



Environmental Significance of Perchlorate in Aqueous Systems and its Removal Technologies

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Abstract— Perchlorate (ClO_4^-) is a naturally occurring anion, commonly found in ammonium, potassium, and sodium salts. It is extensively used as an oxidizer in solid rocket propellant, fireworks, batteries and automobile air-bags. Its contamination to environment is generally associated with the release of ammonium perchlorate by defense contractors, military operations and aerospace programs. This anion is very much persistent in the environment due to high activation energy associated with its reduction. At high concentration perchlorate can affect thyroid gland functions, where it is mistakenly taken up in place of iodine. Also, perchlorate has recently been added to the U.S. Environmental Protection Agency's (EPA) drinking water Candidate Contaminant List. It has been found at high concentrations ($>1000 \text{ mg/L}$) in surface water and groundwater. Due to the stability in water systems it is difficult to remove by existing physico-chemical techniques such as adsorption, anion exchange and membrane filtration, therefore bioremediation is a promising method to reduce perchlorate from water systems. Biological perchlorate degradation depends on several environmental factors such as presence of nitrate and chlorate, dissolved oxygen, carbon-source and temperature. In this review, environmental occurrence of perchlorate, its toxicity in various living organism and remediation processes from water environment have been discussed.

Keywords— Perchlorate, anion-exchange, rocket propellant, thyroid, drinking water, bioremediation.

I. INTRODUCTION

At present, perchlorate contamination is known to be a problem only within the United States. While it appears that drinking water can be satisfactorily treated, current analytical methods cannot reach the detection limits suggested by toxicology studies. In addition, it is not possible to accurately estimate the costs associated with treatment since nearly all work has been conducted on laboratory or pilot scales. Accordingly, issues associated with mass production, implementation, capitalization, and economies of scale are unresolved and preclude a satisfactory cost analysis at this time. The EPA added perchlorate to its Contaminant Candidate List (CCL) for drinking water in 1998 following discoveries of its presence in drinking water supplies throughout the southwestern United States (Dollard 1992). The

fundamental physical and chemical nature of perchlorate make it difficult to uniquely analyze for and to remediate, especially at the low concentrations typically encountered (i.e., $<500 \text{ mg mL}^{-1}$). Although ion chromatography is capable of determining very low levels (e.g., 5 ng mL^{-1}), retention time is not considered a unique identifier, and known confirmatory tests have much higher detection limits. Perchlorate ion is unreactive as a ligand and its salts are extremely soluble, even in organic solvents. Despite its strength as an oxidizing agent, perchlorate is nonlabile, that is, very slow to react. While it appears that drinking water can be satisfactorily treated, current analytical methods cannot reach the detection limits suggested by toxicology studies. In addition, it is not possible to accurately estimate the costs associated with treatment since nearly all work has been conducted on laboratory or pilot scales. Accordingly, issues associated

with mass production, implementation, capitalization, and economies of scale are unresolved and preclude a satisfactory cost analysis at this time. The objective of this review is to provide an overview of the general chemistry, occurrence, toxicology, remediation technologies available for perchlorate.

II. OCCURRENCE

Most of the perchlorate contamination has been associated with military activities or defense contractors (**Gullic 2001**). Ammonium perchlorate is used as a solid oxidant in rocket propulsion. Perchlorate also turns up in fireworks. Perchlorate has been found in groundwater and in surface waters in several western states of U.S., including the Colorado River. Concentrations ranging from 8 ng mL⁻¹ to 3.7 mg mL⁻¹ have been measured from this location. The extensive use of Colorado River water in this region and the proximity of some of these sites to the river have heightened the concern. Perchlorate salts have been found along the Las Vegas Wash. Although additional toxicological studies are ongoing an action level of 18 ng mL⁻¹ has been adopted by California, U.S. Other states have set alternative concentrations, such as Arizona (14 ng mL⁻¹) and Texas (22 ng mL⁻¹). EPA's Regional offices have also set different limits for clean-up of contaminated sites. Low concentrations of perchlorate have been detected sporadically around the U.S., for example, in New York and Iowa. These sites are not associated with any known defense activities, and the source of this perchlorate is not known. It has been speculated that historical use of Chile saltpeter from decades ago may be responsible for some. It is well-known that caliche ore deposits in Chile (which are refined to make sodium nitrate fertilizer) contain natural perchlorate that persists in the final product as a small residue (**Ericksen, 1983; Schilt, 1979; Urbansky et al., 2001**). Manufacturing changes have further reduced this concentration (currently =100 µg g⁻¹) to 5–10% or less (**Lauterbach, 2001**). At present, natural saltpeter fertilizers and products derived from them make up less than 0.1% of the fertilizer applied in the U.S. Data on the historical use of saltpeters is almost nonexistent.

