas of EPA's Region 9 and were described at a recent meeting. Catts (1998) reported that a pilot-scale bioreactor has been constructed for the Baldwin Park Operable Unit in California using microbes derived from the food-processing industry. Operation of this pilot unit over a period of several months showed that perchlorate and nitrate could be reduced to undetectable levels, i.e., $[\mathrm{ClO_4^-}] \leq 4$ ng mL^{-1}. Ethanol was used as a food source and minerals were added to the system. The perchlorate-reducing microbes were not isolated or characterized. Sase (1998) reported on a specially designed anion exchange system with alternately regenerating columns that is undergoing testing by the Main San Gabriel Basin Watermaster.

Conclusions

Bioremediation and biological or biochemical treatment appear to be the most economically feasible, fastest, and easiest means of dealing with perchlorate-laden waters at all concentrations. Although other techniques may find application to select systems, e.g., point-of-use or small utilities, it appears that biological and biochemical approaches will play the greatest role in solving the perchlorate problem. Some situations may require a combination of technologies to best meet unique needs. This is a complex problem, and many of the standard technologies that have dominated the drinking water industry for the past several decades will not work for this contaminant when used in the conventional ways. Many of the possibly effective technologies have not been applied to drinking water specifically, and the interplay with other treatment technologies required for regulation compliance must be assessed. In addition to rapid implementation of effective and workable technologies, ongoing development will be required to find new technologies and to make them affordable and assimilable into the industry.

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