

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

No information is available in the TRI database on facilities that manufacture or process perchlorates because these chemicals are not required to be reported under Section 313 of the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986) (EPA 1997a).

Commercial interest in perchlorates began in the late 1890s/early 1900s in Europe and the United States as a direct result of the pioneering efforts in rockets and their propulsion systems (Mendiratta et al. 1996). The production of ammonium perchlorate, the largest component of solid rocket propellants, far outpaced that of the other perchlorates listed in Table 4-1. Their commercial manufacture began later, and it was not until 1928 when GFS Chemicals began producing magnesium perchlorate for use as a desiccant (GFS 1997) that these salts became available on the U.S. market. Up until 1940, the total worldwide production of perchlorates had not exceeded 3.6 million pounds. An abrupt change in production was realized with the onset of World War II and the resulting increase in demand for rocket and missile propellants. Annual perchlorate production quickly increased to 36 million pounds because of this demand and remained at a high level thereafter (Mendiratta et al. 1996). By 1974, U.S. perchlorate production had reached 50 million pounds (Vogt et al. 2005).

Recent production data for ammonium perchlorate as well as for the other salts listed in Table 4-1 are lacking. In 1994, U.S. production of ammonium perchlorate was estimated at 22 million pounds or just 36% of capacity (Mendiratta et al. 1996). Actual production volumes for ammonium perchlorate have been historically dependent on the demand of aerospace and military applications due to its predominant use in propellants (Mendiratta et al. 1996). This use has resulted in defining ammonium perchlorate as a strategic chemical (Mendiratta et al. 1996; Vogt et al. 2005), and current worldwide production figures are not readily available.

Approximately 900,000 pounds of ammonium perchlorate in aqueous solution serve as the feedstock for the production of magnesium and lithium salts for use in batteries (Mendiratta et al. 1996). The wide variety of uses for perchlorates (see Section 5.3) suggests that the combined production of the salts listed in Table 4-1 would be significantly higher. U.S. facilities listed in the SRI Directory of Chemical Producers that currently manufacture perchlorates are provided in Table 5-1. According to data listed on

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

Table 5-1. U.S. Manufacturers of Perchlorates

Producer	Aluminum perchlorate	Magnesium perchlorate	Potassium perchlorate	Ammonium perchlorate	Sodium perchlorate	Lithium perchlorate
GFS Chemicals, Inc. Columbus, Ohio	√	√	√		√	√
Western Electrochemical Co. ^a Cedar City, Utah			√	√	√	
Barium and Chemicals, Inc. Steubenville, Ohio			√			

^aWestern Electrochemical is a subsidiary of the AMPAC Corporation.

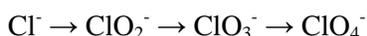
Source: SRI 2007

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

EPA's website, there were 63 Federal agency facilities and 168 non-Federal facilities in the United States that were either known or suspected perchlorate manufacturers/users as of April, 2003 (EPA 2005c).

