

Chapter 2

The Chemistry of Perchlorate in the Environment

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INTRODUCTION

Current interest in the chemistry of perchlorate is primarily due to its presence as a contaminant in groundwater and drinking water. The negatively charged perchlorate ion is composed of one chlorine atom surrounded by four oxygen atoms arranged in tetrahedral geometry. The perchlorate anion (ClO_4^-) commonly originates as a contaminant in the environment from the improper disposal of solid salts of ammonium, potassium, or sodium perchlorate¹. These salts are very soluble in water, and the perchlorate ion is kinetically inert to reduction and has little tendency to adsorb to mineral or organic surfaces. Therefore the perchlorate anion persists in groundwater, and its mobility in surface or groundwater is so high that perchlorate essentially moves with the flow of water (diffusion and convection controlled movement).

Compounds containing perchlorate include the oxidant in solid rocket fuel as well as that in fireworks, military ordinance, flares, airbags, and other applications where an energetic oxidant is required. Ammonium perchlorate is among the most important propellants because it has a high oxygen content and decomposes to the gaseous phases products water, HCl, N_2 , and O_2 , leaving no residue. Salts of perchlorate do not function well in solid-fueled rockets after the salts adsorb too much water, and improper disposal has led to environmental contamination. A report on the occurrence of perchlorate in drinking water by the American Water Works Association² indicates that perchlorate contamination is a national problem with significant concentrations being found in 26 states and Puerto Rico.

The presence of perchlorate in groundwater and drinking water is a potential health concern because perchlorate can impair proper functioning of the thyroid gland.³ The thyroid gland produces hormones that are maintained within narrow concentration limits by an efficient regulatory mechanism. Hormones required for normal development of the central nervous system of

fetuses and infants are secreted by the thyroid gland. These hormones are required for normal skeletal growth and development. In both infants and adults, thyroid gland hormones determine metabolic activity and affect many organ systems. Iodine is a component of the thyroid hormones, and one of the functions of the thyroid gland is to control iodide levels in the bloodstream. Perchlorate competitively inhibits the uptake of iodide ions by the thyroid; in fact, potassium perchlorate has been used to treat hyperthyroidism. In the discussion of the physical properties of the perchlorate ion that follow, it will be seen that the competitive inhibition is a consequence of the hydration energies of the two ions. A recent report by the National Research Council³ concluded that the levels of perchlorate that have been found in groundwater are unlikely to affect a healthy adult. However, the situation may be different for infants, children, pregnant women, and people with pre-existing thyroid disorders. The National Research Council suggested a reference dose of 0.7 $\mu\text{g}/\text{kg}$ of body weight, which is an order of magnitude lower than the dose with no observed effect on iodine uptake by the thyroid. The committee concluded that this reference dose would protect the health of even the most sensitive populations. This reference dose is elevated from the provisional reference dose of 0.1 $\mu\text{g}/\text{kg}$ suggested by the U.S. EPA in 2002. This latter value prompted the State of California to set a maximum contaminant level (MCL) of 6 $\mu\text{g}/\text{L}$ for perchlorate in drinking water. The higher reference dose translates to an MCL for perchlorate in drinking water of 24.5 $\mu\text{g}/\text{L}$.

The environmental chemistry community has an interest in the chemical and physical properties of perchlorate for the purpose of developing analytical methods, separation schemes, and destruction technologies. A number of reviews^{4,5,6,7} of perchlorate chemistry from this perspective have been published in recent years as well as the proceedings of a symposium.⁸ A recent review paper⁹ discusses bioremediation approaches to perchlorate contaminated waters. This chapter will not discuss bioremediation other than to comment on the mechanism of reduction.

REDOX PROPERTIES OF CHLORINE COMPOUNDS

Perchloric acid is the highest oxidation state of the element chlorine. A Latimer diagram¹⁰ for chlorine in acid solution (Figure 1) is a convenient way to summarize the redox potentials relating stable compounds of chlorine. The standard reduction potentials¹¹ in Figure 1 refer to 1 M acid solution at 25°C. The convention is that if a reaction combined from one or more half-reactions of complementary electron count has a positive change in reduction potential (ΔE), then the reaction as written is thermodynamically favorable.

The Gibbs free energy change for a combination of half-cell reactions at 25°C can be computed from the equation

$$\Delta G = -nF\Delta E$$

where ΔG is the Gibbs free energy change, n is the number of electrochemical equivalents in the half-cell reaction, and F is the Faraday constant equal to $9.6485 \times 10^4 \text{ J V}^{-1} \text{ mol}^{-1}$.

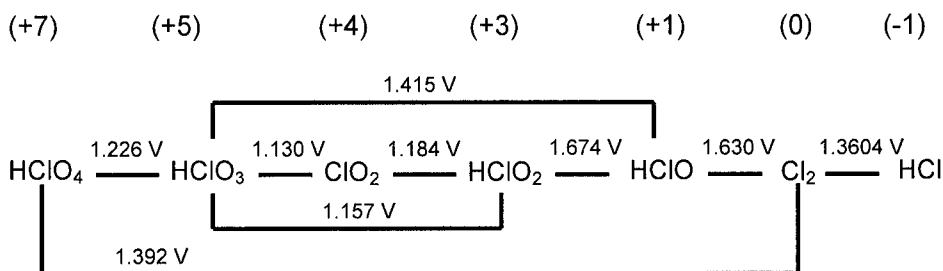
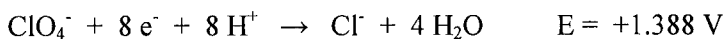


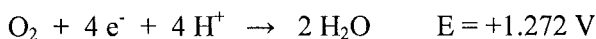
Figure 1. Latimer diagram giving the standard reduction potentials of the stable species of chlorine in aqueous acid solution at 25°C. The formal oxidation state of chlorine is given by the Arabic numeral above each species.

The Latimer diagram is particularly convenient for assessing the thermodynamic stability of individual species. If the potential to the right of a species shown in Figure 1 is more positive than the potential to the left, then the species is unstable to disproportionation. The perchlorate anion is formally in the +7 oxidation state of chlorine in which all valence electrons of chlorine have been lost. A striking observation is that all of the higher oxidation states of chlorine are relatively strong oxidizing agents with respect to the chloride ion.

The half-reactions relating perchlorate (ClO_4^-), chlorate (ClO_3^-), chlorite (ClO_2^-), hypochlorite (ClO^-), and chloride (Cl^-) can be combined to derive the thermodynamic potential for the eight-electron reduction of perchlorate to chloride



In comparison to the potential for oxidation of water to oxygen,¹¹



it is apparent that perchlorate is unstable with respect to the evolution of oxygen from water. Perchlorate reduction to chloride by this reaction does not occur spontaneously at ambient temperatures. In fact, concentrated perchloric acid is stable for many years. One of the authors has a bottle of high purity 72% perchloric acid that has lost none of its acid titer nor built up any chloride ion in a period of around 25 years. The failure of this reaction to occur spontaneously illustrates that reactions involving oxyanions of chlorine require oxygen atom transfer as well as electron transfer. For this process to occur, a mechanism must be available.

Frequently, the species of chlorine dissolved in solution are not in equilibrium, although some do exist in a rapidly established equilibrium. The reactions of HClO , Cl_2 , and Cl^- occur rapidly, and in acid solution HClO reacts with Cl^- to produce Cl_2 . Users of household bleach will realize that in a neutral or slightly alkaline solution, however, the situation is reversed and Cl_2 is the unstable species with respect to OCl^- and Cl^- .