III. TOXICITY

The perchlorate ion is similar in size to the iodide ion and can therefore be taken up in place of it by the mammalian thyroid gland. In this way, perchlorate can disrupt the production of thyroid hormones and thus disrupt metabolism. Additionally, other physiological systems may be indirectly affected.

In 1992, the U.S. Environmental Protection Agency (EPA) reviewed and assessed the health effects of perchlorate administered chemotherapeutically to patients with hyperthyroidism (**Dollarhide, 1992, 1995 and Stanbury, 1952**). This study showed a no observable adverse effects level (NOAEL) of 0.14 mg kg⁻¹ day⁻¹. Doses of 6 mg kg⁻¹ day⁻¹ or more for periods of at least 2 months led to fatal bone marrow changes. The EPA study recommended the following safety/error factors: 10 (nonchronic study), 10 (sensitive persons), 10 or 3 (database error margin) and allowed for two possible uncertainty factors, 1000 and 300. Using the somewhat arbitrary, but relatively accepted, uncertainty factor of 300, the California DHS established 18 ng mL⁻¹ as the action level for initiating remediation and stopping water usage (**Cal DHS, 1997b**). This cut-off assumes a 70-kg person consuming 0.5 mg perchlorate for each kilogram body mass who drinks 2 L of water daily (18 ng mL⁻¹ × 0.016 mg mL⁻¹ = 0.14 mg kg⁻¹ day⁻¹ × 70 kg × 1 day/2 L, 300). The 0.5 mg number introduces a rounding error that was carried through (**Cal DHS, 1997b**). This 18 ng mL⁻¹ action level has been adopted informally by other governmental agencies in the region as well. Using the same assumptions, we would calculate that harmful thyroid effects begin to occur at 49 mg mL⁻¹, and fatalities occur at 210 to 490 mg mL⁻¹. Meanwhile, the European Communities (1982) set a maximum admissible guide level of 20 mg NaClO₄ mL⁻¹ for drinking water. This corresponds to 16 mg ClO₄⁻ mL⁻¹. Perchlorate exerts its most commonly observed physiological effects on or through the thyroid gland. The primary effect is a decrease in thyroid hormone output. The thyroid gland takes up iodide ion from the bloodstream and converts it to organic iodide in the form of hormones that regulate metabolism. The mechanism responsible for this process, the cellular iodide pump, preferentially selects for anions on the basis of ionic volume: I⁻ » SCN⁻ < ClO₄⁻, TcO₄⁻ (**Chiovato et al., 1997; Cooper, 1991; Foye, 1989 and Orgiassi, 1990**). Consequently, the presence of any large anion in the serum reduces thyroid hormone production. This phenomenon was once used pharmaceutically to treat hyperthyroidism, which is known as Graves' disease (**Foye, 1989; Chiovato et al., 1997; Cooper, 1991 and Orgiassi, 1990**). Chemotherapeutic use of perchlorate was reduced substantially in the United States after several instances of aplastic anemia and renal damage were observed (**Foye, 1989 and Hobson, 1961**). Domestic perchlorate use is now restricted almost exclusively to use as a diagnostic tool for the evaluation of thyroid hormone production. As a diagnostic tool, perchlorate is still the standard for evaluating thyroid activity; the protocol at the University of California, Los Angeles (UCLA) requires a dose of 0.6 g (pediatric) or 1 g (adult) (UCLA, 1997). Although

