

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

5.1 PRODUCTION

Chlorine dioxide is always manufactured on site because of the risk of rapid decomposition. In all processes, chlorine dioxide is produced in strong acid solutions from either sodium chlorite or sodium chlorate. Small- and medium-scale industrial production of chlorine dioxide utilizes sodium chlorite as the raw material. This is typical of water treatment and disinfection applications that require high purity (i.e., chlorine-free) waters. Other applications not requiring high purity waters utilize sodium chlorate. This is typical of pulp bleaching where large quantities of chlorine dioxide are necessary. There are several processes used to generate chlorine dioxide from sodium chlorate. In the R2 process, chlorine dioxide is produced from sodium chlorate and sulfuric acid, with sodium chloride as the reducing agent. Chlorine dioxide is absorbed from the gas phase in packed towers in cold water, and chlorine leaves the system as a by-product. In the Mathieson process, a sulfur dioxide-air mixture is diffused into a solution of sodium chlorate and sulfuric acid. Sulfur dioxide is used as the reductant to produce chlorine dioxide with a much lower chlorine content. The process also produces sulfuric acid, reducing the overall acid requirement. Exit gases from the Mathieson process are passed through a scrubber to remove any unreacted sulfur dioxide. The Solvay process uses sodium chlorate and sulfuric acid, with methanol as the reducing agent. Products from this process are chlorine dioxide, formic acid, and carbon dioxide. In improved Solvay processes, sulfuric acid demand is reduced by crystallizing out the by-products sodium sulfate, sodium sesquisulfate, or sodium bisulfate (Kaczur and Cawlfeld 1993; Vogt et al. 1986).

The production volume of chlorine dioxide can be accurately estimated from the total sodium chlorate consumption for chemical pulp bleaching because this accounts for >95% of all chlorine dioxide production. The annual production of chlorine dioxide in the United States was estimated to be 79, 81, 146, 226, and 361 kilotons for the years 1970, 1975, 1980, 1985, and 1990, respectively (Kaczur and Cawlfeld 1993).

Table 5-1 lists the facilities in each state that manufacture or process chlorine dioxide, the intended use, and the range of maximum amounts of chlorine dioxide that are stored on-site. There are 118 facilities that produce or process chlorine dioxide in the United States. Current estimates for the amounts of chlorine dioxide stored on-site as a by-product or impurity range from 99 to 9,999,999 pounds/year (45–

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Table 5-1. Facilities that Produce, Process, or Use Chlorine Dioxide

State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
AL	9	10,000	999,999	1, 3, 6, 10, 11, 12
AR	4	10,000	9,999,999	1, 3, 10, 11
CA	3	0	99,999	1, 3, 10, 12
CO	1	1,000	9,999	1, 3, 12
FL	7	0	9,999,999	1, 3, 10, 11, 12
GA	8	100	999,999	1, 3, 5, 10, 11, 12
ID	1	10,000	99,999	1, 3, 10
IL	1	0	99	1, 3, 12
KY	3	10,000	999,999	1, 3, 6, 12
LA	5	1,000	999,999	1, 3, 6, 10, 11
MA	1	0	99	1, 3, 12
MD	1	10,000	99,999	1, 3, 10
ME	6	10,000	9,999,999	1, 3, 6, 10, 11, 12
MI	3	10,000	99,999	1, 3, 7, 10, 11
MN	2	10,000	99,999	1, 3, 10
MS	4	10,000	999,999	1, 3, 8, 10
NC	8	0	9,999,999	1, 3, 5, 6, 10, 12
NY	2	1,000	99,999	1, 3, 10, 12
OH	1	10,000	99,999	1, 3, 10
OR	3	10,000	999,999	1, 3, 10
PA	6	1,000	999,999	1, 2, 3, 10, 11, 12
SC	6	0	99,999	1, 3, 6, 10, 11, 12
TN	2	10,000	99,999	1, 3, 6, 10
TX	4	1,000	99,999	1, 3, 5, 10, 11
VA	3	1,000	999,999	1, 3, 10, 12
VT	1	0	99	1, 3, 12
WA	7	0	99,999	1, 3, 6, 10, 11, 12
WI	3	100	99999	1, 3, 4, 10, 11, 12

