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CHLORINE OXYGEN ACIDS AND SALTS, CHLOROUS ACID, CHLORITES, AND CHLORINE DIOXIDE

Sodium chlorite [7758-19-2], $NaClO_2$, an oxidizing agent, is manufactured and distributed worldwide in commercial quantities as aqueous solution, flake, and powder products. The primary use for sodium chlorite is on-site generation of chlorine dioxide [10049-04-4], ClO_2, through oxidation and/or acidification of an aqueous chlorite solution. Sodium chlorite is used to produce chlorine dioxide economically in quantities of less than 2000 kg/d. Sodium chlorate [7775-09-9] $NaClO_3$, is the preferred raw material for producing larger quantities of chlorine dioxide (see Chlorine oxygen acids and salts, chloric acid and chlorates).

Chlorine dioxide is finding increasing use as an oxidizing bleaching agent in the pulp (qv) and paper (qv) industry, replacing chlorine [7782-50-5], Cl_2, and aqueous sodium hypochlorite, [7681-52-9], NaOCl (see Bleaching agents). Use of ClO_2 significantly reduces the quantity of adsorbable organically-bound halide (AOX) effluents produced in paper pulp bleaching processes. Chlorine dioxide is also increasing use as a disinfectant or biocide in municipal and industrial water (qv) treatment (see Disinfectants and antiseptics) as well as an oxidizer in oil field and pollution abatement processes (see Petroleum). Chlorous acid [13898-47-0], $HClO_2$, is a short-lived chemical intermediate generated in acidified sodium chlorite solutions and is involved in the chemistry of the production and use of chlorine dioxide in oxidation and bleaching processes.

1. Chlorine Dioxide

1.1. Physical Properties

Chlorine dioxide, ClO_2, is a greenish yellow gas having a pungent odor that is distinctive from that of chlorine. Liquid chlorine dioxide has a deep red color and is explosive at temperatures above $-40°C$. Selected physical and thermodynamic properties of chlorine dioxide are given in Table 1.

Chlorine dioxide exists as a free-radical monomer (2–5). The chlorine–oxygen bonds have a double-bond character (6), O–Cl–O angle of about 117.5°, and a chlorine–oxygen bond length of 0.147 nm (5, 7–12). The aqueous ultraviolet absorption spectrum of chlorine dioxide has a broad absorption band. The maximum is near 360 nm and the molar extinction coefficient, given as 1150 $(M{\cdot}\mathrm{cm})^{-1}$, is more accurately valued at 1250 $(M{\cdot}\mathrm{cm})^{-1}$ when using high resolution, narrow bandwidth spectrophotometers (13–18). The extinction coefficient is independent of temperature from 25 to 50°C, and from acid concentrations ranging from 0.2–4 N, ionic strength, 2–4 M, and chloride ion concentrations up to 0.3 M (16). The chlorine dioxide absorption spectrum in aqueous or organic solutions is the same as the gas-phase spectrum (13).

Chlorine dioxide is soluble in water, forming a yellow to yellow-green color solution that is quite stable if kept cool and in the dark. Various crystalline hydrates of chlorine dioxide have been described including a hexahydrate (19), an octahydrate (20), and an orange colored decahydrate (21). The partition coefficient between water and ClO_2 gas is about 21.5 at 35°C and 70.0 at 0°C (22). Data on the solubility of chlorine dioxide in water at various chlorine dioxide gas partial pressures (23) have been published. Chlorine dioxide

Table 1. Physical and Thermodynamic Properties of Chlorine Dioxide[a]

Property value	Values
mol wt	67.452
critical temperature, K	465
critical pressure, kPa[b]	8621.6
mp, K	213.55
triple point temperature, K	213.55
triple point pressure, kPa[b]	1.2544
bp at 101.3 kPa[b], K	284.05
liquid molar volume, m^3/kmol	4.1852×10^{-2}
density of liquid, g/mL	
−55°C	1.773
0°C	1.640
10°C	1.614
ideal gas heat of formation, kJ/mol[c]	102.5
ideal gas Gibbs energy of formation, kJ/mol[c]	120.5
ideal gas entropy, kJ/(mol·K)[c]	0.257
standard net heat of combustion (gas), kJ/mol[c]	−102.5
dipole moment, C·m[d]	5.9500×10^{-30}
acentric factor	0.35638
radius of gyration, m	2.8030×10^{-10}

[a] Ref. 1. All temperatures at 298.15 K unless otherwise noted.
[b] To convert kPa to mm Hg, multiply by 7.501.
[c] To convert J to cal, divide by 4.184.
[d] To convert C·m to debyes, divide by 3.336×10^{-30}.

solubilities in water at partial pressures to 20 kPa (150 mm Hg) from experimental data (24) having a better internal consistency are shown in Figure 1.

An equation for calculating the partial pressure of chlorine dioxide above specified chlorine dioxide solutions at various temperatures based on the data from reference 24 has been developed (25):

$$p_{\mathrm{ClO_2}} = (\mathrm{g/L\ ClO_2})\, e^{[10.717-(3102/T)]} \qquad (1)$$

where $p_{\mathrm{clo_2}}$ is the partial pressure of chlorine dioxide gas in kPa, g/L ClO_2 is the chlorine dioxide solution concentration in grams per liter, and T is the absolute temperature in Kelvin. Reference 24 gives chlorine dioxide partial pressure values that are about 10–12% higher than those of reference 23.

1.2. Chemical Properties

Chlorine dioxide gas is a strong oxidizer. The standard E° reversible potential is determined by the specific reaction chemistry. The standard E° potential for gaseous ClO_2 in aqueous solution reactions where a chloride ion is the product is -1.511 V, but the potential can vary as a function of pH and concentration (26):

$$\mathrm{ClO_2} + 4\,\mathrm{H^+} + 5\,e^- \longrightarrow \mathrm{Cl^-} + 2\,\mathrm{H_2O} \qquad (2)$$

$$E = -1.511 + 0.0473\ \mathrm{pH} - 0.0118 \log\left\{\left(p_{\mathrm{ClO_2}}\right)/\left[\mathrm{Cl^-}\right]\right\} \qquad (3)$$

