SECTION 2
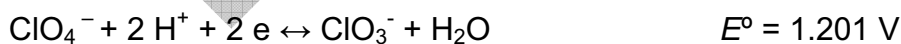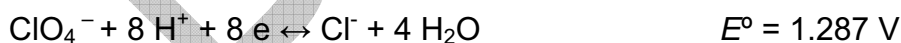**CHEMISTRY AND TOXICOLOGY OF PERCHLORATE**

I. INTRODUCTION

The Perchlorate Contamination Prevention Act (AB 826, Jackson) defines "perchlorate" as "all perchlorate-containing compounds" and defines "perchlorate material" as "perchlorate and all perchlorate-containing substances, including, but not limited to, waste perchlorate and perchlorate-containing waste." Within the context that DTSC is typically involved, terms such as "material", "substance", and "waste" assume very specific definitions that are usually applied rigorously. The Perchlorate Contamination Prevention Act, however, applies the plain language meaning of these terms. It is, therefore, necessary to discuss "perchlorate" and "perchlorate-containing material" in terms of both plain language and technical language commonly accepted by industry and the sciences. To that end, the following will provide an overview of "Perchlorate" including the forms of perchlorate, the toxicology of perchlorate, and the environmental fate and transport of perchlorate.

II. PHYSICAL AND CHEMICAL PROPERTIES OF PERCHLORATE AND PERCHLORATE COMPOUNDS

A. Perchlorate Ion[1, 2]

Chemically, the term perchlorate refers to the anion consisting of a chlorine molecule in a +7 valence state combined with four oxygen molecules in a typical sp3 tetrahedron. Identified by the chemical formula "ClO_4^- ", perchlorate represents the highest oxidized form of chlorine and is, therefore, a strong oxidizer. Despite its oxidative potential, the perchlorate anion is surprisingly stable and typically requires high activation energy in order to overcome the kinetic barrier to its reduction. These characteristics distinguish perchlorate compounds, and are responsible for their preferred use in many applications.

Perchlorate's oxidative ability is evidenced by the reduction potentials for its reduction to chloride and chlorate:

$$ClO_4^- + 8\ H^+ + 8\ e \leftrightarrow Cl^- + 4\ H_2O \qquad E^o = 1.287\ V$$

$$ClO_4^- + 2\ H^+ + 2\ e \leftrightarrow ClO_3^- + H_2O \qquad E^o = 1.201\ V$$

Based on thermodynamics alone, perchlorate is expected to be a powerful oxidizer. Perchloric acid, for example, should be able to oxidize water to oxygen (E^o = -1.229 V). The stability of perchlorate in aqueous solutions is, therefore, governed by kinetics and not a result of thermodynamics. The kinetic barrier to perchlorate's reduction is, however, not insurmountable. Wet ashing organic material with perchloric acid may be accomplished but requires the addition of heat and concentrated acid. Perchlorate may also be reduced by metal cations.

Several researchers have investigated the kinetics of the reaction of metal cations with perchlorate. Notable is the study by Liu (1984) which investigated the reaction of perchlorate with N-(hydroxyethyl)ethylenediamine-N,N',N'-triacetatopentaaquotitanium(III) ion (Ti(Hedta)). The net reaction is:

$$8\ Ti(Hedta) + ClO_4^- + 8\ H^+ \leftrightarrow 8\ Ti(IV) + Cl^- + Hedta^{3-} + 4\ H_2O$$
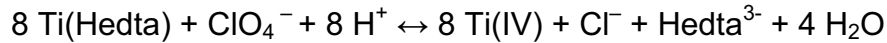
This reaction is significant because Ti(III) is reasonably stable in air and because Ti(IV) will, over the course of hours to days, form fine suspended crystallites of non-toxic TiO_2. Liu developed the following rate equation:

$$Rate = -\,d[Ti^{III}]\,/\,dt = (k\,[ClO_4^-]\,[H^+]^2 + k')(Ti(Hedta))$$

Where $k = 2 \times 10^{-3}\ M^{-2}\,s^{-1}$ and $k' = 2 \times 10^{-8}\ s^{-1}$

While Liu's research offers a possible treatment option for perchlorate contamination in aqueous mediums, reaction rates may be too slow to be practical in water treatment facilities. Other reductants have, also, been investigated, including methylrhenium dioxide (CH_3ReO_2) and other metal cations; however, chemical reductants typically have two characteristics that limit their application in industrial processes: they oxidize when exposed to atmospheric oxygen, and their rates of reaction are relatively slow. While these two limitations may be overcome by utilizing anaerobic conditions and increasing detention times, chemical reduction of perchlorate has found limited application in environmental remediation.

Perchlorate may also be reduced electrochemically. The electrochemical reduction of perchlorate ion has also been reported for a variety of cathodes, including platinum, tungsten carbide, ruthenium, carbon doped with chromium (III) oxide or aluminum oxide, aluminum, and titanium.

Biological reduction of perchlorate has also been investigated. Several bacteria species are known to produce perchlorate reductases capable of overcoming perchlorate's kinetic barrier to reduction. Unfortunately, these bacteria tend to prefer oxygen and tend to selectively reduce nitrate and chlorate. Despite these tendencies, some species are capable of reducing perchlorate in the presence of nitrate. In environmental remediation application biological reduction will in most cases be complicated by the presence of other oxidants which could act to slow (or stop) perchlorate reduction.

Because perchlorate exists as a charged particle in aqueous environments, the perchlorate anion is susceptible to ion exchange techniques. Typically, ion exchange resins are non-specific in that they unselectively remove all ions (anion in the case of perchlorate removal). However, more selective resins have been developed that preferentially select perchlorate, leaving bicarbonate, sulfate silicate, and other native background ions behind.

Membrane processes such as reverse osmosis and nanofiltration are also possible techniques usable for perchlorate separation. However, these processes are unselective and tend to completely demineralize water.

Perchlorate is widely known as a poor complexing agent. The perchlorate ion in non-polar, and the negative charge of the ion is evenly dispersed over the ion including the four exterior oxygen atoms. This charge dispersion may account for perchlorate's inability to bind to cations and result in perchlorate's extremely high solubility in both aqueous and non-aqueous media.

B. Perchloric Acid[3]

Perchloric acid, $HClO_4$, is the strongest simple acid. It is commonly available as an aqueous solution but can be produced as a pure anhydrous compound by vacuum distillation. Perchloric acid in a pure anhydrous form is unstable and has the potential to explosive. It is a colorless liquid which freezes at -112ºC and boils at 16ºC and 2.4 kPa without decomposition. Distillation at atmospheric pressure results in an azeotropic solution containing 72.4% $HClO_4$. Perchloric acid forms a number of hydrates commonly referred to as hydronium or oxonium perchlorates. When cold and dilute, perchloric acid is a weak oxidizing agent; when hot and concentrated, its oxidizing power increases and may react explosively in the presence of a reducing agent. Because of its oxidizing ability, ionic strength, and the high solubility of perchlorate salts perchloric acid is a common and useful analytical reagent.

C. Perchlorate Salts[3]

Perchlorate exists primarily as a salt. In addition, the heats of formation of metal and ammonium perchlorates are comparable to those for the corresponding chlorides. As a result, the reduction of these perchlorate compounds occurs with little net energy change. This characteristic is desirable in many applications which require a strong yet stable oxidizing agent such as perchlorate.

i. Ammonium Perchlorate

Ammonium perchlorate is a colorless, crystalline compound with a molecular weight of 117.5 and a density of 1.95 g/mL. Its solubility in water is 19.7 mass percent of solute[4]. It is synthesized by a double displacement reaction between sodium perchlorate and ammonium and ammonium chloride, and crystallized from water as the anhydrous salt.