Perchloric acid has a long history in analytical chemistry as an oxidant for destroying organic material by fuming at elevated temperature.¹² As will be noted later in this chapter, the active oxidizing agent in these reactions is molecular perchloric acid, not the perchlorate anion. The methodology for wet-ashing of organic materials for the determination of trace levels of metals is well-established.

The prevalence of perchlorate in drinking water has led to speculation that chlorine used to disinfect water is the source of perchlorate. A combination of individual half-reactions indicates that the disproportionation of Cl_2 to ClO_4^- and Cl^- is not favorable in acid solution. Gaseous ClO_2 has also been used as a disinfectant for water.¹³ The Latimer diagram indicates that this species is unstable to the formation of chlorate and chlorite in solution. The formation of perchlorate by disproportionation of ClO_2 , driven by the formation of HClO , is a thermodynamically favorable reaction:



However, even though this reaction is thermodynamically favorable, there is no clear evidence in the literature that the reaction occurs. A simple bimolecular reaction involving the transfer of two oxygen atoms has not been observed, and the mechanism of a process such as this will require intermediates that are not well understood. Since there is a fairly good database on the occurrence of perchlorate in drinking water,² it would be interesting to correlate reported perchlorate levels with the method of disinfection.

A draft report by the Massachusetts Department of Environmental Protection¹⁴ presented evidence that perchlorate is spontaneously generated in both commercial strength (15%) hypochlorite solutions and in household bleach. The suggestion was made that sodium hypochlorite spontaneously decomposes to chlorate by the reaction



which is not a thermodynamically favorable reaction in acid solution, but which is thermodynamically favored in alkaline solution ($\Delta G = -159.8 \text{ kJ mol}^{-1}$). The spontaneous decomposition of chlorate to form perchlorate was claimed, i.e.,



This is of potential significance since 15% commercial bleach solutions are used by some municipalities for disinfection of drinking water. Although hypochlorite is made by an electrochemical process, commercial bleach solutions are made by bubbling chlorine gas into a NaOH solution, precluding the introduction of perchlorate as an electrochemical reaction byproduct. As previously noted, just because a reaction is thermodynamically favorable does not mean it occurs fast enough to be significant at ambient temperatures. A kinetic pathway with an activation energy accessible at ambient temperature is necessary, and the formation of perchlorate by this route seems dubious.

Salts of chlorate have been used as defoliants, leading to speculation that these could be sources of perchlorate in groundwater.¹⁵ From the Latimer diagram in Figure 1, it is immediately apparent that the disproportionation of chlorate to perchlorate and chlorite in acid solution is not thermodynamically favorable. However, the potential for the $\text{HClO}_2/\text{HClO}$ redox couple is quite positive, which provides the driving force for the net reaction



to be thermodynamically favorable. The Latimer diagram indicates that chlorite is unstable to chlorate and hypochlorite in acid solution. However, chlorite is sufficiently stable kinetically that it is a readily identified and well-characterized species. The spontaneous formation of perchlorate and hypochlorite from chlorite,



is thermodynamically favorable in acid. The mechanism (or even a detailed sequence of reactions) by which either of these reactions might occur is unknown. Although chlorate may not disproportionate to produce perchlorate at ambient temperatures, perchlorate could be present in chlorate as a byproduct from manufacturing, as will be discussed later.

GENERAL PHYSICAL AND CHEMICAL PROPERTIES OF PERCHLORIC ACID AND THE PERCHLORATE ANION

Perchloric acid is among the strongest acids, and this species is completely dissociated in water. Simply stated, an acid is a proton donor and a base is a proton acceptor (Bronsted theory). The perchlorate anion is the conjugate base of perchloric acid. Within this framework, acid strength may be defined as the tendency to give up a proton. Acid-base reactions occur when an acid reacts with the conjugate base of a weaker acid to transfer a proton. When acid-base reactions occur between acids of comparable strength, the reaction proceeds to a measurable equilibrium that allows the relative strength of the two acids to be measured. In Table 1, relative strengths of a series of inorganic acids are given. For the very strong acids, pK_a values are approximate but relative strengths of the various acids are accurately known. The conjugate base of perchloric acid, the ClO_4^- anion, has its negative charge distributed equally over four oxygen atoms, and this delocalization of the conjugate base contributes to the increased acidity of perchloric acid. Perchloric acid occupies a unique position in the development of

Table 1. Inorganic Acid pK_a Values.^a

Acid	Conjugate Base	Approximate pK_a ^b
FSO_3H	FSO_3^-	<-12
HClO_4	ClO_4^-	-10
HI	I^-	-10
H_2SO_4	HSO_4^-	-10
HBr	Br^-	-9
HCl	Cl^-	-7
H_3O^+	H_2O	-1.74
HNO_3	NO_3^-	-1.4
HSO_4^-	SO_4^{2-}	1.99
HF	F^-	3.17

^aData from Smith, M. B. and March, J. *March's Advanced Organic Chemistry: Reactions, Mechanism, and Structure*, 5th Ed. New York: John Wiley and Sons, 2001, p 329.

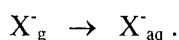
^bValues relative to water.

superacids.¹⁶ This designation was given to a solution of perchloric acid in glacial acetic acid. Concentrated perchloric acid is commercially available as a 70 to 72% solution, which corresponds to $\text{ClO}_4 \cdot 2\text{H}_2\text{O}$. Anhydrous perchloric acid can be prepared by vacuum distillation of concentrated acid in the presence of a dehydrating agent such as $\text{Mg}(\text{ClO}_4)_2$. However, the anhydrous acid is stable only for a few days at low temperature, decomposing to give $\text{HClO}_4 \cdot \text{H}_2\text{O}$ (84.6% acid) and ClO_2 .¹⁶ Perchloric acid in the absence of sufficient water is a very powerful oxidizing agent and a potent dehydrating agent. Contact between organic material and anhydrous or concentrated perchloric acid can produce explosions.¹²

Inorganic chemists, studying metal ions in solution, and electrochemists have long prized perchlorate salts and perchloric acid for use as an inert electrolyte because perchlorate is generally a non-complexing anion that is a poor nucleophile and is also kinetically inert to oxidation and reduction. The poor coordinating ability and low nucleophilicity are consistent with the delocalization of the negative charge of the perchlorate anion over four oxygen atoms. Although perchlorate complexes of metal ions are known, the stability constants are quite low. Because of its poor coordinating ability, perchlorate is widely used as a counter-ion in studies of metal ion complexation. It is used to adjust the ionic strength in kinetic studies involving transition metals where other electrolytes might complex the metal ion.⁴

The ClO_4^- ion is kinetically inert to exchange of oxygen atoms with water. The exchange of ^{18}O -labeled water with HClO_4 of normal isotopic composition at a concentration of 9 mol/L is insignificant after 63 days at 100°C . Based on these measurements, the half-life for exchange at room temperature is estimated to be greater than 100 years.¹⁷ By analogy to the other oxyanions of chlorine, the rate of exchange is anticipated to be at least first order in acid. Thus, the rate of exchange in neutral groundwater is expected to be negligible. This is anticipated because exchange can occur only by expansion of the coordination sphere of chlorine, a pathway expected to have a very high activation energy, or by protonation of the perchlorate anion, an unlikely possibility given the acidity of perchloric acid.