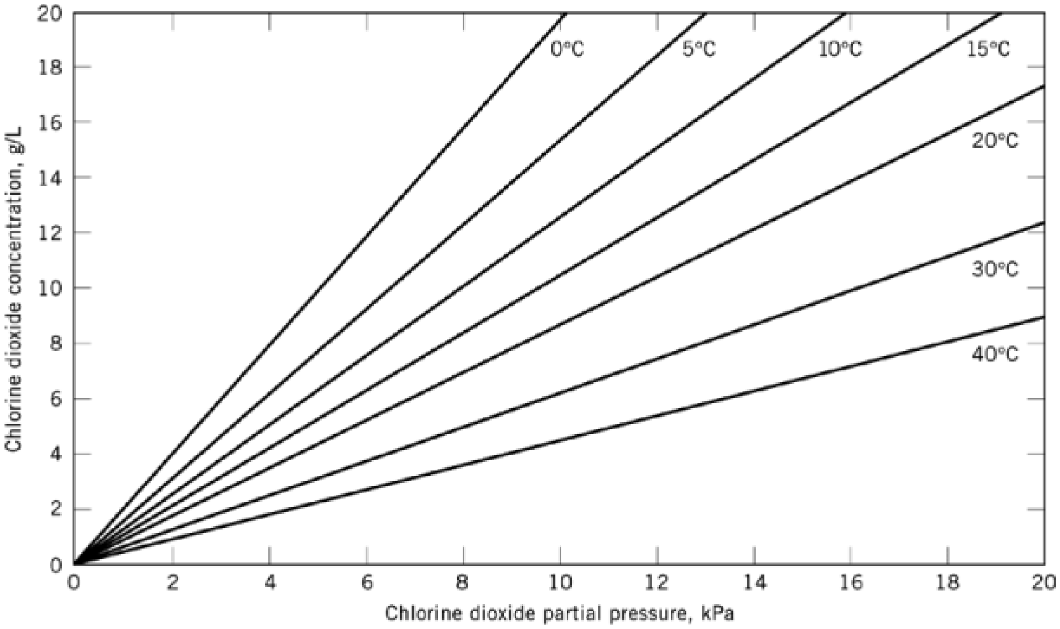

Fig. 1. Solubility of chlorine dioxide in water. To convert kPa to mm Hg, multiply by 7.501.

In reactions where chlorite is the product, the standard potential is -1.160 V and the potential varies according to:

$$ClO_2 + e^- \longrightarrow ClO_2^- \qquad (4)$$

$$E = -1.160 - 0.0591\log\{(p_{ClO_2}) / [ClO_2^-]\} \qquad (5)$$

In gaseous reaction systems where HCl gas is formed, the standard potential E° is -1.436 V and the potential varies according to:

$$ClO_2 + 5\ H^+ + 5\ e^- \longrightarrow HCl + 2\ H_2O \qquad (6)$$

$$E = -1.436 + 0.0591\ pH - 0.0118\log[(p_{ClO_2}) / (pHCl)] \qquad (7)$$

1.2.1. Thermal Decomposition of ClO_2

Chlorine dioxide decomposition in the gas phase is characterized by a slow induction period followed by a rapid autocatalytic phase that may be explosive if the initial concentration is above a partial pressure of 10.1 kPa (76 mm Hg) (27). Mechanistic investigations indicate that the intermediates formed include the unstable chlorine oxide, Cl_2O_3. The presence of water vapor tends to extend the duration of the induction period, presumably by reaction with this intermediate. When water vapor concentration and temperature are both high, the decomposition of chlorine dioxide can proceed smoothly rather than explosively. Apparently under these conditions, all decomposition takes place in the induction period, and water vapor inhibits the autocatalytic phase altogether. The products of chlorine dioxide decomposition in the gas phase include chlorine, oxygen, HCl, $HClO_3$, and $HClO_4$. The ratios of products formed during decomposition depend on the concentration of water vapor and temperature (27).

Surface area can accelerate the decomposition of chlorine dioxide up to a point, but sufficient area appears to inhibit catalytic decomposition by adsorption of the intermediates. For example, the presence of fluffed wood pulp or glass wool is reported to stop the explosive decomposition of chlorine dioxide (27).

In solution, chlorine dioxide decomposes very slowly at ambient temperatures in the dark. The primary decomposition process is hydrolysis of chlorine dioxide into chlorite and chlorate ions. The hydrolysis rate is a function of the concentration of hydroxyl ions and temperature, proceeding rapidly at solution pH values above 10:

$$2\ ClO_2 + 2\ OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O \qquad (8)$$

Decomposition of chlorine dioxide solutions occurs more rapidly in the presence of chlorine and hypochlorite, producing chlorate and HCl (28):

$$2\ ClO_2 + HOCl + H_2O \longrightarrow 2\ ClO_3^- + 3\ H^+ + Cl^- \qquad (9)$$

1.2.2. Photochemical Reactions

The photochemistry of chlorine dioxide is complex and has been extensively studied (29–32). In the gas phase, the primary photochemical reaction is the homolytic fission of the chlorine–oxygen bond to form ClO and O. These products then generate secondary products such as chlorine peroxide, ClOO, chlorine, Cl_2, oxygen, O_2, chlorine trioxide [17496-59-2], Cl_2O_3, chlorine hexoxide [12442-63-6], Cl_2O_6, and other oxychlorine species. In aqueous solutions, chlorine dioxide photolyzes in a complex manner. Chlorate, $ClO_3{}^-$, chloride, Cl^-, and hypochlorite, OCl^-, anions are the principal stable products (33–35).

1.2.3. Organic Chemistry

The chemistry and mechanisms of reactions of chlorine dioxide with organic compounds have been extensively reviewed (36–39). A compilation of kinetic data is also available (40). The reactions of chlorine dioxide with organic compounds must be distinguished with regard to the specific reaction conditions. For example, reactions may take place using chlorine dioxide in the gas phase or dissolved in aqueous or nonaqueous solutions. In addition, the reaction pH conditions may be low or high at corresponding reactant and oxidant concentrations. Chlorine dioxide typically reacts with organics as an oxidant with little or no chlorination. The breaking of organic carbon–carbon bonds is generally not extensive in most of the reactions so that the oxidation by-products are also organics. Saturated aliphatic hydrocarbons do not react with aqueous chlorine dioxide, and ClO_2 does not react with carboxylic acids, R–COOH, where R is a saturated alkyl group.

In aqueous solutions, primary and secondary amines react very slowly or not at all with chlorine dioxide (36, 41). Chlorine dioxide rapidly oxidizes tertiary amines, producing a secondary amine and an aldehyde. It rapidly oxidizes phenolic compounds, first by oxidation to quinones and eventually by ring opening reactions. However, ClO_2 has a relatively low oxidizing activity toward olefins (37). Alcohols and carbonyl compounds react somewhat more slowly with chlorine dioxide to produce carboxylic acids. Organic sulfides react with chlorine dioxide to form sulfonyl compounds and oxygen-containing products, thus effectively eliminating many odors (37, 39). Chlorine dioxide has also been found to react with some chlorinated phenolic compounds, reducing toxicity (39). Partial oxidation of phenol with chlorine dioxide can produce mono- and dichlorinated benzoquinones. But when sufficient chlorine dioxide is used to fully oxidize phenol, the primary products are oxalic and maleic acids as well as carbon dioxide.