Ammonium Perchlorate has been use extensively as a solid oxidizer in rocket propellants. As a result, the chemical, thermodynamic, and kinetic properties of ammonium perchlorate have been comprehensively investigated.
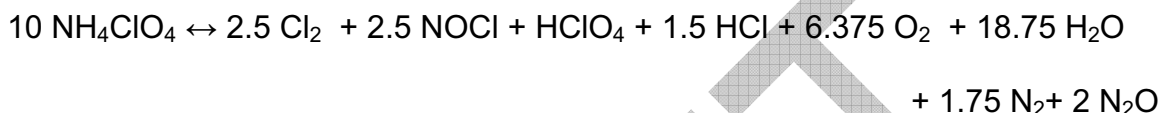
The activation energy required to initiate the decomposition of ammonium perchlorate has been observed to occur at one of three levels depending on temperature: 123.8kJ/mol (29.6 kcal/mol) for temperatures below 240ºC, 79.1

kJ/mol (18.9 kcal/mol) for temperatures above 240ºC, and 307.1 kJ/mol (73.4 kcal/mol) for temperatures between 400-440ºC.

The decomposition reaction is also dependent on temperature. For temperatures below 300ºC, the primary reaction is

$$4\ NH_4ClO_4 \leftrightarrow 2\ Cl_2 + 3\ O_2 + 8\ H_2O + 2\ N_2O$$
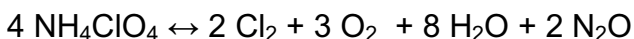
with the proportion on nitric oxide increasing at temperatures above 300ºC. Above 350ºC, the reaction seem to convert to

$$10\ NH_4ClO_4 \leftrightarrow 2.5\ Cl_2 + 2.5\ NOCl + HClO_4 + 1.5\ HCl + 6.375\ O_2 + 18.75\ H_2O$$
$$+ 1.75\ N_2 + 2\ N_2O$$

ii.   Alkali Metal Perchlorates

Alkali metal perchlorates are known and many are commonly available. Alkali metal perchlorates are typically either white or colorless crystalline compounds and may exhibit high solubility. Sodium perchlorate, $Na\ ClO_4$, has the highest water solubility of the group with a mass percent of solute of 67.2. Lithium, rubidium, and cesium perchlorate are also known in addition to the related ammonium perchlorate. Potassium perchlorate, $KClO_4$, is noteworthy because of its current and historical use in pyrotechnics and because it contains the highest percentage of oxygen (60.1%).

iii.   Group 11 (IB) Perchlorates

Copper and silver perchlorates are known. Copper (I) perchlorate, $CuClO_4$, and copper (II) perchlorate, $Cu(ClO_4)_2$, for a variety of complexes with ammonium, pyridine, and their organic derivatives and are reported to be effective as a burn-rate accelerator in solid propellants. Silver perchlorate, $AgClO_4$, is deliquescent and forms a light-sensitive monohydrate that is soluble in a variety of organic solvents. Silver perchlorate has been reported to react explosively.

iv.   Alkaline-Earth Perchlorates

Anhydrous alkaline-earth perchlorates have been prepared by heating ammonium perchlorate with the corresponding oxide or carbonate. Hydrates may be prepared by treating the metal oxides or salts with aqueous perchloric acid. Basic salts, of the form $M(OH)ClO_4$, have also been prepared where M is magnesium (Mg), calcium (Ca), or barium (Ba). Solubility of the alkaline-earth perchlorates tends to exceed 50 mass percent of solute at 25ºC.

v.   Group 12 (IIB) Perchlorates

Zinc perchlorate, cadmium perchlorate, mercury (i) perchlorate, and mercury (II) perchlorate are known

vi.   Group 13 (IIA) Perchlorates

Perchlorate compounds of boron and aluminum are known. Aluminum perchlorate forms a series of hydrates.