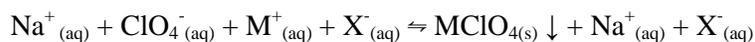
Potential source contributions of perchlorate from its intended uses and from its content as an impurity in various non-military products have been analyzed (Aziz et al. 2006; Dasgupta et al. 2006). Dasgupta et al. (2006) used data from the U.S. Government Accountability Office (GAO) and production capacities of individual plants to estimate ammonium perchlorate production and use within the United States. Based upon their analysis, an average annual perchlorate production rate of approximately 1.06×10^7 kg per year had been estimated from 1951 to 1997 (Dasgupta et al. 2006). Potassium perchlorate is an important ingredient in fireworks and road safety flares. Using statistical data regarding total flare sales, average cost per flare and an assumed concentration of 3.6 g of perchlorate per flare, a perchlorate source contribution of 1.4×10^5 kg per year was estimated (Dasgupta et al. 2006). No quantitative estimates were made for firework usage since the amounts of perchlorate in fireworks vary greatly. The perchlorate composition by weight percentage has been estimated to range from 4 to 70%, depending upon the type of firework (Aziz et al. 2006; SERDP 2005). Perchlorate is recognized as an impurity in the production of electrochemically produced chlorine products, including sodium chlorate. The pulp and paper industry uses most of the sodium chlorate consumed in the United States for on-site production of chlorine dioxide to bleach cellulose fibers (Aziz et al. 2006; SERDP 2005). Sodium chlorate has also been used as a non-selective contact herbicide and a defoliant for cotton, sunflowers, sundangrass, safflower, rice, and chili peppers (Aziz et al. 2006; SERDP 2005). Using a sodium chlorate consumption rate of approximately 10^9 kg per year and a 0.01% perchlorate content, a source strength of roughly 10^5 kg per year was calculated (Dasgupta et al. 2006). Perchlorate is also found as an impurity in other common consumer products that may ultimately lead to human exposure and release to the environment. The occurrence of perchlorates in these products as well as natural sources of perchlorate in the environment are discussed in Chapter 6.

The predominant commercial method for the manufacture of perchlorates begins with the production of the most soluble salt, sodium perchlorate. Electrochemical oxidation of an aqueous solution of sodium chloride is the most common method of producing sodium perchlorate (Schilt 1979; Vogt et al. 2005). Many variations for this process have been described over the years. They differ in the amount of current used, electrode composition, ionic strength of the bath, or temperature, although they all proceed via the following series of two-electron oxidations:



5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

The manufacture of all other perchlorate salts, including those listed in Table 4-1, is accomplished by selectively re-crystalizing the perchlorate salts that are less soluble than sodium perchlorate. Thus, adding common salts to a solution of sodium perchlorate leads to a metathesis (ion exchange) process that is driven to the right as the desired product precipitates out of solution:



where M is magnesium, potassium, lithium, or ammonium; X is chloride, sulfate, or carbonate; and $\text{MClO}_{4(\text{s})}$ is the desired perchlorate. The majority of sodium perchlorate produced in the United States is converted to ammonium perchlorate using this process (Grotheer 1994).

Given that the manufacture of perchlorates is typically accomplished in aqueous solution, the resulting perchlorate is produced as a hydrate. The anhydrous salt is required for pyrotechnic applications, and water molecules are removed from the hydrate by a number of methods including controlled heating, displacement of the water molecules by volatile amines (which are subsequently removed at reduced pressure or elevated temperatures), or through the use of a strong desiccant (Kamienski et al. 1995). High purity perchlorate salts are produced by a wide variety of methods. For example, lithium perchlorate may be prepared by direct electrochemical oxidation of lithium chloride or by reaction of 70% perchloric acid with lithium carbonate (Kamienski et al. 1995; Schilt 1979). A more recent approach in the production of high purity ammonium perchlorate involves the electrolytic conversion of chloric acid to perchloric acid, which is then neutralized by ammonia gas (Mendiratta et al. 1996). The ammonium perchlorate is spray dried to the desired crystal size at air temperatures below 150 °C.

5.2 IMPORT/EXPORT

The U.S. Census bureau does not list perchlorates as a separate, reportable item on its schedule B book on imports or exports. Instead, perchlorates are listed under the general category of perchlorates; bromates and perbromates; iodates and periodates. The total amount of imports for this category were 1.867×10^6 , 1.881×10^6 , and 1.281×10^6 kg for 2005, 2006, and 2007, respectively (USITC 2008). Exports totaled 1.349×10^6 , 2.067×10^6 , and 1.927×10^6 kg in 2005, 2006, and 2007, respectively (USITC 2008).