1.3. Manufacture

1.3.1. Laboratory Preparation

Pure chlorine dioxide is easily prepared in small quantities by the addition of dilute sulfuric acid into a solution of sodium chlorite (42). A purified air or nitrogen stream passed through a potassium iodide solution or chromium(II) solution is used to sparge the generated ClO_2 gas through a scrubber containing a sodium chlorite solution for the removal of any chlorine contaminants. The gas can then be used directly or absorbed into high purity deionized water. An alternative generation method involves passing a 4–6 vol % mixture of dilute chlorine gas in nitrogen through a dry, packed column of sodium chlorite (43, 44). The preparation and solution storage of chlorine dioxide should be done in the absence of uv or strong visible light. The solutions should be kept cold to minimize vapor losses from the solution. Chlorine dioxide easily permeates many polymers, including fluoropolymers.

1.3.2. Small- and Medium-Scale Industrial Production

Sodium chlorite is the preferred raw material for chlorine dioxide production in quantities of less than about 2000 kg/d. This is typical for water treatment and disinfection applications. Other applications not requiring high purity, ie, chlorine-free, chlorine dioxide can use chemical generation methods reacting sodium chlorate and hydrochloric acid, sulfuric acid, and mixtures containing sodium chloride. High conversions of chlorate can be achieved by the addition of large excesses of acid and a reducing agent (45). Some of these processes prevent the separation of chlorine dioxide from the highly acidic generator solution by maintaining sufficient pressure.

1.3.3. Large-Scale Industrial Production

Large amounts of chlorine dioxide are used in pulp bleaching and smaller quantities are used for the manufacture of sodium chlorite. In these applications, sodium chlorate is the only commercially available raw material. Chlorine dioxide production from sodium chlorate is achieved by the reduction of the chlorate ion in the presence of strong acid. The reaction consumes acid, so that acid and reducing agents must be constantly added to maintain the reaction.

1.3.4. Chloride Reductant

Processes prior to 1945 used hydrochloric acid as both the acid and reducing agent. Hydrochloric acid is oxidized to chlorine gas and chlorate is reduced to chlorine dioxide. The overall stoichiometry produces a 2:1 molar ratio of chlorine dioxide to chlorine. Sodium chloride is a by-product:

$$2\ NaClO_3 + 4\ HCl \longrightarrow 2\ ClO_2 + Cl_2 + 2\ NaCl + 2\ H_2O \qquad (10)$$

This reaction is not driven to completion unless there is a large excess of HCl; thus the HCl consumption is substantially higher than the stoichiometry would imply.

Sulfuric acid is an economical alternative source of acid and many commercial generators substitute concentrated sulfuric acid for HCl. Furthermore, the required chloride ion needed as the reductant is already present or added as NaCl in the chlorate solution or crystal obtained from the chlorate manufacturer. This process, popular in the 1960s and 1970s, produces substantial amounts of liquid effluent containing 20–35% sulfuric acid, 20–25% sodium sulfate, and minor amounts of sodium chloride and unreacted chlorate that must be neutralized with alkali.

An integrated process for producing chlorine dioxide that can consume chlorine (46) involves the use of hydrochloric acid as the reductant. The spent chlorine dioxide generator liquor is used as feed for chlorate production, and hydrogen gas from chlorate production is burned with chlorine to produce hydrochloric acid. The principal disadvantage in the integrated hydrochloric acid-based processes is that the chlorine dioxide gas contains 1/2 mole of chlorine for each mole of chlorine dioxide produced. A partial purification is achieved by absorption in chilled water in which the solubility of chlorine is less than chlorine dioxide; however, this product still contains 10–15% chlorine on the basis of total chlorine and chlorine dioxide.

1.3.5. Sulfur Dioxide Reductant

The Mathieson process uses sulfur dioxide, sodium chlorate, and sulfuric acid to produce chlorine dioxide gas with a much lower chlorine content. The sulfur dioxide gas reductant is oxidized to make sulfuric acid, reducing the overall acid requirement of the process. Air is used to dilute the chlorine dioxide produced by this process. The exit gases flow through a scrubber to which chlorate is added in order to remove any unreacted sulfur dioxide. Spent liquor, containing some unreacted chlorate, sulfuric acid, and sodium sulfate, continuously overflows from this process.

Small amounts of chlorine, amounting from 1 to 5% of the chlorine dioxide, are present in the chlorine dioxide gas product from the Mathieson process. The purity of the chlorine dioxide gas can be increased at the expense of higher chlorate content in the spent liquor if NaCl is not used in the reactor and a small amount of sulfur dioxide gas is present in the generator chlorine dioxide product gas stream.

Various improvements in the sulfur dioxide reduction processes have been commercialized, including the Canadian International Paper Process (1946) and the Kesting, Persson, and Holst processes. A variation combining both chloride and sulfur dioxide reductant processes was developed and patented by KemaNord AB (47).

1.3.6. Organic Reductant Processes

A wide range of organic compounds can be used as reducing agents in the production of chlorine dioxide from sodium chlorate. Carboxylic acids, alcohols, and carbohydrates have been reported as reducing agents, but methanol is the only organic reductant used in commercial generators. Methanol, first used in the Solvay process, is employed in processes licensed by Albright and Wilson Americas and Eka Nobel. These processes use sulfuric acid as the acid source and produce chlorine dioxide containing low levels of chlorine.

$$\mathrm{CH_3OH + 4\ ClO_3^- + 4\ H^+ \longrightarrow HCOOH + 4\ ClO_2 + 3\ H_2O} \qquad (11)$$

In improved methanol reductant processes, sulfuric acid demand is reduced by crystallizing out by-product sodium sulfate, sodium sesquisulfate, or sodium bisulfate. The particular sodium sulfate salt that is formed depends on the operating temperature and acidity of the generator. The most popular generators use a single vessel operating both as a generator and crystallizer operating under a vacuum. Vacuum operation allows water to evaporate from the generator solution to maintain steady-state concentrations in the generator liquor and to dilute the chlorine dioxide gas.

Chlorine dioxide decomposition occurrences in the generator system are less explosive when operating under reduced pressure with water vapor present. Generator operation events can sometimes occur, referred to as white-outs, during which production from the generator suddenly stops, and the gas produced contains significant amounts of chlorine.

Chlorine dioxide produced from the methanol reductant processes contains carbon dioxide and small amounts of formic acid. For this reason, sulfur dioxide and chloride-based chlorine dioxide processes are still used for sodium chlorite production. This problem has been addressed by recycling a portion of the vapor from methanol-based generators so that formic acid further reacts to carbon dioxide:

$$\mathrm{HCOOH + 2\ ClO_3^- + 2\ H^+ \longrightarrow CO_2 + 2\ ClO_2 + 2\ H_2O} \qquad (12)$$

Improvements to the methanol reductant processes may be found in the patent literature. These include methods of operation to reduce acidity in the crystallization zone of the generator to promote crystallization of sodium sulfate and to reduce sulfuric acid consumption (48). Other improvements sought are the elimination of formic acid and chlorine impurities from the chlorine dioxide, as well as methods of recovering acid and sodium hydroxide, or acid and neutral sodium sulfate from the solid sodium sesquisulfate salt waste stream (48–52).