   vii.   Group 3 (IIIB) and inner Transition-Metal perchlorates
Yttrium, lanthanum, uranium, and tetravalent cerium perchlorate are known.

   viii.   Group 14 (IVA) Perchlorates
Organic carbon perchlorates are known as are diazonium perchlorates, oxonium perchlorates and perchlorate esters. Organic peroxides are known to decompose violently when heated, contacted with other reagents, or subjected to mechanical shock. In 1910, diazonium perchorate was reported to be the most explosive substance known.

   ix.   Group 4 (IV) Perchlorates
Titanium tetraperchlorate has been prepared, but the compound explodes when heated to 130ºC.

   x.   Group 15 (VA) Perchlorates
Nitrogen perchlorates have been used as oxidizers in rocket propellants. Hydrazine perchlorate and hydrazine diperchlorate have also been investigated for use as oxidizers for propellants. Nitronium perchlorate (NO_2ClO_4), nitrosyl perchlorate ($NOClO_4$), and phosphonium perchlorate ($P(OH)_4ClO_4$) are also known.

   xi.   Other Perchlorates
Group 16 (VIA), Group 5 (VB), Group 6 (VIB), Group 17 (VIIA) perchlorates are known as are perchlorates of the other transition elements.

III. TOXICOLOGY OF PERCHLORATE AND PERCHLORATE COMPOUNDS

(The information provided in this subsection has been paraphrased from "Public Health Goals for Perchlorate in Drinking Water" prepared by the California Office of Health Hazard Assessment (2004). See the original report for a more detailed analysis and a listing of cited research literature.)

   A. Metabolism and Pharmacokinetics[5]
Because perchlorate compounds are almost completely disassociated in aqueous environments, the metabolic and pharmacokinetic characteristics of perchlorate are dependent on the characteristics of the perchlorate ion (ClO_4^-) and are assumed to be independent of the source compound.

   i.   Absorption
Current data suggests that perchlorate is absorbed primarily through the gastrointestinal tract as a result of ingestion. Research indicates that a high percentage of perchlorate administered to human subjects is adsorbed and excreted in urine within 48 hours.

Based on its ionized state in aqueous environments, it is unlikely that perchlorate is significantly permeable through intact skin. Dermal adsorption is, therefore, expected to be limited.

Because of perchlorate's low vapor pressure, adsorption via inhalation is probably limited to exposures involving particulate inhalation. While occupational exposure of airborne perchlorate particles may represent a significant exposure route in industries that use or manufacture perchlorate materials, it is unclear what role inhalation plays in non-occupational exposures. In uses as an oxidizer, perchlorate residuals are known to remain in the solids and fumes of spent flares, solid rockets, and fireworks. While these materials would be expected to quickly fall to the ground where they would no longer represent an inhalation exposure risk, the exposure potential to individuals using manufactured products containing perchlorate materials is unknown. Proximity to these products during use may provide an opportunity for inhalation exposure as in individuals near burning flares or those viewing fireworks displays. Because of perchlorates low vapor pressure and the relatively large droplets produces in bathing showers, showering in water contaminated with perchlorate is not likely to represent a significant exposure route.

ii. Distribution

In the preponderance of animal studies, perchlorate has been found to concentrate in thyroid tissues. Perchlorate has also been found to concentrate in salivary gland and in the testes. This effect is most significant at lower dose levels with tissues levels matching plasma levels at higher doses. There is conflicting research that suggests that chlorate (rather than perchlorate) is what is being concentrated.

iii. Metabolism

Research suggests that perchlorate is adsorbed and subsequently excreted in tact. Results showed that orally administered perchlorate was not reduced in vivo.

iv. Excretion

Research indicates that approximately 95 percent of a dose of sodium perchlorate administered orally to human subjects was eliminated in the urine within 48 hours of being administered. Research further indicates an elimination half-life for humans of approximately 6 to 9 hours.

v. Physiological/Nutritional Role

Perchlorate has no known nutritional role. Early researchers observed that perchlorate displaced iodide in animal thyroid. Perchlorate has since been widely used to study thyroid activity and iodide uptake.