Using import/export volumes of substances in which perchlorates are contained may yield an indirect estimate of how much perchlorate is imported into the United States either from its intentional use in a

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

specific product or unintentionally as an impurity of a product or commodity. For example, the import of Chilean nitrate fertilizer, which contains perchlorate as a natural component, peaked around 1920 and has dropped significantly since the 1960s. The total amount of Chilean nitrate fertilizer imported into the United States from 1930 to 1993 was estimated as 2.4×10^{10} kg (Dasgupta et al. 2006). Assuming an average perchlorate content of approximately 0.2%, the total amount of perchlorates imported over this time was approximately 4.8×10^7 kg. Perchlorates are used in fireworks (see Section 5.3) and in 1997, U.S. imports of these pyrotechnic devices totaled \$93 million (U.S. Census Bureau 1999). U.S. exports of fireworks in 1997 totaled \$6.2 million. In 2003, 221 million pounds (approximately 1×10^8 kg) of fireworks were consumed in the United States, with an estimated 3% produced domestically and the remainder (214 million pounds) imported from China (Aziz et al. 2006; SERDP 2005). Using data from the U.S. Trade Commission (USITC 2008), the import/export volumes for fireworks, signal flares, and propellant powders from 2005 to 2007 are provided in Table 5-2. The actual volume of perchlorates represented by these figures is difficult to estimate since the content of perchlorate in these commodities is not known or is highly variable.

5.3 USE

The predominant uses of perchlorates take advantage of their strong oxidizing power and relative stability at moderate temperatures (Conkling 1996; Mendiratta et al. 1996; Schilt 1979; Vogt et al. 2005). On heating, perchlorates decompose into chlorine, chlorides, and oxygen. As the reaction proceeds and temperatures increase, decomposition becomes self-propagating. In the presence of organics and other oxidizable materials (the fuel), large amounts of energy are released. The decomposition of ammonium perchlorate differs from that of the metal salts listed in Table 4-1 because it produces only the neutral products chlorine, water, oxygen, and nitrous oxide (or nitrogen oxide at high temperatures) and leaves no solid residue (e.g., sodium chloride residue is produced by the decomposition of sodium perchlorate).

Ammonium perchlorate is the largest volume perchlorate used in the United States (Mendiratta et al. 1996). Its primary use is as an oxidant for solid rocket boosters. The solid propellant used in the booster rockets on the U.S. Space Shuttle is approximately 70% ammonium perchlorate by weight (Conkling 1996). According to the Interstate Technology and Regulatory Council (ITRC) (2008), "Solid rocket products developed and manufactured by Aerojet consisted primarily of jet-assisted take-off motors; tactical rockets such as Falcon, Hawk, Harpoon, Sidewinder, Maverick, Bullpup, Genie, Sparrow, AMRAAM, Tartar, and Navy Standard Missile; ballistic missiles Minuteman I, II, and III, Polaris, Midgetman, Peacekeeper, and space boosters; and sounding rockets." DOD's use of perchlorates in

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

Table 5-2. Import and Export Data for Products that may Contain Perchlorate

Product or commodity	2005	2006	2007
Imports (amount in kg)			
Fireworks	1.248x10 ⁸	1.234x10 ⁸	1.082x10 ⁸
Signal flares	3.152x10 ⁶	2.333x10 ⁶	1.885x10 ⁶
Propellant powders	3.755x10 ⁶	4.755x10 ⁶	3.150x10 ⁶
Exports (amount in kg)			
Fireworks	2.39x10 ⁵	3.98x10 ⁵	3.07x10 ⁵
Signal flares	4.36x10 ⁵	3.35x10 ⁵	3.54x10 ⁵
Propellant powders	1.824x10 ⁶	2.446x10 ⁶	2.210x10 ⁶

Source: USITC 2008

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

weapon systems over the last 5 years was 6–8 million pounds per year, much of which is recovered and recycled (DOD 2007) (see Section 5.4)

The other perchlorates listed in Table 4-1, most notably potassium perchlorate, also find use as oxidants in solid booster rockets (Lindner 1993). Oxidant mixtures developed using metal perchlorate salts are less powerful than those using ammonium perchlorate (Schilt 1979).