1.3.7. Other Reductants

Sulfur, carbon, and carbon monoxide have been identified as potential reducing agents for chlorate, but no processes using these have been commercialized. Several recent patents describe chlorine dioxide generator processes using hydrogen peroxide [7722-84-1] as a reducing agent in combination with sodium chlorate and acid. Generator operation in an acid normality range of 2–5 N produces a neutral sodium sulfate by-product salt (53), whereas a sodium sesquisulfate salt is made operating in a range of 5–11 N (54).

1.3.8. Electrochemical Reduction and Catalytic Processes

Electrochemical reduction methods for producing pure chlorine dioxide from acidic solutions containing sodium chlorate have been developed (55–60). At low acidities, chloride ion must be present in order to promote the reduction of chlorate. The need for addition of chloride ion indicates that chlorine dioxide is actually being formed by chloride reduction followed by the electrolytic reduction of chlorine to chloride ion (55). The electrolytic reduction process may be catalyzed using platinum group metal oxide coated cathodes in an acid solution containing sodium chlorate (56). More complex electrochemical processes have been proposed using multiple membrane separated cell compartments to reduce acidified sodium chlorate electrochemically to chlorine dioxide with coproduction of sodium hydroxide (57, 58). Electrochemical reduction processes producing chlorine dioxide from chloric acid [7790-93-4], $HClO_3$, have also been developed. One process uses chloric acid from the ion exchange of sodium chlorate (59). Another reduction process employs chloric acid produced from the thermal or electrochemical oxidation of hypochlorous acid [7790-92-3], HOCl (60). Catalytic methods of producing chlorine dioxide in acid and sodium chlorate solution mixtures using platinum group metal oxide catalysts have also been described (61–63).

1.3.9. Other Significant Process Developments

Increasing chlorine dioxide bleaching substitution levels in the pulp mills, as well as the need for chlorine-free chlorine dioxide, are the driving forces for future process/design changes in commercial generator systems using sodium chlorate. The trends in the chlorine dioxide generator systems are being driven toward the reduction or elimination of the sodium sulfate by-product salt cake because of limited recovery boiler capacity in many pulp mills in the United States and Canada. One method of resolving this problem is converting the by-product sodium sulfate salt cake to sulfuric acid and sodium hydroxide by employing electrochemical salt-splitting technology (64, 65) (see Electrochemical processing).

Alternative technology developments are focusing on the use of chloric acid as a generator feed in place of sodium chlorate, thus reducing the requirement for acid addition and minimizing or eliminating salt cake by-product. Methods for the formation or *in situ* production of chloric acid from sodium chlorate by ion exchange (qv) (59), electrodialysis (qv) (66, 67), or by integrating an electrochemical cell with a generator (66, 68, 69) may be found in the literature. Other methods of chloric acid production are by the thermal decomposition or electrochemical oxidation of hypochlorous acid (60, 70). In an alternative development, an electrochemical process producing variable composition chloric acid/sodium chlorate mixtures from sodium chlorate with the coproduction of sodium hydroxide, has been developed (71). The mixtures can be directly fed into a generator to balance the daily sulfur requirements of individual pulp mills as required.

A process for producing chlorine-free chlorine dioxide, called the O1 PROCESS technology, was announced by Olin Corp. in early 1992 (72). The process uses a pure chloric acid feedstock and proprietary catalysts that utilize water as the reducing agent. The overall reaction chemistry of the process is

$$2\ HClO_3 \longrightarrow 2\ ClO_2 + 1/2\ O_2 + H_2O \qquad (13)$$

Table 2. Chlorine Dioxide Production in North America, 10^3 t / yr[a]

Year	United States	Canada	Total
1970	79	47	126
1975	81	63	144
1980	146[b]	122	268
1985	226	130	356
1990	361	200	561

[a] Ref. 74.
[b] Estimated value.

The process requires water vapor removal from the generator to be balanced with the water introduced with the chloric acid feed. Significantly greater chlorine dioxide generator capacity is achievable than using the older design generators.

1.3.10. Other ClO_2 Generation Methods

A method of generating chlorine dioxide has been described using a high temperature inert gas plasma reaction using a chlorine and oxygen gas mixture having at least a 2.5:1 molar ratio of oxygen to chlorine (73).

1.4. Production and Shipment

In all cases, chlorine dioxide is produced at the point of use either from sodium chlorite or sodium chlorate. Production volume can be accurately estimated from total sodium chlorate consumption for chemical pulp bleaching because this use accounts for greater than 95% of all chlorine dioxide production. The annual North American production of chlorine dioxide since 1970 is given in Table 2.

1.5. Economic Aspects

The costs of manufacturing chlorine dioxide from sodium chlorate vary for different processes depending on the degree of integration with chlorate manufacture and the need for by-products produced from chlorine dioxide production. The principal costs of chlorine dioxide manufacture are determined by the consumption of sodium chlorate, acid, and reducing agent, together with the fixed costs of operating and maintaining the facility. Estimates in 1992 ranged from $1100 to $1800 per metric ton.

The cost of manufacturing chlorine dioxide from sodium chlorite is about two to four times higher than that from sodium chlorate. However, the fixed operating costs of small-scale chlorate-based processes are much higher. The production costs from sodium chlorite are governed by the cost of the chlorite, and the related costs of the handling and storage of the oxidizing agents and/or acids used to generate the chlorine dioxide.

1.6. Uses

The uses for chlorine dioxide take advantage of the high oxidizing power and broad-spectrum disinfection capability.

1.6.1. Pulp Bleaching

Wood pulp bleaching is the largest use of chlorine dioxide, which is a uniquely selective oxidizer for lignin. Unlike other oxidizing bleaches such as ozone, hydrogen peroxide, oxygen, or chlorine, chlorine dioxide does not attack cellulose and thus preserves the mechanical properties of bleached pulp. Chlorine dioxide bleaching is more effective than other methods at removing incompletely defibered wood or shives (75–78). Compared with other oxidative bleaching chemicals, chlorine dioxide is the most expensive to produce, but it can actually reduce overall bleaching costs under certain conditions (78).

Pulp bleaching is normally performed in several oxidative stages separated by alkaline extraction stages and washing. In final oxidative bleaching stages, chlorine dioxide is the most frequently preferred bleaching chemical. Pulp bleaching practice in the United States makes use of mixtures of chlorine and chlorine dioxide in first-stage bleaching to reduce the formation of organic chlorine compounds in the bleaching process while minimizing total chemical cost (75, 77, 78).