Ammonium perchlorate has been reported to cause weight gain in farm animals. This effect is currently considered to be a result of thyroid hormone inhibition (hypothyroidism).

B. Toxicology[5]

Perchlorate competitively blocks iodide at the thyroid gland. Adverse effects of perchlorate exposure in the low dose range are, therefore, expected to mimic those of iodide deficiency. These effects can be seen in geographic regions where iodine intake is inadequate.

Iodine deficiency results in declining thyroid hormone synthesis and secretion. This decrease causes the pituitary gland to increase production of Thyroid Stimulating Hormone (TSH), which in turn causes thyroid hypertrophy and iodine deficiency goiter. Manifestations of endemic iodine deficiency range from goiter or mild mental retardation in euthyriod subjects to severe mental deficiency and neurological effects in those with variable degrees of hypothyroidism. Children with severe iodine deficiency may suffer cretinism. Endemic cretinism is described as, neurologic cretinism and myxedematous cretinism. Neurologic cretinism is more common and is characterized by delayed growth of long bones, neurological complications such as deaf mutism, mental retardation, and spasticity. Myxedematous cretinism is characterized by delayed long bone growth, myxedema, and sometimes goiter.

i. Acute Toxicity

The acute lethal oral dose of perchlorate is estimated to be 214 mg/kg for a 70-kg for an adult human. Autopsy findings of animals subjected to acute toxicity testing include necrosis and hemorrhaging of the mucous membranes of the stomach, intestinal damage, pulmonary edema, vascular dilation, and congestion of the spleen, brain, and sinuses.

ii. Subchronic Toxicity

Perchlorate, historically, has been used as a pharmaceutical in the treatment of Graves' disease in humans. Graves' disease is an immune disorder in which immunoglobulins bind to TSH receptors of thyroid cells resulting in hyperthyroidism. Perchlorate has been used to reduce the production of thyroid hormones by inhibiting the uptake of iodide by the thyroid. The side-effects of these clinical studies provide examples of short duration oral exposure to perchlorates in dose ranges of 600 to 2,000 mg/day (sodium perchlorate). Reported side-effects include gastrointestinal irritation, nausea, sore throat, skin rash, lymphadenopathy, and agranulocytisis. Leukocyte counts of the single patent displaying agranulocytisis returned to normal when perchlorate treatment was discontinued. A number of animal studies have shown perchlorate to disrupt thyroid hormone regulation, induce hypertrophy and hyperplasia in thyroid follicular cells, and increase thyroid weight. More recent research also reports that perchlorate exposure decreases circulating 3,5,3'–triiodothyronine (T3) and L-thyroxine (T4) and increases serum TSH.

iii. Genetic Toxicity

No research on the genetic toxicity of perchlorate on humans was found. A variety of in vitro and in vivo genotoxicity tests of ammonium perchlorate indicate no mutagenic or clastogenic results.

iv. Developmental and Reproductive Toxicity

A number of toxicity studies have shown that perchlorate exposure causes a variety of adverse health effects in the offspring of test animals. Enlargement of both maternal and fetal thyroid have been observed. Other observations include morphometric changes to the brain (striatum, cerebellum, and corpus callosum); thyroid colloid depletion, hypertrophy, and hyperplasia; thyroid hormone disruption (T3 and T4); and increases in motor activity.

