

Perchlorate Environmental Occurrences, Health Effects, and Remediation Technologies

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Abstract

Perchlorate is a widespread pollutant in the environment. It can be produced naturally by atmospheric photochemical reactions or synthesized in large quantities for industrial, military, and pyrotechnic applications. Perchlorate can affect human thyroid function by interfering with iodide uptake and thus has significant public health ramifications. This presentation will provide the current state of science and technology with respect to the source and occurrence of perchlorate in natural environments, its risk assessment, and recent advances in treatment technologies to remove perchlorate from contaminated water. Although perchlorate is a powerful oxidant, it is highly soluble and stable in water and soil and can thus persist in the environment. The discussion will focus on various treatment technologies such as selective ion exchange, reverse osmosis, and biological reduction which can be used to remove perchlorate from contaminated water and thus to minimize its health risks to the public.

Perchlorate contamination in groundwater and soil is an emerging environmental concern in many parts of the world. For many decades, synthetic perchlorate in the form of ammonium perchlorate (NH_4ClO_4) or potassium perchlorate (KClO_4) salts has been widely used as the primary oxidant in a variety of solid rocket propellants and explosives produced for military and aerospace applications (Gu & Coates, 2006). Besides military propellants and explosives, synthetic perchlorate has also been used in many commercial products, including fireworks, air bags, pyrotechnics, matches, safety flares, and perchloric acid (Aziz et al., 2006). As a result, widespread contamination of perchlorate has been found in soil, lakes and rivers, and even in drinking water and some food products, and thus has significant ramifications ranging from public-health concerns to potential impacts on agriculture, crop production, and environmental cleanup.

Man-made perchlorate is perhaps the largest source of contamination, and it is mostly synthesized via electrolysis. However, perchlorate has also been found in nature as a minor component in nitrate salt deposits in the hyperarid Atacama Desert in northern Chile (sometime referred to as Chilean caliche) (Bao & Gu, 2004; Ericksen, 1981) and other parts of the world (Böhlke et al., 2005; Dasgupta et al.,

2005; Jackson et al., 2005). The Chilean caliche contains an average concentration of perchlorate about 0.1% of the salt, but with concentrations as high as about 6% reported (Dasgupta et al., 2005; Ericksen, 1981). It was used previously as a source of inorganic nitrogen fertilizer. In California alone, it was reported that more than 477,000 metric tons of Chilean nitrate were used as fertilizer between 1923 and 1998 and may thus have contributed significantly to perchlorate contamination in soil and groundwater. Perchlorate is highly soluble in water, and this characteristic results in its ability to move from surface soil into groundwater when it enters the environment. Perchlorate is an anion (ClO_4^-) or an ionic substance and, therefore, it does not volatilize from water or soil surfaces. It is very stable and known to remain unreacted in the environment for a long period of time, unless it is under highly reducing conditions where some anaerobic microorganisms can cause degradation of perchlorate to other substances such as chloride.

Perchlorate can affect human thyroid function by interfering with iodide intake or absorption. Iodine is a nutrient required for the synthesis of thyroid hormone, which regulates certain body functions after it is released into the blood. Children and developing fetuses are more sensitive to be affected by perchlorate than adults because thyroid hormones are essential for normal growth and development. People exposed to high levels of perchlorate for a long time may develop a low level of thyroid activity, so-called hypothyroidism. On the other hand, perchlorate also has been used as a drug to lower thyroid hormone levels to treat people with overactive thyroid glands, so-called hyperthyroidism.

While costly, various treatment technologies are available to remove perchlorate from contaminated water and soil and thus to minimize its health risks to the public. Among these treatment technologies, ion exchange, reverse osmosis, and biological reduction are perhaps among the most widely used, although each treatment technology has its own advantages and disadvantages with respect to the treatment efficiency and cost effectiveness. Their pros and cons have been described in detail by Gu & Coates (2006). In general, reverse osmosis is a physical separation technique, in which a high pressure is applied on one side of the semi-permeable membrane to force water molecules to pass through the membrane, leaving behind the salts and contaminants. It is effective in removing perchlorate but is energy intensive and costly. Additionally, the presence of dissolved organic and particulate matters in water could easily cause fouling or plugging of the membrane so that it must be replaced frequently.