The formation of chlorinated organic compounds in the pulp is measured as absorbable organic halides (AOX) or as total organically bound chlorine (TOCl). The amount formed during bleaching appears to be a linear function of the chlorine and chlorine dioxide added. Chlorine dioxide contributes about 1/5 the chlorinated organic compounds, as does chlorine. However, when individual chlorinated compounds are measured, a more complex, nonlinear relationship is found. Formation of the most toxic highly polychlorinated phenolic compounds, particularly dioxins and chlorofurans, can be eliminated with only partial substitution of chlorine dioxide for chlorine (see Chlorocarbons and chlorohydrocarbons, toxic aromatics). As chlorine dioxide is substituted for chlorine, the distribution of chlorinated species shifts from polychlorinated compounds to dichloro and monochlorinated compounds. Even when pure chlorine dioxide is used, some amounts of monochlorinated organics are formed during bleaching (78, 79).

The stoichiometric relationship between chlorine dioxide added and color removed during bleaching is nonlinear, but it is independent of temperature, pH, and pulp concentration under conditions normally used. Models used to explain the kinetics and stoichiometry show a strong dependence on chromophore concentration that probably results from differences in the reaction rates of the various chromophores present in the pulps (80).

When chlorine dioxide is used for pulp bleaching in conjunction with the Kraft (sulfide) process for chemical pulping, by-product sodium sulfate can be used as a source of makeup sulfur and sodium consumed in the chemical cycle. The demand for sodium and sulfur in pulp bleaching is related to the loss of these chemicals through carryover in unbleached pulp. As process improvements have sought to reduce pollution from pulp mills, less sodium sulfate makeup is required. The trends in pulp bleaching to increase substitution of chlorine with chlorine dioxide have caused an oversupply of sodium sulfate, so that this by-product is often regarded as waste (81).

Where pressured to provide bleaching alternatives that avoid the use of chlorine containing compounds entirely, pulp producers have developed bleaching processes that use ozone in place of chlorine dioxide. However, when bleaching kraft pulps, ozone must be used in conjunction with oxygen delignification and does not produce pulp having the same combination of brightness and strength as using chlorine dioxide. However, combinations of chlorine dioxide and ozone have demonstrated better bleaching, resulting in less loss of pulp yield and strength than for ozone alone. These processes also demonstrate exceptionally low AOX per metric ton of pulp produced (82–85).

Pulp bleaching with chlorine dioxide is most often performed at an acidic pH, so that the final pH of the bleach liquor is in the range of 2–5. Under these conditions, the residual concentration of chlorite and chlorate ions in the bleach liquor are minimized and chloride ion is the predominant chlorine species in the spent bleach (77). In addition to direct addition to pulp in bleaching, chlorine dioxide also finds use in wastewater treatment from pulp mill operations as a means to remove effluent color (85).

1.6.2. Other Uses

As a biocide, chlorine dioxide is more effective than chlorine over a wider pH range. Chlorine dioxide is also less corrosive and more compatible with some materials of construction. Chlorine dioxide has a wide variety of small applications in drinking water, food processing (qv), cooling towers, and oil recovery. In these areas, chlorite is the preferred source of chlorine dioxide.

1.7. Toxicology

Gaseous chlorine dioxide is explosive at concentrations above 10.1 kPa (76 mm Hg) partial pressure (10 vol %) in air. Explosions may be caused by an electrical discharge including static electricity, hot surfaces, metal oxides, or organics, and may be self-initiated after an induction period. Flame propagation velocities for explosive decomposition are a function of the initial partial pressure of chlorine dioxide and range from 1 m/s at 16.7 kPa (125 mm Hg), to more than 5 m/s at 40 kPa (300 mm Hg) (23, 86). Explosions are much more violent and may occur at lower concentrations when organic vapors are present. When involved in a fire, chlorine dioxide is a source of oxygen. The decomposition reactions of chlorine dioxide may produce hazardous by-products such as hydrochloric acid, chlorine, and chloric acid.

The threshold limit value–time integrated average, TLV–TWA, of chlorine dioxide is 0.1 ppm, and the threshold limit value–short-term exposure limit, STEL, is 0.3 ppm or 0.9 mg/m^3 of air concentration (87, 88). Chlorine dioxide is a severe respiratory and eye irritant. Symptoms of exposure by inhalation include eye and throat irritation, headache, nausea, nasal discharge, coughing, wheezing, bronchitis, and delayed onset of pulmonary edema. Delayed deaths occurred in animals after exposure to 150–200 ppm for less than one hour. Rats repeatedly exposed to 10 ppm died after 10 to 13 days of exposure. Exposure of a worker to 19 ppm for an unspecified time was fatal. The ingested systemic effects of low concentration chlorine dioxide solutions are similar to that of chlorite.

Chlorine dioxide solutions are normally stored cold at concentrations of less than 10 g/L in order to keep the concentration of gaseous chlorine dioxide above the aqueous solutions below the explosive limit. Chlorine dioxide solutions are corrosive to the skin and eyes, and solutions must be handled with adequate ventilation to avoid exposure to the gas. Protective equipment required for chlorine dioxide are impervious clothing, neoprene gloves and boots, gas-tight chemical splash goggles and face shields, as well as other appropriate clothing to prevent the possibility of skin contacting aqueous solutions or vapor. Clothing contaminated with chlorine dioxide should be removed immediately and thoroughly washed. In the event of spills or leaks, personnel not wearing appropriate safety equipment should be immediately evacuated from the area. NIOSH/MHSA-approved respiratory protection is required for chlorine dioxide concentrations above 0.1 ppm. For ClO_2 concentrations above ~ 10 or unknown ppm, self-contained breathing apparatus is required for entry and escape and in firefighting. All sources of ignition should be removed and the area of the leak or spill should be ventilated and the source of the leak stopped. Any residual material should be flushed with large quantities of water. Contaminated material and residues should be disposed of in a manner approved for this material. Manufacturer MSDS data sheets and technical information should be consulted (87, 88).

1.8. Analytical and Test Methods

Reagents similar to those used in the analysis of chlorine are commonly employed in the quantitation of gaseous and aqueous chlorine dioxide as well as its reaction coproducts chlorine, chlorite, and chlorate. The volatility of the gas from aqueous solutions as well as its reactivity to light must be considered for accurate analysis. Other interferences that must be taken into account include other oxidizers such as chloramine, hydrogen peroxide, permanganate, and metal impurities such as ferrous and ferric iron.