Clinical data regarding human developmental toxicity is limited. A single study is reported that observed the thyroid size of infants born to mothers treated with potassium perchlorate. The study observed a single slightly enlarged thyroid in the 12 infants studied. Because the study involved mothers being treated for hyperthyroid, it is unclear how (or if) these results may correlate to the general population. Several ecological and epidemiological studies have been reported. In general, these studies have calculated estimated dose rate from estimated perchlorate concentrations of drinking water by geographic region. Estimated dose rates where then compared to existing serum thyroid hormone data. Interpretation of the subsequent findings is challenging and results conflict. Researchers have pointed out that there are considerable uncertainties regarding estimations of perchlorate exposure in all available historical studies, and, in most cases, the studies include confounding factors that were either not controlled or only partially controlled.

v. Immunotoxicity

Interpretation of existing immunotoxicity data is difficult because of technical problems encountered in the studies, apparent inconsistency of high-dose study results, and the unknown biological significance of observed response enhancement. However, U.S. EPA, in its 2002 external draft Benchmark Dose Technical Guidance Document, found that three immune function parameters were altered by ammonium perchlorate exposure: suppression of in vitro peritoneal macrophage phagocytosis of L. monocytogenes; enhancement of the plaque-forming cell assay response to sheep red blood cells; and enhancement of local lymph node assay to 2,4-dinitrochlorobenzene. Other research found that perchlorate has a significant immunosuppressive activity in humans. Investigators found that perchlorate at 1.0 to 10 mmol/L inhibited IgG production and at 10 mmol/L inhibited IgM production.

vi. Hematological Effects

The use of perchlorate in the treatment of Grave's disease was discontinued in the early 1960s when it was noted that patients "occasionally" developed fatal

aplastic anemia. Typical treatment included perchlorate doses in the range of 6 to 14 mg/kg-day administered for three to eight months. Nonfatal agranulocytosis has also been reported in human patients treated with 14 mg/kg-day perchlorate for 12 days. Patients given similar doses for a two month period have been reported to have developed leucopenia. Similar adverse hematological effects have not been reported in rodents exposed to 30 mg/kg-day or 100 mg/kg-day, suggesting that humans may be more sensitive to these effects.

vii. Carcinogenicity

Several animal studies have been reported that have investigated the carcinogenicity of perchlorate. While these studies have suggested that perchlorate exposure may promote both benign and malignant thyroid tumors, the studies results are subject to interpretation because of the small number of animals per dose group, short duration of exposure and observation, lack of multiple dose groups, and co-exposure to other carcinogenic agents.

Several studies have attempted to correlate the prevalence of thyroid diseases (including malignancies) in humans to historical exposure to drinking water contaminated with perchlorate. These studies found no significant increase in the occurrence of thyroid disease (including cancer).

viii. Adverse Health Effects Associated with Iodide Deficiency and Low Thyroid Hormone levels

The most notable effect of perchlorate exposure is the reduction of iodide uptake by the thyroid. While the results of research documenting the effects of perchlorate exposure is limited, an extensive body of research exists that documents the health effects associated with iodide deficiency in humans. This research may provide persuasive evidence regarding the effects of reduced iodide uptake caused by perchlorate exposure.

A number of human studies have indicated that pregnancy stresses the thyroid, increasing the risk of abnormally low serum T3 and T4, thyroid enlargement, and goiter in pregnant women. The nature of these risks and the severity of effect is increased in areas of iodine deficiency. For these reasons, the National Academy of Sciences determined an Estimated Average Requirement of 160 µg/day and a Recommended Dietary Allowance of 220 µg/day for pregnant women, which is approximately 50 percent higher than those determined for adults in general.

Iodine deficiency disorders range from endemic goiter and less sever forms of brain damage to endemic cretinism characterized by mental and growth retardation, rigid spastic motor disorders, and deaf mutism. The impact of iodine deficiency depends on the degree of deficiency and differs depending on the effected individual's stage of growth. Fetuses, neonates, and infants suffer the most sever effects of iodine deficiency because of the irreversible impacts caused during a period of rapid structural and behavioral development. Cognitive

impairment is the most common finding in offspring of mothers suffering iodine deficiency and thyroid disorders during pregnancy.