Perchlorates are used extensively in pyrotechnic devices such as fireworks, safety flares, and blasting explosives (Aziz et al. 2006; SERDP 2005). Ammonium perchlorate is used in small amounts in gun powder (Lindner 1993). Ammonium perchlorate is used in a mixture with sulfamic acid to produce a dense smoke or fog for military applications. Perchlorates are also used in civilian explosives.

It has been widely published in the scientific literature that perchlorates are used in airbag inflator systems (see, for example, Cowan 2000; Lamm et al. 1999; Logan 2001; Smith et al. 2001; Von Burg 1995). When used in this application, a chlorine scavenger would be required to prevent this gas from entering the passenger compartment (Mausteller 1996). Encyclopedic sources limit their discussion of airbag inflator systems to sodium azide (Antonsen 1996; Conkling 1996; Jansen 1992; Jobelius and Scharff 1989; Stiefel 1995), although potassium perchlorate has been used in compositions described as suitable for this purpose (Schilt 1979). Airbag inflators containing perchlorate have been described in the patent literature (see, for example, Scheffee and Wheatley 1999). According to the Automotive Occupant Restraint Council, perchlorate-containing airbag initiators are sealed from the environment prior to deployment and during an accident in which they are deployed, and the perchlorate is destroyed through the combustion process, essentially resulting in little or no release of perchlorate (CADTSC 2005).

Perchlorates have also found use in a wide variety of other applications. They are used as oxygen generating systems (oxygen candles) for enclosed environments, such as submarines, spacecraft, and civilian and military aircraft (Vogt et al. 2005). Anhydrous perchlorates, most notably the magnesium salt, are used as a highly efficient drying agent for gases as well as for scrubbing the last traces of polar compounds from inert gases (Schilt 1979). Lithium and magnesium perchlorate have been used in batteries due to their low weight and high energy density. Potassium perchlorate, mixed with a reactive metal such as iron or zirconium, has been used in heat pellets for the activation of reserve battery cells (Cohen 1993). Perchlorate salts are being investigated as additives for conducting polymers although they have been problematic due to their explosive nature (Druy 1986).

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

A novel use of ammonium perchlorate is as a component of temporary adhesives for steel or other metallic plates (Vogt et al. 2005). Ammonium perchlorate is mixed with an epoxy resin, which, after curing, forms the adhesive bond between the plates. When separation of the plates is required, they are heated to initiate the self-propagating perchlorate decomposition, which, in turn, decomposes the epoxy adhesive (Vogt et al. 2005).

Perchlorates find frequent use to adjust the ionic strength of electroplating baths (Schilt 1979; Vogt et al. 2005). Metals that have been used in this process include aluminum and its alloys, iron, steel, nickel and its alloys, tin and lead alloys, and zirconium and its alloys. Perchlorate electrolysis baths are specifically used in plating razor blades. Perchlorates are also routinely used to adjust the ionic strength of aqueous solutions of analytical and investigative procedures of metal solutions (Nair et al. 1997; Papini and Majone 1997; Puls and Powell 1992; Sposito and Traina 1987). They are used in this application because of the tendency of perchlorates not to form metal complexes in solution and, therefore, not to interfere with the chemical dynamics of the investigation (Cotton and Wilkinson 1980).

Perchlorates were widely used in the treatment of hyperthyroidism during the 1950s and early 1960s especially for people with Graves' disease (Von Burg 1995). Perchlorate is also available in the United States for administration (200–400 mg orally) to block radioactive technetium ($^{99}\text{TcO}_4^-$) uptake in the thyroid, choroid plexus, and salivary glands during medical imaging of the brain, blood, and placenta (Gibbs et al. 1998). Potassium perchlorate is currently used as part of a treatment to counter the thyroid effects of the drug amiodarone (Martino et al. 2001).