The iodometric analysis method for ClO_2 and its coproducts is based on the pH-dependant oxidation of potassium iodide to selectively distinguish the various oxychlorine species from each other (42, 89). The reactions of the oxidizer species with iodide at various pH buffered conditions are

$$Cl_2 + 2\,I^- \longrightarrow I_2 + 2\,Cl^- \qquad \text{pH } 7,\ 2,\ <0.1 \qquad (14)$$

$$2\ \mathrm{ClO_2} + 2\ \mathrm{I^-} \longrightarrow \mathrm{I_2} + 2\ \mathrm{ClO_2^-} \qquad \text{pH 7} \qquad (15)$$

$$2\ \mathrm{ClO_2} + 10\ \mathrm{I^-} + 8\ \mathrm{H^+} \longrightarrow 5\ \mathrm{I_2} + 2\ \mathrm{Cl^-} + 4\ \mathrm{H_2O} \qquad \text{pH 2, <0.1} \qquad (16)$$

$$\mathrm{ClO_2^-} + 4\ \mathrm{I^-} + 4\ \mathrm{H^+} \longrightarrow 2\ \mathrm{I_2} + \mathrm{Cl^-} + 2\ \mathrm{H_2O} \qquad \text{pH 2, <0.1} \qquad (17)$$

$$\mathrm{ClO_3^-} + 6\ \mathrm{I^-} + 6\ \mathrm{H^+} \longrightarrow 3\ \mathrm{I_2} + \mathrm{Cl^-} + 3\ \mathrm{H_2O} \qquad \text{pH <0.1} \qquad (18)$$

Use of a pH buffer of 8–9 has been suggested as a substitute for the pH 7 buffer for more accurate analysis. Sodium thiosulfate [10102-17-7], $Na_2S_2O_3$, or phenylarsine oxide [637-03-6], C_6H_5AsO, are the typical titrants.

$$\mathrm{C_6H_5AsO} + \mathrm{I_2} + 2\ \mathrm{H_2O} \longrightarrow \mathrm{C_6H_5AsO\,(OH)_2} + 2\ \mathrm{H^+} + 2\ \mathrm{I^-} \qquad (19)$$

$$2\ \mathrm{Na_2S_2O_3} + \mathrm{I_2} \longrightarrow \mathrm{Na_2S_4O_6} + 2\ \mathrm{Na^+} + 2\ \mathrm{I^-} \qquad (20)$$

These titrations can be done manually using a starch indicator for end point detection or more accurately by amperometric methods.

Ion chromatography is being qualified as a standard method for chlorite and chlorate analysis (90). Flow injection analysis methods have also been developed based on the iodometric pH adjusted reaction chemistry illustrated in equations 14–18 using spectrophotometric detectors (91, 92). A colorimetric method using *N,N*-diethyl-*p*-phenylenediamine [93-05-0] (DPD), $C_{10}H_{16}N_2$, (42) is popular but is subject to interferences from other oxychlorine oxidizing species present. Colorimetric methods using chlorophenol red [4430-20-0] have been found to be specific for ClO_2 without interferences from chlorine (93, 94). A detailed review of the various oxychlorine analytical methods is available (95).

Commercially available process analyzers have been developed for the online measurement and control of chlorine dioxide gas and aqueous solution generation systems. A gas chromatography method has been described for measuring Cl_2 and ClO_2 in gases (96). Near uv spectroscopic methods are the most common, suitable for aqueous ClO_2 in the 0.05–10 g/L range and in the ppm to vol % ranges for gaseous ClO_2. Amperometric and oxidation–reduction potential (ORP)-based sensors (qv) are commercially available for ClO_2 solutions and gases in the ppm and mg/L and lower ranges.

2. Chlorous Acid and Chlorites

2.1. Physical Properties

2.1.1. Chlorous Acid

The physical properties of $HClO_2$ have been determined using acidified alkali metal chlorite solutions. The existence of $HClO_2$ is based on spectroscopic evidence (6, 13, 97).

2.1.2. Sodium Chlorite

The Cl–O bond lengths in the chlorite ion are about 0.156 nm and the bond angle is between 108–110° (98–101). The uv absorption spectra of aqueous chlorite solutions have a maximum at about 260 nm. The crystallization of sodium chlorite from aqueous solutions yields solid sodium chlorite trihydrate [49658-21-1], $NaClO_2 \cdot 3H_2O$, at temperatures below 37.4°C. Anhydrous $NaClO_2$ [7758-19-2] forms above 37.4°C. The anhydrous form is not hygroscopic (102, 103) and is slightly soluble in methanol. Analytical-grade $NaClO_2$ (mol wt = 90.442) is a colorless crystalline solid that decomposes as it melts between 180–200°C. Technical-grade (80 wt % assay) $NaClO_2$ is a white solid that may have a slight greenish tint from trace amounts of ClO_2 or metals such as iron.

2.2. Chemical Properties

2.2.1. Chlorous Acid

The chemical properties of $HClO_2$ have been determined from the acidification of alkali metal chlorites. The K_a acid dissociation constant of chlorous acid at 25°C, reported to be about 1.1×10^{-2} (104, 105), has been measured using rapid scan spectrophotometric methods and determined to be 1.9×10^{-2} (106). The standard enthalpy, Gibbs free energy, and standard entropy for $HClO_2$ at 298.15 K are $\Delta H^\circ = -51.9$ kJ/mol (− 12.4 kcal/mol), $\Delta G_f^\circ = 5.9$ kJ/mol (1.4 kcal/mol), and $S^\circ = 0.1013$ kJ/(moK) (0.024 kcal/(moK)), respectively (107). The overall disproportionation of chlorous acid in acidic solutions in the absence of chloride ion has been reported as:

$$4\ HClO_2 \longrightarrow 2\ ClO_2 + ClO_3^- + Cl^- + 2\ H^+ + H_2O \qquad (21)$$

In the presence of added chloride, chlorate ion is formed in negligible amounts.

$$5\ HClO_2 \longrightarrow 4\ ClO_2 + Cl^- + H^+ + 2\ H_2O \qquad (22)$$

equation 22 gives the maximum theoretical obtainable chlorine dioxide from the disproportionation of $HClO_2$. Experimentally, differences in the stoichiometry have been reported. This is because the chloride formed in equation 21 can catalyze the reaction to form more chlorine dioxide as in equation 22. Proposed mechanisms for these reactions and the kinetics under various conditions have been described (16, 108).

2.2.2. Sodium Chlorite

The standard enthalpy, Gibbs free energy of formation, and standard entropy for aqueous chlorite ions are $\Delta H^\circ = -66.5$ kJ/mol (− 15.9 kcal/mol), $\Delta G_f^\circ = 17.2$ kJ/mol (4.1 kcal/mol), and $S^\circ = 0.1883$ kJ/(moK) (0.045 kcal/(moK)), respectively (107). The thermal decomposition products of $NaClO_2$ in the 175–200°C temperature range are sodium chlorate and sodium chloride (102, 109):

$$3\ NaClO_2 \longrightarrow 2\ NaClO_3 + NaCl \qquad (23)$$

About 5 wt % of the chlorite goes to oxygen. At higher temperatures, the by-product sodium chlorate melts at about 260°C and decomposes above about 448°C. Sodium chlorite is not shock sensitive unless contaminated with organics. Commercial alkaline sodium chlorite solutions are stable so long as light is excluded. Solutions can even be boiled with little assay loss. Hydrogen peroxide reduces chlorite very slowly in a pH range between 3 and 9 (102).