Source: TRI01 2003

^aPost office state abbreviations used^bAmounts on site reported by facilities in each state^cActivities/Uses:

- | | | |
|--------------------------|--------------------------|-----------------------------|
| 1. Produce | 6. Impurity | 11. Chemical Processing Aid |
| 2. Import | 7. Reactant | 12. Manufacturing Aid |
| 3. Onsite use/processing | 8. Formulation Component | 13. Ancillary/Other Uses |
| 4. Sale/Distribution | 9. Article Component | 14. Process Impurity |
| 5. Byproduct | 10. Repackaging | |

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4,500,000 kg/year) (TRI01 2003). The data from the Toxics Release Inventory (TRI) listed in Table 5-1 should be used with caution, however, since only certain types of facilities were required to report (EPA 1995). This is not an exhaustive list.

The commercial manufacture of sodium chlorite is based almost entirely on the reduction of chlorine dioxide gas in a sodium hydroxide solution containing hydrogen peroxide as the reducing agent. The chlorine dioxide is generated from the chemical or electrochemical reduction of sodium chlorate under acidic conditions. The product is a 33 weight percent solution of sodium chlorite, which is then converted to a dry solid containing approximately 80% of sodium chlorite with other added salts (e.g., sodium chloride), which act as diluents for increased safety in storage and handling (Kaczur and Cawfield 1993; Vogt et al. 1986).

In 1991, the production capacity of sodium chlorite was 7,700 metric tons for 80% assay basis sodium chlorite (Kaczur and Cawfield 1993). In the United States, sodium chlorite is produced by International Dioxide, Inc. (North Kingstown, Rhode Island) and Vulcan Materials Co. (Wichita, Kansas) (SRI 2001).

5.2 IMPORT/EXPORT

In all cases, chlorine dioxide is produced at the point of use. No import or export of this chemical occurs (Kaczur and Cawfield 1993; Vogt et al. 1986).

Import/export data on chlorites from the U.S. Department of Commerce are combined with data for hypochlorites and hypobromites (ITA 2002). Separate data on the import/export of chlorite were not located.

5.3 USE

Wood-pulp bleaching is the largest use of chlorine dioxide, which is a uniquely selective oxidizer for lignin. In general, the trend in the pulp industry has been to eliminate chlorine and hypochlorite as bleaching agents and replace them with chlorine dioxide. Since chlorine dioxide functions via an oxidative reaction rather than a chlorinating reaction, the formation of chlorinated organic compounds is limited. Also, unlike other oxidizing agents, chlorine dioxide does not attack cellulose, and thus preserves the mechanical properties of bleached pulp. In the final stages of the pulp-bleaching processes,

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chlorine dioxide is the most frequently used bleaching chemical. A unique whiteness can be achieved using chlorine dioxide in kraft pulp, sulfite pulp, and soda pulp processes. In the United States, the first-stage of the pulp-bleaching process makes use of mixtures of chlorine and chlorine dioxide to reduce the formation of organic chlorine compounds (EPA 2002c; Kaczur and Cawlfeld 1993; Vogt et al. 1986).

In the textile industry, chlorine dioxide is used as a bleaching agent and produces high-quality textile fibers with additional qualities. For example, “shrinkproof” wool owes its qualities to the reaction of chlorine dioxide with the cross-linking sulfur atoms of the wool.

In industrial and municipal waste-water treatment, chlorine dioxide is more effective than chlorine as a biocide over a wide pH range. It is also less corrosive and more compatible with some construction materials. Some municipal water systems use chlorine dioxide to eliminate taste and odor problems from drinking waters (EPA 2002c; Kaczur and Cawlfeld 1993; Vogt et al. 1986). The advantage of using chlorine dioxide, rather than chlorine or ozone, is that chlorine dioxide does not react with organic matter to form trihalomethanes (THMs); it also does not transform bromide into hypobromite (OBr^-), which could react with organic matter to form bromoform (CHBr_3) or bromate (BrO_3^-) (Aieta and Berg 1986; Stevens 1982; WHO 2000). As part of the EPA Information Collection Rule (ICR), 5.1% of the water treatment facilities serving more than 100,000 people in the United States reported that chlorine dioxide was used in 1995 (Hoehn et al. 2000). Table 5-2 summarizes the number of facilities utilizing chlorine dioxide for water treatment in each state. However, the percentage of facilities using chlorine dioxide would be higher if smaller facilities (i.e., those serving less than 50,000 people) were also included in this value.