Many published human studies have demonstrated that maternal thyroid deficiency during pregnancy affects neuropsychological development of the child. Animal studies have demonstrated that orally administered perchlorate may cause significant changes in the size of several brain regions. Animal studies have also shown that sever iodine deficiency causes abnormal fetal brain development in a number of animal species.

IV. FATE AND TRANSPORT

Atmospheric
A recent study [6] suggests that Chilean deposits, the largest known natural reservoir of perchlorate, originated primarily from atmospheric deposition of particles produced by gas to particle conversion over a period of 0.2 to 2.0 million years. The exact origin of the Chilean deposits is not completely understood yet. Although some researchers [7], ascribed a biological origin to Chilean nitrate, others have concluded that the nitrogen and oxygen isotopic analysis data were consistent with virtually all the nitrate being of atmospheric origin [8, 9].

Perchlorate can enter air from its production, use, accidental spills during loading and unloading for shipment, and accidental spills during transport. Perchlorate compounds have negligible vapour pressures but can exist in air for a short time as particulate matter. Perchlorate-containing particles are removed from the atmosphere mainly by gravitational settling or by rain. Soil particulate matter containing perchlorate can be transported in air. The fate and transport of perchlorate in air is largely determined by the size and density of the particles and by wind speed and direction.

Fireworks particles may vary from smoke size all the way up to chunks of the fireworks items themselves. And based on their size and weight, they fall out at different locations. Recent studies have detected perchlorate in soils, groundwater and/or surface water following fireworks displays, and therefore, the potential environmental impact of perchlorate from fireworks displays warrants further scientific study. [10]

Groundwater
Perchlorate has been considered the perfect conservative tracer in water, although this hypothesis has not yet been systematically tested in contaminated soils. The perchlorate anion's high solubility in water coupled with its limited propensity to adsorb to most soil surfaces leads to high mobility in aqueous environments. Perchlorate can persist in the environment for many decades under typical groundwater conditions because of its resistance to reactions with other available constituents in the subsurface. Once perchlorate has dissolved,

these characteristics lead to the formation of long and persistent contaminant plumes when released into either ground water or surface water. Dilution and precipitation are considered to be the two most important processes influencing the fate and transport of perchlorate in natural aqueous environments [11].

Adsorption processes are often influenced by pH, soil mineralogy, organic content, ionic strength, and competing ions [12,13]. The ionic salts of perchlorate are extremely soluble in water. Salts of perchlorate have different solubility in water, with potassium perchlorate being the least soluble.

In dilute concentrations typically found in groundwater, perchlorate behaves conservatively, with the center of mass of the plume moving at the same average velocity as the water. Dispersion will result in the contaminant front actually moving faster than the average groundwater velocity. Perchlorate is kinetically very stable under environmental conditions and will not react or degrade in solution under ambient conditions. Biodegradation of perchlorate in groundwater will not occur unless significant levels of organic carbon are present, oxygen and nitrate are depleted, and perchlorate-degrading anaerobic bacteria are present.

If perchlorate is released as a high concentration brine solution, the movement of the brine in a groundwater system may be controlled by density effects [14]. Flowers and Hunt (2000) explain that, depending on site release history, perchlorate can be distributed in the subsurface as a source area of undiluted perchlorate-contaminated brine, along with a plume of more dilute perchlorate-contaminated groundwater.

Perchlorate ions are very dense, so concentrated solutions tend to sink in slow-moving liquids [15]. The density contrast between the brine and ground water may cause the brine to move vertically with minimal influence by groundwater movement and little or no dilution. Brine pools may form on top of confining layers and significant perchlorate mass may move into low permeability confining layers by diffusion. The brine pools and perchlorate mass absorbed by the confining layers may serve as a long-term source of dissolved contaminant as perchlorate is released to the groundwater by diffusion. This type of release may occur where perchlorates have been manufactured, at rocket motor washout facilities, or other locations where perchlorate has been slurried or handled in concentrated brines. ITRC (2002) noted that in high-enough concentrations, perchlorate will precipitate out of solution, but the salts formed will re-dissolve readily.