Many of the metal chlorites are not particularly stable and will explode or detonate when struck or heated. These include the salts of Hg^+, Tl^+, Pb^{2+}, Cu^+, and Ag^+. Extremely fast decomposition with high heat evolution has been noted for barium chlorite [14674-74-9], $Ba(ClO_2)_2$, at 190°C, silver chlorite [7783-91-7], $AgClO_2$, at 120°C, and lead chlorite [13453-57-1], at 103°C (109). Sodium chlorite can be oxidized by ozone to form chlorine dioxide under acidic conditions (110):

$$2\ NaClO_2 + O_3 + H_2O \longrightarrow 2\ ClO_2 + 2\ NaOH + O_2 \qquad (24)$$

The proposed mechanistic details are (111):

$$ClO_2^- + O_3 \longrightarrow ClO_2 + O_3^- \qquad (25)$$

$$O_3^- + H_2O \longrightarrow OH + O_2 + OH^- \qquad (26)$$

$$ClO_2^- + OH\cdot \longrightarrow ClO_2 + OH^- \qquad (27)$$

The generated ClO_2 has a competing reaction with excess ozone to form chlorate. Mechanistically,

$$ClO_2 + O_3 + H_2O \longrightarrow ClO_3^- + O_3^- + 2\ H^+ \qquad (28)$$

$$O_3^- + H_2O \longrightarrow OH + O_2 + OH^- \qquad (29)$$

$$ClO_2 + OH\cdot \longrightarrow ClO_3^- + H^+ \qquad (30)$$

yielding the net equation:

$$2\ ClO_2 + O_3 + H_2O \longrightarrow 2\ ClO_3^- + O_2 + 2\ H^+ \qquad (31)$$

Sodium chlorite is used to produce chlorine dioxide by chemical oxidation, electrochemical oxidation methods, or by acidification with acids. Most of the commercial methods employ chlorine or sodium hypochlorite.

2.2.3. Acid–Sodium Chlorite System

The addition of a strong inorganic acid into an aqueous sodium chlorite solution produces chlorous acid, which rapidly disproportionates into chlorine dioxide. One proposed set of reactions using hydrochloric acid is (110):

$$NaClO_2 + HCl \longrightarrow HClO_2 + NaCl \qquad (32)$$

$$HClO_2 + 3\ HCl \longrightarrow 2\ Cl_2 + 2\ H_2O \qquad (33)$$

$$4\ NaClO_2 + 2\ Cl_2 \longrightarrow 4\ ClO_2 + 4\ NaCl \qquad (34)$$

yielding the net equation:

$$5\ NaClO_2 + 4\ HCl \longrightarrow 4\ ClO_2 + 5\ NaCl + 2\ H_2O \qquad (35)$$

A secondary reaction path produces by-product chlorate and has a proposed net reaction of:

$$4\ NaClO_2 + 2\ HCl \longrightarrow 2\ ClO_2 + NaClO_3 + 3\ NaCl + H_2O \qquad (36)$$

The maximum chlorite to chlorine dioxide theoretical molar yield using HCl is only 80%. In practice, 85–90% of the 80% molar theoretical yield is obtained using a 300% molar excess of strong HCl (112). A patented generator design employs a strong acid stream and a concentrated chlorite solution using a water eductor system to draw off and dilute the high concentration chlorine dioxide gas containing liquid stream (113). Chlorine dioxide yields from chlorite by acidification using sulfuric acid generally does not exceed about 60–70% of the theoretical 80% molar yield. The methods using hydrochloric acid give increased conversion yields because of the presence of chloride ion. The acid–chlorite generating systems are commonly used in very small-scale operations for convenience.

2.2.4. Hypochlorous Acid–Sodium Chlorite System

In this method, chlorine gas is educted into water forming a hypochlorous acid solution which then reacts with aqueous sodium chlorite to produce chlorine dioxide (114–116). Hypochlorous acid, formed from the disproportionation of chlorine gas in water:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl \qquad (37)$$

reacts with sodium chlorite to produce ClO_2:

$$2\ NaClO_2 + HOCl + HCl \longrightarrow 2\ ClO_2 + 2\ NaCl + H_2O \qquad (38)$$

Demonstrated chlorine dioxide yields from chlorite are 95% or higher in properly operated systems. Excess hypochlorous acid is commonly used to achieve a high conversion.

2.2.5. Chlorine Gas–Sodium Chlorite System

In this method, chlorine gas reacts directly with a concentrated sodium chlorite solution under a vacuum and chlorine dioxide gas is removed from the reaction chamber using a water-based eductor (117). The reaction has a 100% theoretical molar conversion of chlorite:

$$2\ NaClO_2 + Cl_2 \longrightarrow 2\ ClO_2 + 2\ NaCl \qquad (39)$$

Chlorine dioxide yields of 95% or greater have been demonstrated. The use of chlorine as an oxidant has distinct advantages because it is usually present in municipal water treatment plants for water disinfection.

2.2.6. Sodium Hypochlorite–Acid–Sodium Chlorite System

In this method, hydrochloric or sulfuric acid is added into a sodium hypochlorite [7681-52-9], NaOCl, solution before reaction with the sodium chlorite (118).

$$HOCl \rightleftharpoons OCl^- + H^+ \qquad (40)$$

The acid addition shifts the chlorine solution equilibrium to favor molecular chlorine. The hypochlorous acid–chlorine equilibria is

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (41)$$

The pH of the chlorine dioxide reaction mixture must be maintained in the 2.8–3.2 pH range, otherwise decreased conversion yields of chlorite to chlorine dioxide are obtained with by-product formation of chlorate. Generator efficiencies of 93% and higher have been demonstrated. A disadvantage of this system is the limited storage life of the sodium hypochlorite oxidant solution.

2.2.7. Photochemical Generation of Chlorine Dioxide from Chlorite

Several methods of generating chlorine dioxide by the photochemical oxidation of chlorite have been reported in patents. The chlorite solution is irradiated using a light source and the chlorine dioxide generated is swept from the solution using an inert gas stream. Low concentrations of ClO_2 gas are produced (119, 120). In another method, ultraviolet light is used in conjunction with salts or hydrogen ions added to a chlorite solution (121).