Chlorine dioxide has been recognized for its disinfectant properties since the early 1900s. Chlorine dioxide kills microorganisms by disrupting the transport of nutrients across the cell wall. In 1967, EPA first registered the liquid form of chlorine dioxide for use as a disinfectant and sanitizer. Liquid formulations are used as disinfectants in a variety of applications (e.g., on pets and farm animals; in bottling plants; and in food processing [fruit and vegetable washing, meat and poultry disinfection, disinfection of food processing equipment], handling, and storage plants). In industrial processes, chlorine dioxide is used as a disinfectant in water treatment (cooling systems/towers), ammonia plants, pulp mills (slime control, paper machines), oil fields, scrubbing systems, odor-control systems, and the electronics industry. In 1988, EPA registered chlorine dioxide gas as a sterilant. Chlorine dioxide gas is

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Table 5-2. Publicly Owned Treatment Works (POTW) Utilizing Chlorine Dioxide for Water Treatment in 1995

Number of facilities	States ^a
0	AK, DE, FL, HI, ID, MD, MN, MS, ND, NV, OR, UT, VT, WI, WV
1–5	AL, AR, AZ, CA, CO, CT, IN, KS, LA, ME, MI, MT, NE, NH, NJ, NM, NY, OK, PA, RI, SD, TN, WA, WY
6–10	IA, KY, MA, NC, VA
11–15	GA, MO, SC
21–25	OH
72	TX

Source: Hoehn et al. 2000

^aPost office state abbreviations used

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registered for sterilizing manufacturing and laboratory equipment, environmental surfaces, tools, and clean rooms. (EPA 2002c; Kaczur and Cawlfeld 1993; Vogt et al. 1986).

Chlorine dioxide is one of many antimicrobial agents being considered for use in some anthrax decontamination efforts because of its effectiveness against spore-forming bacteria. Section 18 of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) authorizes EPA to allow certain state and federal agencies to use a pesticide for an unregistered use for a limited time if EPA determines that emergency conditions exist. On November 9, 2001, EPA issued a crisis exemption for the limited sale, distribution, and use of EPA-registered pesticide products containing aqueous chlorine dioxide for cleaning surfaces contaminated with anthrax. Under the crisis exemption, only registered stabilized chlorine dioxide products may be sold or distributed to employees of EPA, other federal, state, or local government agencies, and the U.S. Postal Service. Application of the pesticide products under crisis exemption are limited to specific buildings or treatment sites identified by EPA, other federal, state, or local government agencies, and the U.S. Postal Service (EPA 2002c).

More than 80% of all sodium chlorite produced is used for the generation of chlorine dioxide. Sodium chlorite is also used in disinfectant formulations and for sterilization. Like chlorine dioxide, it must be registered with EPA under FIFRA for each specific application use as a disinfectant. Sodium chlorite is used in other industrial settings (e.g., in scrubber systems used to remove NO_x and SO_x from combustion flue gas; in the treatment and removal of toxic and odorous gases such as hydrogen sulfide and mercaptans; and as an aqueous formulation used to oxidize copper surfaces in multilayer circuit boards) (Kaczur and Cawlfeld 1993).

5.4 DISPOSAL

Chlorine dioxide is a strong oxidizer and will not persist in the open environment for long periods. At concentrations $>10\%$, chlorine dioxide is easily detonated by sunlight (O'Neil et al. 2001). It can remain for short periods of time in clean distribution systems (Kaczur and Cawlfeld 1993; NRC 1980; Vogt et al. 1986). No further information on the disposal of chlorine dioxide was located.

Chlorite ions and salts are strong oxidizers. Responsible care should be undertaken during disposal of chlorite ion solutions and salts. For example, solid sodium chlorite is unstable and can form explosive mixtures with oxidizable materials, such as organic compounds. Chlorite ion solutions should not be allowed to dry on textiles because this may result in a flammable combination (Kaczur and Cawlfeld

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1993; Vogt et al. 1986). No further information on the disposal of chlorite ions and chlorite salts were located.