The hydration energy of perchlorate anions in water is among the lowest of common inorganic anions, a fact that has significant consequences for the separation and analysis of perchlorate. The hydration energy of an anion is the free energy for transfer of the unsolvated gas-phase anion to an aqueous solution, i.e.,



The standard free energy for this process correlates remarkably well with the Born equation, which gives the energy to charge a sphere of radius R in a medium of dielectric constant ϵ as

$$\Delta G_{\text{Born}}^{\circ} = \frac{Bz^2}{R(1-1/\epsilon)}$$

where z is the charge on the ion and B is a constant equal to $-69.47 \text{ kJ nm mol}^{-1}$ at 25°C .¹⁸ Although this equation represents the zeroth-order approximation to the computation of hydration energy, previous workers have empirically improved the fit by adjusting the radius by a constant and adding a small correction term. For singly-charged ions such as perchlorate, the hydration energy is predicted to decrease as the size of the ion increases. This trend is shown very clearly in the data in Table 2 for a series of inorganic anions commonly found in groundwater.

Table 2. Hydration Energies of Common Inorganic Anions^a

Anion, X^-	Thermochemical radius, nm	$\Delta G_{\text{h, obs}}$, kJ mol^{-1}
F^-	0.126	-465
OH^-	0.133	-430
HCO_3^-	0.156	-335
Cl^-	0.172	-340
Br^-	0.188	-315
NO_3^-	0.196	-300
H_2PO_4^-	0.200	-465
I^-	0.210	-275
ClO_4^-	0.240	-205
CO_3^{2-}	0.178	-1315
SO_4^{2-}	0.230	-1295
PO_4^{3-}	0.238	-2765

^aData from Moyer and Bonnesen.¹⁸

One of the most effective processes for the removal of perchlorate contamination from ground and surface waters is sorption on solid phase anion exchange resins. Commercially available anion exchange resins typically are based on cross-linked polystyrene or polyacrylate beads with

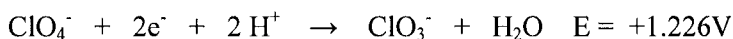
quaternary ammonium exchange sites. The process of transferring an anion from aqueous solution to the organic resin surface can be understood by an electrostatic model of anion transfer, which is discussed in some detail in Chapter 10 and by Diamond and Whitley¹⁹ and by Moyer and Bonnesen.¹⁸ Perchlorate is more strongly sorbed on these organic resins than other anions commonly found in groundwater. For singly-charged anions, this is the expected result based on the hydration energies. A generalization is that anions with small hydration energies are selectively transferred from an aqueous to a nonaqueous phase. Optimizing resin design for the selective sorption of perchlorate from groundwater is discussed in Chapter 10.

The thyroid gland in mammals appears to function as an ion exchanger with a preference for large, poorly-hydrated anions. It seems clear from the relative hydration energies of perchlorate, iodide ion, and pertechnetate and perrhenate anions (TcO_4^- and ReO_4^- , respectively, which have hydration energies very close to that of perchlorate), that these anions have common characteristics in this regard. Radioactive perrhenate and pertechnetate preferentially concentrate in the thyroid, and these anions are similar in size and charge density to perchlorate and iodide. The thyroid is not the only naturally occurring anion exchanger known. Others are noted in the section on perchlorate fate in the environment.

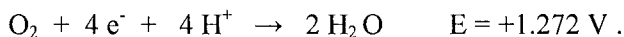
Another consequence of perchlorate's low hydration energy is the ease with which this ion can be separated from more hydrophilic ions for analysis by ion chromatography. Ion chromatography with detection by conductivity change is destined to be the workhorse for potable water analysis in the US for the foreseeable future.⁶ It is a fair statement that the discovery of groundwater contamination with low concentrations of perchlorate can be directly attributed to developments in ion chromatography. Optimization of the sorbant phase is obviously important, but in general, more hydrophilic ions are eluted before less hydrophilic ions.

INDUSTRIAL PREPARATION OF PERCHLORATE

Perchlorates are produced in a two-step electrochemical process in which sodium chloride is first oxidized to sodium chlorate, and then sodium chlorate is oxidized to sodium perchlorate.²⁰ The potential for oxidation of chlorate to perchlorate



is close to the potential for oxidation of water to oxygen



The production process is operated at high voltage in an undivided cell with an anode of either PbO_2 or Pt-coated material. The cell tank is operated as the cathode, which is typically bronze or 316 stainless steel. Sodium dichromate is added to the cell to prevent undesirable reduction of chlorate or perchlorate. Despite the potentially competitive evolution of oxygen, the efficiency at a Pt anode is 90 to 97%. The production of perchlorate (or even the capacity for production) in the United States is difficult to estimate because perchlorates are classified as strategic materials. Immediately following World War II, capacity was thought to be about 18,000 tons per year.

In contrast, the capacity for production of chlorate, an intermediate in the production of perchlorate is well known. For a number of years, the Electrochemical Society has published an annual report on the electrolytic industries, and sodium chlorate production is a major category. The two most recent reports are cited here.^{21,22} Sodium chlorate is produced by electrolysis of an acidic brine solution followed by crystallization to isolate the product. Over 95% of the sodium chlorate produced is used in the pulp and paper industry where it is converted to ClO_2 for use as a bleaching agent. The pulp and paper industry is under environmental pressure to convert to elemental-chlorine-free processes. The capacity for sodium chlorate in North America was 2.1 million tons in 2000, and the world capacity in the same year was estimated to be 3 million tons. For use in the paper industry, sodium chlorate is converted to ClO_2 by reduction with hydrogen peroxide in the presence of sulfuric acid. The similarities in potential for oxidation of brine to chlorate or to perchlorate have led to speculation that commercial grade sodium chlorate is contaminated with perchlorate.¹⁵ It has been reported that laboratory grade sodium chlorate contains 0.2% perchlorate on a weight basis, while the analytical reagent grade chemical has 200 to 900 ppm.²³ Specifications given in authoritative reference works²⁴ indicate that technical grade sodium chlorate is 99.5% pure, and the American Chemical Society analytical reagent specifications do not mention perchlorate as a significant impurity in sodium chlorate. It seems unlikely that perchlorate is present at more than a hundred ppm or so even in technical grade material. Nonetheless, given the large quantities of sodium chlorate used annually by the pulp and paper industry, sodium chlorate cannot be ignored as a possible source of perchlorate contamination in the environment. Salts of chlorate are used as defoliants, and this is also a possible source for the introduction of perchlorate into the environment.

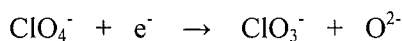
CHEMICAL REDUCTION OF PERCHLORATE

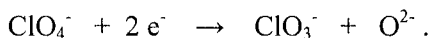
As mentioned previously, perchlorate reduction in aqueous solution is strongly favored thermodynamically, i.e.,



yet the kinetics of the reduction reactions indicate the rates of these processes are inhibited. Earley,²⁵ Espenson²⁶ and others^{27,28} have commented on the unusual lack of reactivity of perchlorate. Chemical reactions that lead to the reduction of perchlorate are of great interest to those seeking economical and efficient methods for the remediation of contaminated groundwater. Perchlorate does not react at an appreciable rate at ambient temperature with reducing agents commonly used in environmental remediation such as sulfite, dithionite, or zero-valent iron. Because of the large kinetic barriers, chemical reduction of perchlorate engenders great academic interest as well. Of notable scientific interest is the fact that some weaker reducing agents react with perchlorate at measurable rates, whereas stronger reducing agents fail to react at all. The fundamental issue is can the reaction rate be predicted, even if only to the precision of several orders of magnitude, from the properties of the reactants.