The ion exchange technology is commonly used, particularly for drinking water treatment at low perchlorate concentrations. In this process, perchlorate anion is exchanged with chloride adsorbed on ion exchange resins. The technology has been used widely for water treatment for more than half a century because of its simplicity and capability of operating at a high flow rate. However, different ion exchange resins are available commercially for perchlorate removal from contaminated water. They can be generally categorized as: (1) selective but non-regenerable strong-base

anion-exchange resins, (2) nonselective or low-selective anion-exchange resins with sodium chloride (NaCl) brine regeneration, and (3) highly selective and regenerable strong-base anion-exchange resins. In the first case, the spent resin cannot be regenerated using conventional brine washing technique (Gu & Coates, 2006), so it is either discarded or incinerated after reaching its sorption capacity. The resin bed must then be replaced after reaching its capacity. The change-out time for the resin depends on the feed perchlorate concentration and water quality. In the second case, the resin is regenerated by flushing with concentrated brine solution. However, because of its relatively low selectivity (or low sorption efficiency and capacity for perchlorate), the resin removes other common anions indiscriminately, such as sulfate (SO_4^{2-}) and nitrate (NO_3^-). Because these anions exist in contaminated groundwater or surface water usually at orders of magnitude higher concentrations than perchlorate, they occupy most of ion-exchange sites on the resin (>99%), resulting in an extremely low efficiency for perchlorate removal (Batista et al., 2000; Gu & Coates, 2006). Therefore, the spent resin bed must be regenerated frequently, producing large volumes of secondary brine wastes containing perchlorate. These factors contribute to relatively high capital and operating costs of conventional ion-exchange technologies.

Therefore, selective ion exchange is usually the preferred technology for treatment of drinking water with low perchlorate concentrations because of its treatment efficiency, longevity, simplicity, and minimal impact on water quality. The selective and regenerable ion-exchange technology is based primarily on the use of so-called bifunctional anion-exchange resins developed at the Oak Ridge National Laboratory and University of Tennessee (Gu et al., 2000; Gu & Coates, 2006). The bifunctional resin consists of two trialkylammonium functional groups optimized for its performance and sorption capacity. The technology has been demonstrated in both laboratory and field studies to have high efficiency and longevity in removing perchlorate from contaminated water at very low concentrations. It can treat about 100,000 bed volumes of water before a breakthrough of perchlorate occurs at an influent perchlorate concentration of about 50 $\mu\text{g}/\text{L}$ (Gu et al., 2000; Gu et al., 2007). This translates to a treatment period of about 5 months if it operated at 0.5 bed volumes per minute or about 1 year at 0.2 bed volumes per minute prior to resin replacement or regeneration. It is also important to note that the regeneration technology allows the resin to be reused while producing minimal secondary wastes and can therefore substantially reduce the capital and operational costs (Gu & Coates, 2006).

Biological treatment of perchlorate is also commonly used, in which perchlorate is break down by certain species of anaerobic bacteria when supplied with sufficient quantities of nutrients as electron donors (e.g., acetate or lactate), whereas perchlorate serves as the electron acceptor. The technology could be cost-effective and efficient, especially for treatment of groundwater or wastewater containing relatively high concentrations of perchlorate, dissolved organic matters, and/or high

total dissolved solids required for the growth of microorganisms. The technology has been used for both ex-situ water treatment and in-situ soil/groundwater treatment, such as the source contamination area containing high perchlorate concentrations. However, biological degradation could be ineffective or costly for treating drinking water with low concentrations of perchlorate (e.g., at tens or hundreds of $\mu\text{g/L}$ concentrations). This is mainly because biological reduction of perchlorate requires a high reducing environment, in which a highly active biomass must be maintained by continuously supplying nutrients (both electron donors and acceptors) to the treatment system. Additionally, post-treatment is often required in order to remove residual nutrients, anaerobic microbes and potential pathogens in water.

In summary, while perchlorate can form naturally, especially at Atacama desert, synthetic or manmade perchlorate is perhaps the largest source, which has resulted in widespread contamination of perchlorate in soil and water in the world. Perchlorate can impair human thyroid function by inhibiting iodide uptake or thyroid hormone production. Children and developing fetuses are particularly sensitive because thyroid hormones are essential for normal growth and development. Various treatment technologies are available to remove perchlorate from contaminated water, although it is important to consider site specific conditions (e.g., water quality, perchlorate concentrations, etc.), treatment criteria, cost and feasibility, regulatory requirements, and ecological concerns when selecting the most appropriate technology for removing perchlorate.

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Bio-note

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