The solubility of perchlorate salts are many orders of magnitude greater than drinking water standard. Consequently perchlorates have been released to the subsurface in a concentrated form. Perchlorate brine density severely limits recovery by mass transfer. As a consequence, groundwater extraction alone is inefficient for recovery and time scales are on the order of a hundred years. Long

term pump and treat approaches are not going to be economically efficient or protective of groundwater basins as a drinking water source [16].

Perchlorate is thermodynamically a strong oxidizing agent, with chlorine in the +7 oxidation state. However, it is unreactive toward most abiotic reducing agents in cold and dilute environments [17]. In contrast, a body of research has evolved that demonstrates that perchlorate is vulnerable to biotically induced reactions [18,19]. Specifically, perchlorate can be used as an electron acceptor in biologically mediated reactions under reducing conditions and be reduced to chlorate and, ultimately, chloride. The most common natural degradation pathway for perchlorate is respiratory microbial reduction. For this to occur, oxygen and nitrate must be depleted and an appropriate electron donor must be present. If reducing conditions exist or can be created in a perchlorate-contaminated aquifer, biotransformation of perchlorate into its less-toxic reaction products may occur. This phenomenon holds promise as a means to remove perchlorate from contaminated aquifers using in-situ bioremedial approaches.

Soil
Sorption is not expected to attenuate perchlorate concentrations because it absorbs weakly to most soil minerals. Both soil particles and perchlorate are negatively charged. The accepted mechanism for perchlorate adsorption to soil particles is through outer-sphere complexes, where the ions engage in simple electrostatic bonds [20] (Vanderwaals) and serve to balance electric charge on the surface [21,22].

Natural chemical reduction in the environment is also not expected to be significant. As a salt, perchlorate exhibits the characteristics of high solubility with the exception of potassium perchlorate which is sparingly soluble. The movement of perchlorate in soil is largely a function of the amount of water present. Perchlorate does not bind to soil particles. Perchlorate salts that are released to the soil in solid form will readily dissolve in whatever moisture is available. If sufficient infiltration occurs, the perchlorate will be completely leached from the soil. No partitioning coefficients or degradation rates in the environment are reported in the literature.

Perchlorate biodegradation in soil
Perchlorate is so stable in water that there are no natural factors to decompose it, only except some series of bacteria. Generally, perchlorate biodegradation results from microbially mediated redox reactions where perchlorate serves as the electron acceptor and is reduced via chlorate to chlorite. Chlorite then undergoes a biologically mediated dismutation reaction, releasing chloride and oxygen. The oxygen is subsequently reduced, provided sufficient electron donors are available. [23,24,25]

The electron donor in soil may be all kinds of organic matters, including alcohols (e.g., ethanol, methanol), volatile fatty acids (e.g., acetate) and so on. Research

suggest that bacteria capable of perchlorate reduction are ubiquitous in subsurface environments. [26]

Plants
Soil moisture containing perchlorate in solution, can be taken up by plants through the roots and several ecological studies have demonstrated the tendency of some plants to concentrate the perchlorate in plant tissues. Some perchlorate may be held in solution in the vadose zone by capillary forces. In arid regions, crystallized perchlorate salts may accumulate at various horizons in the soil due to evaporation of infiltrating rainfall that leaches perchlorate from shallower depths.

At this time, the ecological impact of perchlorate is not well known, and as such, it is premature to speculate what measures, if any, might be appropriate. In addition, measures to abate perchlorate will be influenced by a number of factors, including rainfall and irrigation, dilution, natural attenuation, soil adsorption, and bioavailability.

Site characterization is crucial to assess the influence of soil physicochemical characteristics on the sorption behavior of the perchlorate ion. Settings such as river and stream valleys, fractured rock, and karst strata offer many challenges. Fate and transport modeling should be developed according to site-specific field conditions.

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