Taube²⁸ has noted that there are no examples of the removal of oxygen from perchlorate by typical nucleophilic reducing agents, and all of the well-characterized examples of perchlorate reduction under ambient conditions involve metal ions. The perchlorate anion is resistant to the solvated electron in both water and ammonia. This stability in the presence of such a strong and kinetically active reducing agent is understandable because perchlorate has no low-lying unfilled molecular orbitals, and thus it cannot readily take an electron to form the ClO_4^{2-} ion. Considering again the nucleophile as a reducing agent, the electrophile in this case is the chlorine center of perchlorate. For reaction with a nucleophilic reducing agent, the coordination environment of the tetrahedrally bound chlorine center must expand to five-coordination, and this seems to be an extremely high energy intermediate. However, perchlorate can be reduced if the reductant can accept or stabilize an O^{2-} group as a part of the reaction. Most evidence suggests that perchlorate is reduced only when atom transfer accompanies a change in the oxidation state of chlorine, i.e., when an oxygen atom is transferred to the reducing agent in a mechanism involving bonding of both chlorine and the reducing species to the transferring oxygen atom in the activated complex. In the case of perchlorate reduction, atom transfer can occur in both one- and two-electron processes as





There are well-defined examples of each process that have been described in the literature. Fairly detailed kinetic studies have been conducted involving the reduction of perchlorate by aquo ions of Ti(III),^{29,30} Ru(II),³¹ V(II), and V(III).³² Detailed studies of reactions between perchlorate and complex metal ions, including an HEDTA chelate of Ti(III)³³ and the Ru(II) complex $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$, have also been conducted.³⁴ Among the aquo metal ions, the order of reactivity is $\text{Ru(II)} > \text{Ti(III)} > \text{V(III)} \approx \text{V(II)} > \text{Cr(II)} \approx \text{Eu(II)} \approx 0$. The aquo ions of Cr(II) and Eu(II) do not appear to be reduced by ClO_4^- at measurable rates ($k < 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ at 25°C), despite the fact that both ions are thermodynamically powerful reducing agents. These facts led Taube to postulate that metal ions for which the transferring oxygen atom is stabilized by multiple bond formation with the metal ion – that is by formation of an “yl” complex* – are the most kinetically active. For certain metal ions there is an abrupt change in the acidity of water bound to the metal ion with an increase in oxidation state. For metal ions that form “yl” complexes in higher oxidation states, the disassociation constant of the protons bound to water are such that both are lost, and a strong multiple bond between oxygen and the metal ion forms. It is this bonding that influences the rate of perchlorate reduction. The aquo ions of Cr(III), Eu(III), and V(III) do not form “yl” complexes at normal pH values, but Ti(IV), V(IV), and Ru(IV) are thought to exist either predominantly in this form or within a readily established equilibrium.

The reaction of the Ti(III) aquo ion with perchlorate is a particularly well-defined example of a one-electron redox process since titanium exists only in oxidation states (III) and (IV) in aqueous solution. The rate expression for this reaction is given by

$$\text{rate} = -\frac{d[\text{Ti(III)}]}{dt} = (k + k'[\text{H}^+])[\text{Ti(III)}][\text{ClO}_4^-]$$

where $k = 1.9 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ and $k' = 1.25 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$. Taube²⁸ suggested that the acid dependent term in the rate expression may be spurious due to the use of Na^+ ion rather than Li^+ to replace H^+ while maintaining constant ionic strength. The reduction of perchlorate by Ru(II) could occur by either a one-electron or a two-electron redox process. The two-electron pathway gives Ru(IV) as an intermediate, which would react rapidly in a subsequent step with Ru(II) to give the observed Ru(III) product. Other complexes of

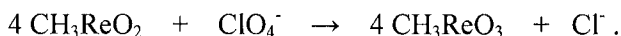
* yl complexes are M=O complexes such as V(IV)O^{2+} , referred to as the vanadyl ion.

Ru(IV) are well-characterized as oxo complexes with multiple bonds between the metal ion and oxygen. It is interesting that both V(II) and V(III) react with perchlorate at roughly the same rate. If the product of both reactions is the V(IV) oxo complex (vanadyl ion), then at first blush it would seem that the V(II) reductant, which is the stronger reducing agent of the two, would react faster in a two-electron process. However, experimental evidence suggests the two-electron pathway offers no advantage over the one-electron process (The first pK_a of V(III) is roughly three,³⁵ and the formation of an oxo complex under reaction conditions is precluded).

To put these reactions in perspective with regard to processing perchlorate-contaminated groundwater, Espenson²⁶ tabulated half-lives for the reaction of 10^{-3} M ClO_4^- with aqua metal ions at 25°C. The most rapidly reacting aqua metal ions among those discussed above are Ru(II) and Ti(III), which have calculated half-lives of 87 and 1470 hr, respectively. Thus, use of these metal ions in a direct or catalyzed process does not seem to offer a feasible method for treating groundwater even moderately contaminated with perchlorate.

A very clear example of a two-electron redox process has been reported by Espenson and coworkers,^{36,37} The unusual organometallic oxide methyltrioxorhenium(VII), CH_3ReO_3 , has been extensively investigated by Espenson and his group,^{38,39} mostly as a catalyst for the oxidation of organic substrates by hydrogen peroxide. This compound and its reduced form, methylrhenium(V) dioxide, undergo facile oxygen atom transfer reactions. The reduced Re(V) form has been shown to be a strong two-electron reducing agent able to abstract an oxygen atom from many substrates including amine oxides, sulfoxides, epoxides, halogenated oxyanions (XO_n^- including perchlorate), and certain metal-oxo species such as VO^{2+} . The coordination geometry of methyltrioxorhenium is tetrahedral, but the exact composition of methylrhenium dioxide is unknown. In aqueous solution, two water molecules appear to be bound to the Re center, and the structure is possibly that shown in Figure 2. Although the oxidation state of rhenium formally changes during these reactions, Espenson and coworkers³⁸ characterize the reactions as atom transfer reactions rather than electron transfer reactions.

The stoichiometry for the net reaction of perchlorate with methylrhenium dioxide is given by the equation



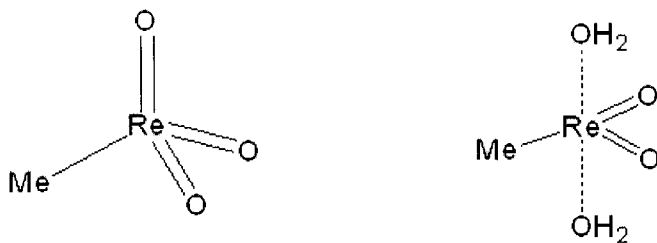


Figure 2. Structure of methylrhenium(VII) trioxide (left) and methylrhenium(V) dioxide (right).