perchlorate has been used as a treatment for hyperthyroidism, under the right circumstances it also can act as goitrogen in rodents and prevent thyroid hormone formation by interfering with iodide uptake (**Capen and Martin, 1989**). The low level of hormone is recognized by the pituitary gland which then stimulates the thyroid gland to work harder, eventually leading to goiter. A recent study of thyroid hormone levels in the Sprague-Dawley rat supported the EPA reference dose of $0.14 \text{ mg kg}^{-1} \text{ day}^{-1}$. Male rats exhibited a thyroid NOAEL of $0.44 \text{ mg kg}^{-1} \text{ day}^{-1}$, but females exhibited a thyroid NOAEL of only $0.124 \text{ mg kg}^{-1} \text{ day}^{-1}$ (**King, 1995**). Potassium perchlorate has been used to treat thyrotoxicosis without toxicity at doses ranging from 40 to 120 mg day^{-1} (**Cooper, 1996**). If we assume a daily intake of 3 L of water, this would correspond to 13 to $40 \text{ mg KClO}_4 \text{ mL}^{-1}$, or about 9 to $12 \text{ mg ClO}_4^- \text{ mL}^{-1}$. This is a factor of about 1000 times the California DHS action level, but close in line with the European Communities level. It is unknown whether secondary effects resulting from decreased thyroid function, indirectly caused by perchlorate, will be consequential.

Perchlorate can directly affect organs and tissues in addition to the thyroid gland. The mouse mammary gland has a mechanism similar to the thyroid iodide pump that is inhibited by perchlorate (**Rillema and Rowady, 1997**); however, it is unclear whether this has any significance for human health. Much of what is known about perchlorate's effects on living organisms is derived from studies of acute toxicity over relatively short periods of time rather than chronic exposure to very low concentrations over a lifetime.

IV. REMEDIATION AND TREATMENT

4.1 Overview

The best choice for any treatment technology will require a careful evaluation of options and probably some combination of techniques. We must remember that the potential for success of any technology is dependent on two factors: the establishment of a safe level of perchlorate and a quantitative chemical analysis that ensures this safe level is in fact achieved.

4.2 Remediation by Physical Processes

Membrane Based Techniques Membrane-based techniques can be effective, but they suffer from several drawbacks. While reverse osmosis (RO) would affect sufficient remediation, it can be impractical for a municipal treatment system because of the fouling of membranes and the associated cost. RO-treated water has to be remineralized with sodium chloride, sodium bicarbonate,

and other salts to prevent degradation of the distribution system and to make the water palatable, since deionized water generally is considered to have an unpleasant taste.

4.3 Anion Exchange Techniques

Perchlorate ion is strongly retained by quaternary ammonium resins but initially in low concentration in most cases. For example, it might be necessary to reduce perchlorate concentration from 1 mg mL^{-1} to 20 ng mL^{-1} . Assuming that a chloride-form resin is used, the presence of phosphates, carbonates, and sulfate remains an issue. Although it may be possible to produce a resin salt that matches the proportions of the major anions in the influent water, to do so would be extremely inconvenient. In addition, the low concentration of perchlorate in the raw water substantially reduces the driving force for its removal. In other words, to adequately remove the perchlorate may require essentially demineralizing and remineralizing the water, depending on its anion content. It is possible to modify resins so as to improve their selectivity for particular anions. **Kawasaki et al. (1993)** have used Dowex 1X-8 to selectively preconcentrate perchlorate; the selectivity of the resin for perchlorate is about 100 times that for chloride and 10 times that for nitrate.

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

4.4 Remediation by Chemical and Electrochemical Processes

Here we refer to reduction specifically in the redox sense of adding electrons. From the previous studies of the oxidation-reduction reactions of perchlorate, it is clear that chemical reduction will play no role in drinking water treatment in the near future. Chemical reduction is simply too slow. Unless safe new catalysts become available, this appears unlikely to change. Commonplace reductants (e.g., iron metal; thiosulfate, sulfite, iodide, and ferrous ions) do not react at any observable rate, and the more reactive species are too toxic (and still too sluggish). In addition, any reductant will necessarily have oxidized by-products. The toxicity of the by-products must be considered. There is more hope for electrochemical reduction. A decided advantage of electrochemical reduction is the large amount of control over kinetics that results from control of the operating potential. Electrode reduction kinetics

reasonably can be viewed as being limited by three factors: (1) diffusion of the ions to the electrode surface, (2) association with the electrode surface, and (3) activation past the overpotential required to reach the transition state. Although overpotential usually is the greatest barrier, it also is the one that can be dealt with best. Because we are not concerned with other reductions (including reducing water to hydrogen), the only barrier is the limit of a negative potential that is practical and safe to apply. Fortunately, most of the materials in raw water are reducing agents. Although some may be affected by electroreduction, this probably does not present a significant obstacle. To date, this option has not been explored for low-concentration treatment at anything approaching pilot scale. Although electrochemical technologies are well established for other industries (e.g., electroplating of metals, electrolysis of brine), they have not yet found a place in drinking water treatment. In this category, it appears that the most successful strategies for remediating perchlorate contamination will utilize metal cation-catalyzed reduction by either chemical or electrochemical means. Several metal chelates have potential at this point, especially if embedded in an electrode for use in electrochemical reduction.