Other uses for perchlorates include matches, etching and engraving agents, photography, and synthetic reagents (Lewis 2001). Lithium perchlorate has been described as a catalyst that should be used with caution for synthetic organic chemistry using the Diels-Alder reaction (Kamienski et al. 1995). Potassium perchlorate was used as an ignition ingredient in flash bulbs (Vogt et al. 2005) and has been approved for use as an additive in rubber gaskets for food containers (FDA 1998). Perchlorates have also been used in weed killers and as growth promoters in leguminous plants. Ammonium, sodium, and potassium perchlorates have also been used as stimulants for increasing the weight of farm animals and poultry (Von Burg 1995).

Chilean saltpeter, a naturally occurring material proven to contain perchlorates (Schilt 1979), has been marketed mainly as a granular product for fertilizers (Laue et al. 1991). Chilean researchers initiated a study in 1967 to establish why soybeans were exhibiting stunted growth, rugose, and crumpled leaves as a

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

result of domestic fertilizer application and to determine what levels of perchlorate these plants could tolerate (Tollenaar and Martin 1972). The saltpeter used to produce the fertilizer at that time contained 0.12–0.26% perchlorate (by weight) as a contaminant. The United States first began importing Chilean saltpeter in 1830 (Hoffmeister 1993). U.S. importers of the refined Chilean nitrate reached historic highs prior to 1980 (Bortle 1996), and current annual imports are at 2 million pounds (Laue et al. 1991). However, this amount represents <0.1% of the total amount of nitrogen fertilizer usage in the United States (Hoffmeister 1993). Fertilizer derived from Chilean saltpeter has been traditionally applied mainly to tobacco plants, but is also marketed for citrus fruits, cotton, and some vegetable crops (Urbansky et al. 2001). The amount of perchlorate present in recent samples of these fertilizers was found to range from 0.7 to 2.0 mg/g, although steps have been taken to reformulate these products to remove perchlorate.

In 1999, perchlorate was also detected in nine different brands of synthetic fertilizer products (Susarla et al. 1999), raising concern for the potential widespread contamination from this source. The results of this study were questioned (Urbansky et al. 2000b) and a reinvestigation of many of the same products purchased at a later date found perchlorate in only one sample at a concentration two orders of magnitude lower than typically found in the original publication (Susarla et al. 2000). Nevertheless, it raised important questions as to why perchlorate would be present in synthetic fertilizers and how frequently it appeared. It also highlighted the difficulty in analyzing for perchlorate in solid samples and other complex matrices. Urbansky and Collette (2001) conducted a survey of approximately 40 fertilizer products comparing the results of six different laboratories. After an evaluation phase to determine the ability of each laboratory to quantify perchlorate in a fertilizer matrix, their results indicated that perchlorate was not detectable in any real-world fertilizer products (including synthetic fertilizers) that were not derived from Chilean caliche. During a survey of 48 fertilizer products collected from representative sites across the United States, perchlorate was detected in only 5 of the products (concentrations ranging from 1,800 to 4,200 $\mu\text{g/g}$) (EPA 2001a).

5.4 DISPOSAL

In 1998, perchlorate was listed in the Drinking Water Contaminant Candidate List. The Safe Drinking Water Act, as amended in 1996, required EPA to publish a list of contaminants that were not subject to other primary drinking water regulation (EPA 1998a). In 1999, perchlorate was subsequently added to the Unregulated Contaminant Monitoring List that required public water systems that serve >10,000 persons, and other representative systems, to monitor for perchlorate and other substances

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

beginning January, 2001 (EPA 1999b). The following year, EPA published a final rule indicating that standard method 314.0 should be used to monitor for perchlorate in drinking water (EPA 2000).