An independent kinetic determination has shown that chlorate reacts with the Re(V) species nearly 10^4 times faster than with perchlorate. The eight-electron reduction of perchlorate is postulated to occur by a series of four step-wise two-electron reduction processes. The rate expression for the reaction of methylrhenium dioxide with perchlorate is deceptively simple

$$\text{rate} = -\frac{d[\text{ClO}_4^-]}{dt} = k[\text{CH}_3\text{ReO}_2][\text{ClO}_4^-]$$

where $k = 7.2 \text{ M}^{-1}\text{s}^{-1}$ and the first of four sequential reactions is the rate-determining two-electron transfer step. This Re(V) species reacts with perchlorate more than a thousand times faster than any other reducing agent observed to date. Espenson²⁶ relates this to practical applications by noting that the half-life of 10^{-3} M perchlorate in the presence of this Re(V) species has been reduced from hours for the aquo metal ions to a few minutes.

Abu-Omar and coworkers^{40,41} have studied the catalytic activity of Re(V) complexes in perchlorate reduction reactions. They used inexpensive reducing agents that might be useable in processing contaminated groundwater. They also investigated the catalytic activity of rhenium coordinated by oxazoline, particularly as applied to the net reaction between perchlorate and organic thioethers. The Re complex acts as a catalyst by oxygen atom transfer from a Re(VII) oxo complex to the organic thioether, producing the active Re(V) species. This complex reduces perchlorate by an oxygen atom transfer process that regenerates the Re(VII) species. Abu-Omar⁴¹ indicates that oxazoline complexes of Re are superior to the methylrhenium trioxide – methylrhenium dioxide catalyst pair for perchlorate reduction because a stronger reducing agent is required to reduce

the methyl complex to Re(V) and furthermore, that reaction becomes rate-limiting in the catalytic process. Methylrhenium dioxide also undergoes a polymerization process that renders it inactive.

A preponderance of the evidence suggests that reduction of perchlorate proceeds by an atom transfer reaction in which the transferring oxygen atom is bound to both chlorine and the reducing center in the activated complex. The only well-documented reactions occur at metal centers. Evidence for both one-electron and two-electron mechanisms has been presented. Taube²⁸ has suggested that rate enhancements occur when the oxidized product is stabilized by multiple bonding between the transferred oxo group and the metal center (formation of an $-yl$ complex). Earley^{25,33} has argued that the rate-determining factor is interaction of polarizable d-orbitals of the metal ion with a chlorine-centered orbital. Reactants in which the symmetry of the orbital donating the electron is appropriate to overlap with the accepting p-orbital (metal t_{2g} orbitals) will show a rate enhancement. Earley^{25,33} points out that effective interaction of the orbitals will not occur unless perchlorate begins to distort in the activated complex in the direction of a more planar geometry, thereby lowering the energy of these orbitals. Therefore, distortion of perchlorate from strict tetrahedral geometry is a precondition for rapid reduction. The ideas of Taube and Earley are not particularly at odds for the identification of reactive metal ions, since those which form stable $-yl$ ions are the same that Earley identified. The acid-dependence of the kinetics of perchlorate reduction by the Ti(III)HEDTA complex is somewhat unusual because it is second-order with respect to the concentration of acid. Liu, Wagner and Earley³³ offer this as a route by which perchlorate distorts from tetrahedral geometry, and they propose a mechanism in which coordinated perchlorate is protonated in the activated complex, a possibility that seems unreasonable given the weak basic character of the perchlorate anion. The kinetics for reduction of perchlorate by Re(V) complexes are completely independent of acid, and any mechanism that assumes protonation of the perchlorate anion as a precondition to reaction is untenable.

The instability of anhydrous perchloric acid and the explosive nature of ammonium perchlorate, in contrast with the kinetic inertness of perchlorate anions in aqueous solution, become understandable when the reaction pathways are considered. Anhydrous perchloric acid becomes kinetically active because a proton bound to oxygen is a legitimate way to stabilize the transfer of an oxygen atom. Ammonium perchlorate, like all ammonium salts of mineral acids, exists as molecular ammonia and perchloric acid when vaporized. Under these circumstances perchloric acid is predicted to be kinetically active.

ELECTROCHEMICAL REDUCTION OF PERCHLORATE

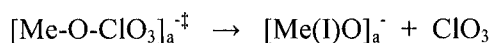
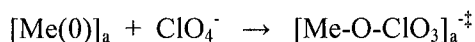
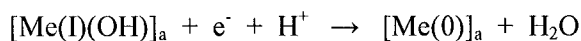
Electrochemical methods of effecting chemical reactions are often cited as potentially “green technologies” because the waste volume from electrochemical processes is usually minimal. Thus, direct electrochemical reduction of perchlorate and reduction via a pathway involving catalysis by a soluble species are potentially attractive routes for remediation of perchlorate-contaminated groundwater. As noted previously in this chapter, the reactivity of perchlorate toward reductants in solution is very low despite the strong thermodynamic driving force for its reduction. Direct electrochemical reduction rates for perchlorate are equally anomalous. Although perchlorate has been utilized as a non-reactive innocent electrolyte, the amount of experimental evidence for perchlorate reduction has been increasing. The literature dealing with electrochemical reduction of perchlorate was recently reviewed by Horányi⁴² and by Láng and Horányi.⁴³

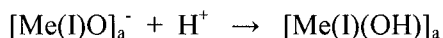
Perchlorate is sufficiently electrochemically inactive in nonaqueous solvents, such that the alkali metals of corresponding alkali metal salts of perchlorates, used in large excess over the reactant of interest as a supporting electrolyte, are reduced before the perchlorate ion.⁴⁴ However, there are definitive examples of the electrochemical reduction of perchlorate in aqueous solution. The electrochemical reduction of perchlorate has been studied, using a number of electrode materials, including Pt,^{45,46} WC,⁴⁷ Ir,^{48,49} Re,⁵⁰ Rh,^{51,52} Ru,⁵³ Tc,⁵⁴ Sn,⁵⁵ Co and Fe,⁵⁶ Ti⁵⁷ and Al.⁵⁸ Following Láng and Horányi,⁴³ these electrochemical reactions may be classified as those occurring at noble metal electrode materials (Pt, Ir, Rh, and Ru), at non-noble electrodes (WC, Re, and Tc), and as perchlorate reduction occurring in conjunction with the corrosion of metals (Co, Fe, Ti, and Al).