4.5 Biological and Biochemical Techniques

Bioremediation is another matter entirely, and it may prove to be the most practical approach. A number of bacteria that contain nitrate reductases (Payne, 1973) are capable of reducing perchlorate (Schilt, 1979). *Staphylococcus epidermidis* is capable of reducing perchlorate in the absence of nitrate. Cell-free extracts of nitrate-adapted *Bacillus cereus* also reduce perchlorate (and chlorate) (Hackenthal, 1965). As would be expected, sodium perchlorate, especially in higher concentrations, has been shown to be toxic to several species of bacteria. Like *S. epidermidis*, *B. cereus* is also pathogenic. *B. cereus* is known for food poisoning, ocular infections, and pneumonia with other sites sometimes affected (Tuazon, 1995). Rikken et al. (1996) reported that perchlorate and chlorate are reduced to chloride by *Proteobacteria* with acetate as a nutrient (reductant) at near-neutral pH. Specifically, they concluded that a dismutase is responsible for all elimination of toxic chlorite from the cell, catalyzing its disproportionation to dioxygen and chloride. However, the uncatalyzed disproportionation of chlorite to chloride and chlorate is not necessarily negligible. Korenkov et al. (1976) patented *Vibrio dechloraticans* Cuzenove B-1168 for perchlorate reduction; *V. dechloraticans* is nonsporulating, motile, and gram negative. Malmqvist et al. (1994) showed that *Ideonella dechloratans* can reduce chlorate, but they did not test for perchlorate reduction. Perchlorate can also be

metabolized by *Wolinella succinogenes*, strain HAP-1 (U.S. Air Force, 1994; Wallace and Attaway, 1994). *W. succinogenes* is capable of using either chlorate or perchlorate to oxidize Brewer's yeast. Pilot-scale systems at Tyndall AFB, Florida in USA showed that perchlorate levels could be reduced from 3000 mg mL⁻¹ to below 0.5 mg mL⁻¹ (Hurley et al., 1997). HAP-1 was first isolated from a municipal anaerobic digester. The bacterium is an antibiotic resistant, nonsporulating, motile, Gram-negative, obligately anaerobic bacillus (Wallace et al., 1996). This sort of remediation may be effective at a site where perchlorate concentrations in water are high, but it would be impractical for the treatment of drinking water unless it can be demonstrated to reach even lower perchlorate concentrations. Very little research has been done on perchlorate reductases. It may be possible to isolate these from bacteria and use them directly as reagents without the parent organisms. The mechanisms of these catalysts are not well understood, and the reductases themselves have not been well characterized. It may be possible to synthesize an analogous catalyst based on the reductase, but only if the fundamental bioinorganic chemistry is understood. Although nitrate reductases are based on molybdenum (Coughlan, 1980), it has not been verified whether this is also true for the perchlorate reductases. Several projects are ongoing in the affected areas of EPA (Environmental Protection Agency). Catts (1998) reported that a pilot-scale bioreactor has been constructed for the Baldwin Park Operable Unit in California, USA using microbes derived from the food-processing industry. Operation of this pilot unit over a period of several months showed that perchlorate and nitrate could be reduced to undetectable levels, i.e., [ClO₄⁻] < 4 ng mL⁻¹. Ethanol was used as a food source and minerals were added to the system. The perchlorate-reducing microbes were not isolated or characterized.

V. CONCLUSION

Bioremediation appear to be the most economically feasible, fastest, and easiest means of dealing with perchlorate laden waters at all concentrations. Although other techniques may find application to select systems, e.g., point-of-use or small utilities, it appears that biological and biochemical approaches will play the greatest role in solving the perchlorate problem. Some situations may require a combination of technologies to best meet unique needs. This is a complex problem, and many of the standard technologies that have dominated the drinking water industry for the past several decades will not work for this contaminant when used in the conventional ways. Many of the possibly effective

technologies have not been applied to drinking water specifically, and the interplay with other treatment technologies required for regulation must be assessed. In addition to rapid implementation of effective and workable technologies, ongoing development will be required to find new technologies and to make them affordable into the industry.

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