EPA would consider discarded perchlorate to be a solid waste and depending on the fact-specific circumstances, EPA believes that discarded perchlorate could be a hazardous waste under the Solid Waste Disposal Act (EPA 2006b). Specifically, because perchlorates are oxidizing chemicals, waste discarded chemical formulations of perchlorate and its salts are likely to be classified as D001 Resource Conservation and Recovery Act (RCRA) hazardous waste under 40 CFR 261.23, which regulates wastes that meet the reactivity characteristic. Such a determination is generally based on the nature of the waste at the point of generation; however, characteristic hazardous waste, such as D001, ceases to be hazardous waste once it no longer exhibits a hazardous waste characteristic. In addition, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) 101(14) defines “hazardous substance.” According to that section, “the term hazardous substance means . . . any hazardous waste having the characteristics identified under or listed pursuant to Section 3001 of the Solid Waste Disposal Act. . . .” Therefore, depending on the fact-specific circumstances, discarded perchlorate could be classified as a D001 hazardous waste and therefore, under certain circumstances, EPA would consider perchlorate a CERCLA hazardous substance.

As noted in Section 5.3, of the 6–8 million pounds of perchlorates used annually by DOD in weapon systems, approximately 4 million pounds of ammonium perchlorate is recovered and returned to the manufacturer for use in commercial applications, such as, blasting agents or perchloric acid for glass etching (DOD 2007).

Water treatment technologies, including air stripping, activated carbon adsorption, chemical oxidation, and aerobic biodegradation are not efficient at removing perchlorate from water (Logan 1998; Urbansky 1998). Granular activated carbon columns do not economically remove the perchlorate anion from water. The useful lifetime of these columns was reduced from approximately 18 months to one month while treating tap water at the Texas Street Well facility in Redlands, California (Logan 2001).

The most promising physical removal process for treating perchlorate-contaminated water uses ion exchange technology (DOD 2005c, 2005d; EPA 2005e; Urbansky 2002). Perchlorate can be removed from water using ion exchange columns, although the resulting brine contains 7–12% perchlorate (Logan et al. 2001a). Currently, scientists are finding ways to improve this technology as well as to make it more cost efficient (Logan 2001). An ion exchange treatment facility has been installed at Edwards Air Force

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

Base in California (DOE 2003). The DOD (2005c, 2005d) has reported that more than 9 million gallons of perchlorate contaminated groundwater have been successfully treated (perchlorate <4 ppb) since its implementation.

Perchlorate removal using anaerobic bioreactors has been proven for onsite applications and at the pilot-plant level (Urbansky 1998). Research in this area is active (Bardiya and Bae 2005; Brown et al. 2003; Cramer et al. 2004; Logan and LaPoint 2002; Min et al. 2004). Suspended growth, fixed bed, and fluidized bed bioreactors have been used to degrade perchlorate at influent concentrations ranging from 0.13 to 7,750 ppb (Logan et al. 2001b). Abatement and remediation of perchlorate in soil and groundwater was achieved using a biological permeable reactive barrier system at the McGregor, Texas Naval Weapons Industrial Reserve Plant (Cowan 2000). A biological fluidized bed reactor installed at the Longhorn Army Ammunition Plant in Karnack, Texas has successfully reduced perchlorate levels in groundwater at the site to below the detection limit (<4 ppb) (DOD 2005c, 2005d). Biological fluidized bed reactors are being used to remove perchlorate, with a 99.99% efficiency from contaminated groundwater at the Kerr-McGee site in Henderson, Nevada (EPA 2006a).

Phytoremediation is another method being explored as a possible treatment process for perchlorate-contaminated soil, sediment, and water (Nzengung et al. 1999, 2004; Tan et al. 2004b; Urbansky 2002; van Aken and Schnoor 2002). Plantings of lettuce and willow trees have been shown to reduce the concentration of perchlorate in contaminated soil (EPA 2004b; Nzengung et al. 1999, 2004; Yu et al. 2004). Uptake followed by accumulation was indicated as the main phytoremediation process in lettuce, whereas both uptake and rhizodegradation appear to be an important removal processes associated with woody plants.