The reduction of perchlorate at noble metal electrodes has been studied the most thoroughly, and until the 1990s, it was generally thought that perchlorate was not reactive at these electrodes. From a theoretical point of view, these are perhaps the most interesting results, and several generalizations can be made. Cyclic voltammetry and other transient potential control techniques indicate that current for the reduction of perchlorate is observed only at positive potentials following a negative-potential process involving hydrogen evolution. The reaction requires prior adsorption of perchlorate anion at the electrode surface. Chloride ion reduction products, as well as other anions such as sulfate, inhibit the reaction. The reduction of perchlorate at non-noble electrodes does not have a well-defined pattern. At WC electrodes, perchlorate reduction occurs along with hydrogen evolution, and the process can be described as electrochemically induced hydrogenation. Horányi and co-workers observed perchlorate at electrodeposited Tc⁵⁴ and Re⁵⁰ layers. Reduction was inhibited

due to the formation of chloride ion, leading to speculation that adsorption of perchlorate is required for reduction to occur. The reduction of perchlorate at Sn⁵⁵ electrodes depends on the electrode surface properties and appears to require a surface oxide of Sn(II). The proposed mechanism involves reduction of ClO₄⁻ to surface-bound SnOHCl followed by reduction of this species to Sn liberating the Cl⁻ anion. Recent as well as older studies of the corrosion of some metals in perchlorate-containing acidic solutions indicate that the reduction of perchlorate cannot be assumed insignificant. The reduction of perchlorate occurs during the formation and breakdown of passive oxide layers on Al,⁵⁸ and Cl⁻ was definitively observed as a reduction product. Brown⁵⁷ observed the reduction of perchlorate during active dissolution of Ti metal. Recent observations on the corrosion of Fe and Co metals⁵⁶ in perchlorate-containing solutions indicate that perchlorate reduction occurs concurrently with metal dissolution. The open circuit potential at an actively corroding electrode occurs where the current for metal dissolution is equal to the current for hydrogen evolution. In perchlorate-containing solutions, the current for the cathodic process must include the current required for perchlorate reduction. This latter result has some implications for the processing of perchlorate-contaminated groundwater by finely-divided Fe metal. Although it appears that the reaction may be too slow to be of practical value, the fact that Fe dissolution occurs concurrently with perchlorate reduction and hydrogen evolution should be considered.

Analogous to the reduction of perchlorate in homogeneous solution, the reduction of perchlorate at an electrode (or any surface) must involve oxygen atom transfer. A mechanism for perchlorate reduction at a Ti electrode was proposed by Brown.⁵⁷ The basic principles of this mechanism were generalized by Lang and Horanyi,⁴³ and applied to the reduction of perchlorate at a Rh electrode. The concept of an atom transfer reaction at an electrode is not as well-defined as it is in solution, but for reactions at a normally oxygen- (or hydroxyl-) covered electrode, the first step is adsorption at an oxygen vacancy. Assume for the purpose of discussion that the surface of a generalized metal, Me, is covered with an air- and water-formed surface oxide that will be described as Me(I)OH. In further analogy with the solution chemistry, perchlorate will not react at the electrode at an appreciable rate if the surface is not capable of stabilizing the surface oxide, thus





where subscript “a” indicates a surface-stabilized adsorbed species, and the symbol ‡ indicates the activated complex. In this formulation, the surface species $[\text{Me}(\text{O})]_a$ represents an oxygen vacancy. The oxidation state of the predominant surface species varies with the metal species, and adjustment of the model should be made accordingly. Several concrete predictions arise from this model that can be tested experimentally. If perchlorate reduction occurs by a one-electron mechanism as shown in the four equations above, then the potential dependence of the current (Tafel slope) is predicted to be 120 mV per decade of current. If a two-electron process is indicated, then the Tafel slope is predicted to be 60 mV per decade at 25°C. The pH-dependence of the current will be governed by the pH-dependence of the predominant species on the electrode surface. Perchlorate is a very poor nucleophile, and other anions in solution are predicted to displace it from the oxygen vacancy.

The prognosis for remediation of groundwater or drinking water contaminated with low concentrations of perchlorate by direct electrochemical reduction of perchlorate is not favorable. Direct electrochemical reduction is slow enough to be controlled by reaction kinetics, thereby requiring a large surface area electrode. The reaction will proceed only with a large overpotential, and the reduction of protons to hydrogen, as well as other reactions, will invariably be competing reactions that are also promoted by high surface area. An electrochemical reaction catalyzed by a solution redox couple is also possible, but this process is controlled by the kinetics of the solution processes, which were shown to be kinetically sluggish in the previous section. However, the process discussed by Gu et al. in Chapter 16 may be feasible. In this reaction, perchlorate is removed from solution by sorption on an ion exchange resin, and a reducing agent generated in an electrochemical process is circulated through the resin to reduce the sorbed perchlorate.⁵⁹

FORMATION OF PERCHLORATE IN THE ENVIRONMENT

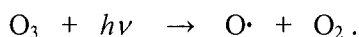
Perchlorate is known to occur naturally within extensive caliche deposits of the Atacama Desert in Chile. These deposits have been extensively mined for NaNO_3 and were the major source of nitrogen fertilizer in the world prior to 1930. Some ore processing is performed to improve NaNO_3 purity, yielding a product containing from 0.07 to 0.2 weight percent perchlorate. To gauge the magnitude of these deposits consider that Ericksen⁶⁰ indicates about 25 million metric tons of NaNO_3 were produced from this area between 1830

and 1980. Although the deposits have the appearance of evaporate minerals, the ^{14}N - ^{15}N and ^{16}O - ^{17}O - ^{18}O ratios have values characteristic of mass-independent fractionation, suggesting an atmospheric origin of the nitrate in which ozone was the oxidant. As discussed in Chapter 5, the perchlorate recovered from these naturally occurring ores also has an isotopic signature that indicates atmospheric ozone was involved in their formation. These factors point to a long term atmospheric deposition process as the source of nitrate and perchlorate in Chilean caliche.

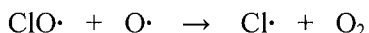
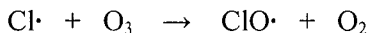
It is now well-established that atmospheric ozone carries a unique isotopic signature.⁶¹ Reactions with ozone occur in both the upper troposphere and the lower stratosphere. The air in the troposphere cools with increasing altitude above the earth's surface until a minimum temperature is reached at the tropopause, which is the boundary between the troposphere and the stratosphere at an altitude of approximately 10 km. The temperature increases with altitude in the stratosphere due to excess kinetic energy released by solar-driven photochemical reactions, extending to an altitude of approximately 50 km. Reactions involving ozone are the primary heat-generating reactions in this layer. The maximum concentration of O_3 occurs between 15 and 25 km above the surface of the earth, depending on latitude and season.⁶² Ozone is formed in the atmosphere by a three-body reaction in which oxygen atoms react with oxygen molecules to form a vibrationally excited ozone molecule that may either dissociate back to reactants or collide with an inert molecule M to form stable ozone:



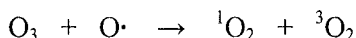
Photolysis of ozone to oxygen atoms and oxygen molecules also occurs:



The principle chlorine-containing species in the upper troposphere and lower stratosphere are hydrochloric acid, chlorine monoxide, and hypochlorous acid.⁶³ The species ClONO_2 is prominently mentioned in the literature as well. The chemistry of chlorine in the atmosphere has been extensively studied in the past two decades, in particular the influence of chlorine compounds on ozone depletion. Chlorofluorocarbon refrigerants are relatively unreactive in the troposphere and insoluble in water. Thus, they are neither oxidized in the lower atmosphere nor removed by rain. Photochemical reactions of these compounds in the stratosphere are a source of chlorine radicals that are responsible for catalytic cycles that lead to decreased levels of ozone, particularly in the polar regions. One of the catalytic cycles leading to ozone loss is the reaction sequence

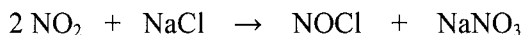


The combination of these two reactions represents the catalytic reaction of oxygen atoms with ozone to form two oxygen molecules, i.e.,

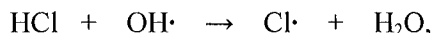


Although anthropogenic sources of chlorine may significantly influence the chemistry of chlorine in the present day atmosphere, they cannot be responsible for the naturally occurring perchlorate in Chilean desert deposits.

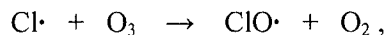
The chemistry of ozone and NO_2 is important in the troposphere, but the hydroxyl radical is generally acknowledged as the most important free radical in the lower atmosphere and appears to drive the oxidation chemistry of most species emitted into the atmosphere during the day.⁶⁴ The chemistry of halogens derived from sea water has been reviewed recently by Finlayson-Pitts.⁶⁵ Sea salt is a major source of halogens in the atmosphere of marine areas due to airborne particles generated by wave action. A number of reactions have been suggested that lead to chlorine atoms from NaCl aerosols, such as



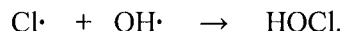
in which the nitrosylchloride species is known to photochemically dissociate to form NO and chlorine atoms. The nitric acid reacts with sea salt aerosols to form HCl that can react with hydroxyl radicals as



although this reaction is thought to be too slow to serve as a significant source of chlorine atoms. A more likely source of atomic chlorine is the reaction of hydroxyl radicals with solid NaCl crystallites to produce molecular chlorine, which is then photolyzed to chlorine atoms. Chlorine atoms rapidly react with ozone to form chlorine monoxide as follows



and chlorine atoms also react with hydroxyl radicals to form hypochlorous acid, HOCl:



Another reaction of importance is that of chlorine monoxide with NO_2 :



HOCl , ClO , and ClONO_2 along with HCl all have sufficiently long lifetimes and mobility to be transported to the stratosphere. Volcanic activity can be another significant source of chlorine compounds in the troposphere and lower stratosphere.

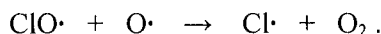
The Atacama Desert is extremely dry, receiving on average less than 3 mm of rain annually. The nitrate mineral beds lie in the rain shadow between the coastal range (altitude 1 to 3 km) to the west and the Andes Mountains to the east. One of the reasons the extensive nitrate beds exist is that this area has not had significant rainfall for millions of years. Michalski et al.⁶⁶ summarize the evidence for a photochemical process involving ozone leading to the generation of nitrate. They conclude that the extensive deposits are the result of atmospheric deposition of the solid phase produced by gas to particle conversion. These deposits could have accumulated from atmospheric deposition over a period of 200,000 to 2 million years under hyper-arid conditions such as those currently found in this area. The perchlorate in these nitrate beds must have been formed at the same time under similar conditions.

Isotopic ratios in the Chilean nitrate deposits suggest that perchlorate formed in the atmosphere by a process involving ozone as the oxidant. Older literature⁶⁷ suggests that HClO_4 may be a sink for atmospheric chlorine since it is not as susceptible to photodissociation as are lower oxidation states of chlorine. Researchers proposed that HClO_4 was formed by reaction of hydroxyl radicals with ClO_3 :

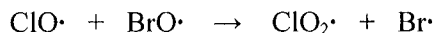


although proponents of this theory acknowledged that the reaction had never been observed even in the laboratory. Evidence for the possible presence of perchloric acid in the stratosphere was provided by balloon-borne FTIR spectroscopy at an altitude of 15 to 20 km in September 1993.⁶⁸ A significant fraction of the inorganic chlorine could not be accounted for by the sum of the species HCl , ClONO_2 , and HOCl . The reaction of ClO in sulfuric acid aerosols to form perchloric acid was proposed to account for the remaining reservoir of inorganic chlorine. Direct observation of perchloric acid in the stratosphere by laser ionization mass spectroscopy was reported, and the maximum concentration occurred at 19 km, which generally corresponds to the altitude at which ozone and ClO have concentration maxima.

The photochemistry and chemistry of chlorine oxides in the atmosphere has been studied in some detail,⁶³ and it is difficult to produce and maintain substantial quantities of either ClO₂ or ClO₃. There is little evidence for the latter species in the atmosphere, and the former is rapidly photolyzed to ClO and atomic oxygen. In fact, chlorine oxide reacts with oxygen atoms to form chlorine atoms and O₂ as follows



Chlorine atoms react with ozone to form ClO, thereby imparting the “ozone signature” to the oxygen atom. Chlorine dioxide can be generated in the atmosphere by reaction of ClO with BrO (generated by the reaction of ozone with bromine atoms) as



in a reaction that imparts to both oxygen atoms of ClO₂ the “ozone signature.” The characteristic photochemical reaction of ClO₂ in the gas phase is photodissociation to form ClO and oxygen atoms. However, the photochemistry in the condensed phase is different. In solution or a matrix, the photolysis products are chlorine atoms and oxygen molecules. Further reaction to produce higher oxidation states of chlorine appears to be possible only if the ClO₂ is sorbed to an ice crystal, sulfuric or nitric acid aerosol, or volcanic aerosol particle of some sort. Chlorine dioxide has a favorable partition coefficient to equilibrate into the condensed phase. We have previously noted that ClO₂ is unstable to disproportionation to HClO₃ and HClO₂. Furthermore, ClO₂ is thermodynamically unstable to disproportionation to HClO₄ and HOCl, although a reaction pathway leading to these products is difficult to envision. In aqueous solution, ozone is known to react rapidly with ClO₂ to form HClO₃. Thus, there appear to be ample precedents in the literature to oxidize chlorine atoms to HClO₃ by processes involving ozone as the source of the oxygen atoms. Ice crystals and acid aerosols containing water are fairly abundant in the atmosphere at the tropopause. Any reaction producing perchloric acid from chloric acid would be purely speculative, but for the sake of completeness, we will suggest ozone or oxygen atoms as the oxidant that takes HClO₃ to HClO₄. This reaction sequence gives rise to several predictions that could be tested in the laboratory. The conversion of HCl to perchlorate should be catalyzed by bromine and also by the presence of sulfuric acid aerosols.

FATE OF PERCHLORATE IN THE ENVIRONMENT

Despite the strongly oxidizing nature of perchlorate, it is known to be stable and nonreactive in aqueous systems. The high stability of ClO_4^- in water is due to its large kinetic barrier to reduction as well as its reluctance to bind to surfaces (poor nucleophile, poor coordinating ability). Simply lowering the Eh of water to below -200 mV does not induce abiotic reduction of the perchlorate ion.^{4,5} Perchlorate has reportedly been reduced by some transitional metal ions, but concentrations of these reduced transition metal ions in natural waters and geologic media are perhaps too low to impact the fate of ClO_4^- in the environment. Although the reduction of ClO_4^- by Fe(II) has been reported at elevated temperatures,⁶⁹ it does not occur at ambient temperatures and near-neutral pH conditions.⁷⁰ However, perchlorate can be reduced on iron surfaces where mixed valence iron-oxyhydroxides and Fe(II) co-exist.⁷¹ The reaction was found to accelerate under acidic pH conditions but was inhibited by the presence of soluble chloride ion. It seems clear from the results of electrochemical experiments that competitive adsorption at an active site is the mechanism of inhibition, as discussed in an earlier section. Recent studies have also revealed that nano-size iron powder significantly enhances the reduction rate of ClO_4^- , particularly at elevated temperatures⁷². The average size of iron nanoparticles used was about 57 nm, and they were synthesized in the laboratory by the reduction of ferrous ion using sodium borohydride (NaBH_4). Nevertheless, no measureable reduction of ClO_4^- occurs using bulk iron filings, microscale iron powders, or Fe(II) ion alone so that the role of iron or iron-containing minerals in the natural attenuation of ClO_4^- is also likely to be insignificant in the subsurface environment.

Perchlorate is poorly retained or sorbed by sediment minerals in the subsurface because of its negative charge and its noncomplexing nature with metal ions. Its large ionic size and low charge density reduce its affinity for metal cations and make it highly soluble and thus exceedingly mobile in natural aqueous systems. As such, perchlorate sorption to soils and sediments has not been widely observed nor extensively studied. The most comprehensive study of perchlorate retention and mobility in soils came from Urbansky and Brown,⁷³ who reported the adsorption and release of ClO_4^- in a variety of soils and minerals at varying perchlorate concentrations. Their findings support the widely-accepted view that perchlorate does not appreciably sorb to soils or minerals and that its mobility and fate are largely influenced by hydrologic and biologic factors. However, sorption of perchlorate appears to occur in soils with appreciable anion-exchange capacities (AEC). These soils act like anion exchangers, and perchlorate is sorbed by the replacement of other anions such as chloride, sulfate and

nitrate. Because of the chemical similarities between ClO_4^- , iodide (I^-), and radioactive pertechnetate (TcO_4^-) anions, the sorption behavior of I^- and TcO_4^- may also be used to infer the mobility of perchlorate in soil. A review of the literature indicates that only highly weathered soils dominated by iron and aluminum-oxyhydroxides and kaolinite are capable of exhibiting a significant AEC and, hence, adsorption capacity for I^- and TcO_4^- anions, which increases as pH decreases below the point of zero charge.⁷⁴ Ticknor and Cho⁷⁵ reported no detectable iodide sorption in the pH range of 7.5 to 8 on a wide variety of minerals such as calcite, chlorite, epidote, goethite, gypsum, hematite, kaolinite, bentonite, muscovite, and quartz. Whitehead⁷⁶ found that although freshly precipitated Fe(III) and Al(III) oxides could sorb a substantial amount of I^- at pH below 5.5, sorption decreased to zero as the pH increased to about 7.0. Routson et al.⁷⁷ studied the sorption of TcO_4^- on two highly weathered soils and found that TcO_4^- was poorly sorbed by the soils. Sisson et al.⁷⁸ observed that a sandy loam soil was unable to sorb TcO_4^- even under acidic pH conditions. Therefore, unless appreciable anion exchange capacity is confirmed, sorption and retention of perchlorate in soil sediments will likely be negligible.

The most significant factors affecting perchlorate fate in the subsurface are likely to be dilution as it migrates from the source, biological uptake, and possibly degradation under anaerobic conditions. Like many other contaminants, perchlorate plume concentrations tend to decrease significantly from the source area due to dilution. Flowers and Hunt⁷⁹ modeled the density-driven flow of a highly concentrated perchlorate brine with concentrations as high as 200 g/L (close to the solubility of NH_4ClO_4) exhibiting an estimated density of 1.1 kg/L. They indicated that release from the source would be mass-transfer limited under density-driven flow conditions with a time-scale of approximately 100 years. However, it is noted that at relatively high ClO_4^- concentrations, perchlorate may “salt out” or precipitate with cations such as potassium because potassium perchlorate has a relatively low solubility (~10 g/L at 20°C), thus decreasing its migration potential.

A widely studied mechanism for natural attenuation of perchlorate in the subsurface environment is anaerobic microbial degradation, which is described in detail in Chapters 12 to 14. For example, in a study of the potential of natural wetland systems to remove ClO_4^- , Tan et al.⁸⁰ reported that soil microbial degradation played a more important role in perchlorate attenuation than plant uptake and transformation. Indigenous soil microorganisms also were found to be responsible for rapid degradation of perchlorate under saturated near-surface conditions in a study of the fate of perchlorate in streambed sediments.⁸¹ In the unsaturated zone, microbial reduction of perchlorate may occur if electron donors such as acetate and

hydrogen are added.⁸² It has been reported that the addition of acetate and hydrogen greatly enhance the reduction rate of perchlorate, although a longer lag period is observed for hydrogen (41 d) than for acetate (14 d). The detailed biochemistry of the microbial reduction of perchlorate has not been extensively studied. Based on the previous discussion of perchlorate reduction, the detailed mechanism will surely involve metal ion catalysis.

Perchlorate uptake by plants, trees, forage and edible vegetation is known to occur and thus represents another natural attenuation and redistribution pathway.⁸³ In fact, phytoremediation of perchlorate has been proposed as a technology to remove ClO_4^- from contaminated soils and groundwater, particularly for shallow contamination.⁸⁴ In a field-scale study of perchlorate accumulation in aquatic and terrestrial plants, Tan et al.⁸⁵ reported a large potential for ClO_4^- accumulation in plant species such as smartweed, watercress, and 40 trees such as ash, chinaberry, elm, willow, mulberry, and hackberry. Concentrations of accumulated perchlorate in plant tissues was as much as 100 times higher than the bulk water perchlorate concentration. Furthermore, trees located closer to the stream had higher ClO_4^- accumulations than trees located farther away, likely caused by a relatively high ClO_4^- concentration closer to the stream. The bioaccumulation or concentration factor for ClO_4^- was even greater for wheat stems and heads (230 to 260) and alfalfa (380).³⁰ Because of its high solubility and mobility, perchlorate follows water movement within the plant and tends to accumulate more in leaves, where transpiration occurs, rather than in fruits. For example, perchlorate concentrations in soybean leaves grown in the greenhouse were found to be significantly higher than in the soybean seeds, and concentrations in tomato leaves were also higher than in the fruit³⁰. There is little evidence of perchlorate degradation or biotransformation in plants. The only evidence of ClO_4^- reduction in poplar tree tissue was reported by van Aken and Schnoor²⁹ using radio-labeled $^{36}\text{ClO}_4^-$. Their results indicated that 27% of ClO_4^- was translocated to the leaves, while 67% remained in the solution. Analysis of the radioactivity recovered in solution showed 68% as nontransformed ClO_4^- and about 32% as chloride-36, suggesting ClO_4^- degradation in the rhizosphere. Most of the radioactivity recovered in leaf extracts was nontransformed ClO_4^- , while small amounts of reduced metabolites were identified in the following percentages: Cl^- (1.6), ClO_2^- (2.4), ClO_3^- (4.8), and an unidentified organic compound (1.4). These studies provide evidence of possible perchlorate reduction and transformation inside plant tissues, although the overall impact on natural attenuation of perchlorate in the environment is yet to be determined. Plants which naturally contain anion exchangers should be investigated for perchlorate retention.

CONCLUSIONS

The persistence of perchlorate in groundwater can be understood from its chemical and physical properties and its chemical reactivity. Although perchlorate is a powerful oxidizing agent, its notorious lack of reactivity can be understood from the requirement that reduction involves oxygen atom transfer. Because perchlorate is relatively unreactive, remediation schemes involving direct chemical or electrochemical reduction are not effective. The low hydration energy of perchlorate anions favors sorption on organic anion exchange resins. Remediation methods involving collection on such resins prior to reduction or some other means of disposal are feasible. Biological systems that naturally reduce and degrade perchlorate are also a potentially practical means of remediating perchlorate-contaminated groundwater in a cost-effective manner.

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