2.2.8. Electrochemical Generation of Chlorine Dioxide from Chlorite

The electrochemical oxidation of sodium chlorite is an old, but not well-known method of generating chlorine dioxide. Concentrated aqueous sodium chlorite, with or without added conductive salts, is oxidized at the anode of an electrolytic cell having a porous diaphragm-type separator between the anode and cathode compartments (122–127). The anodic reaction is

$$ClO_2^- \longrightarrow ClO_2 + e^- \qquad (42)$$

The generated chlorine dioxide must be air stripped from the anode compartment in order to achieve high chlorite conversion efficiency. Sodium ions from the anode compartment are transported into the cathode compartment, forming sodium hydroxide [1310-73-2] and hydrogen gas coproducts:

$$2\ Na^+ + 2\ H_2O + 2\ e^- \longrightarrow 2\ NaOH + H_2 \qquad (43)$$

giving a net reaction of:

$$NaClO_2 + H_2O \longrightarrow ClO_2 + NaOH + 1/2\ H_2 \qquad (44)$$

A concentrated waste stream containing chlorate by-product and residual unreacted chlorite is generated from anodic oxidation of ClO_2 and chlorite side reactions to chlorate. Oxidation-resistant perfluorinated ion-exchange membrane separators (see Membrane technology) and solid polymer electrolyte electrodes have improved process performance and reduced by-product formation (128–130). An alternative electrochemical process producing aqueous chlorine dioxide and coproduct sodium hydroxide from the *in situ* acid activation of sodium chlorite has been developed (131). New electrochemical generation technology employing high surface area anodes have also been developed, producing chlorine-free aqueous chlorine dioxide solutions from dilute chlorite solutions. Chlorite to chlorine dioxide conversion efficiencies of 95% or better have been demonstrated in a single flow-through pass with no by-product chlorate–chlorite waste streams (132–134).

2.2.9. Mechanisms in Chlorine Dioxide Generation from Chlorite

The reactions between sodium chlorite and chlorine-based oxidizers and acids are complex and involve the formation of the proposed unsymmetrical intermediate, [Cl_2O_2] (16, 18, 22, 36, 108, 135–140).

The reactions of chlorite and chlorine and/or hypochlorous acid are

$$2\ \mathrm{ClO_2^-} + \mathrm{Cl_2}\ (\mathrm{g}) \longrightarrow 2\ \mathrm{ClO_2}\ (\mathrm{g}) + 2\ \mathrm{Cl^-} \qquad (45)$$

$$2\ \mathrm{ClO_2^-} + \mathrm{HOCl} \longrightarrow 2\ \mathrm{ClO_2}\ (\mathrm{g}) + \mathrm{Cl^-} + \mathrm{OH^-} \qquad (46)$$

Mechanistically, equations 45 and 46 involve the formation of a [Cl_2O_2] intermediate:

$$\mathrm{Cl_2} + \mathrm{ClO_2^-} \longrightarrow \left[\mathrm{Cl_2O_2}\right] + \mathrm{Cl^-} \qquad (47)$$

At high reactant concentrations, this intermediate is favored and rapidly formed. It then decomposes in a second order reaction to form chlorine dioxide and chlorine:

$$2\ \left[\mathrm{Cl_2O_2}\right] \longrightarrow 2\ \mathrm{ClO_2} + \mathrm{Cl_2} \qquad (48)$$

The generated chlorine further reacts with additional chlorite as given in equation 47, so that the net reaction of the intermediate with chlorite can be written as

$$\left[\mathrm{Cl_2O_2}\right] + \mathrm{ClO_2^-} \longrightarrow 2\ \mathrm{ClO_2} + \mathrm{Cl^-} \qquad (49)$$

The reaction chemistry changes when the initial reactant concentrations are low or there is excess hypochlorous acid present. The [Cl_2O_2] intermediate disproportionation route to chlorine dioxide becomes less important (eq. 48), and the route to chlorite formation by hydrolysis predominates as does the reaction with any available excess HOCl to form chlorate and chlorine:

$$\left[\mathrm{Cl_2O_2}\right] + \mathrm{H_2O} \longrightarrow \mathrm{ClO_3^-} + \mathrm{Cl^-} + 2\ \mathrm{H^+} \qquad (50)$$

$$\left[\mathrm{Cl_2O_2}\right] + \mathrm{HOCl} \longrightarrow \mathrm{ClO_3^-} + \mathrm{Cl_2} + \mathrm{H^+} \qquad (51)$$

Large amounts of chlorate are formed when there is a large excess of chlorine or HOCl in relation to chlorite. These chlorate forming reactions are

$$\mathrm{ClO_2^-} + \mathrm{HOCl} \longrightarrow \mathrm{ClO_3^-} + \mathrm{Cl^-} + \mathrm{H^+} \qquad (52)$$

$$\mathrm{ClO_2^-} + \mathrm{Cl_2} + \mathrm{H_2O} \longrightarrow \mathrm{ClO_3^-} + 2\ \mathrm{Cl^-} + 2\ \mathrm{H^+} \qquad (53)$$

The conditions for chlorate formation are high pH, low reactant concentrations, and the presence of excess chlorine or hypochlorous acid. Thus, the addition of free chlorine or hypochlorite to chlorine dioxide treated water, which contains chlorite as a by-product of the chlorine dioxide treatment, predominantly forms chlorate in the pH 5–8 range typically used in water treatment (140).

2.2.10. Organic Reactions

The chlorite ion, ClO_2^-, is mostly a weak and slow oxidizer in alkaline aqueous solutions. Aldehydes (qv) can be readily oxidized to the corresponding carboxylic acids in neutral or weakly acidic solutions. Mixing solid sodium chlorite with combustible organic materials can result in explosions and fire on shock, exposure to heat, or flames.

2.3. Manufacture

Sodium chlorite is the only chlorite compound produced on a commercial scale. Technical-grade sodium chlorite is an 80 wt % assay solid product containing other added salts, such as sodium chloride, which act as diluents for increased safety in storage and handling. The various sodium chlorite solution grades similarly have varying amounts of other salts.

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 [7722-84-1] as the reducing agent. The chlorine dioxide is generated from the chemical or electrochemical reduction of sodium chlorate under acidic conditions.

In the general process, chlorine dioxide gas is absorbed into a cooled (15–20°C) circulating solution containing sodium hydroxide and hydrogen peroxide. The predominant reaction is (141, 142):

$$2\ ClO_2 + 2\ NaOH + H_2O_2 \longrightarrow 2\ NaClO_2 + 2\ H_2O + O_2 \qquad (54)$$

A secondary competing reaction can occur where chlorine dioxide disproportionates in the alkaline solution, producing sodium chlorite and chlorate:

$$2\ ClO_2 + 2\ NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O \qquad (55)$$

The reaction in equation 55 occurs when there is insufficient hydrogen peroxide reductant in the absorber solution. Monitoring of the hydrogen peroxide concentration is important because H_2O_2 is unstable in strong alkaline solutions, decomposing to water and oxygen. A small excess of sodium hydroxide is maintained to stabilize the final chlorite solution product. The yield of sodium chlorite from the absorbed chlorine dioxide is generally 95% or better. Process methods for controlling the hydroxide/peroxide liquid absorber operation using pH and/or redox potential for high yield production of chlorite from the raw materials have been described (141–143).

2.4. Production and Shipment

Solution sodium chlorite is shipped by producers and distributors in specified plastic containers, plastic drums, tote tanks, isotainers, and tank trucks. Dry product is shipped in 45.36 kg, 50 kg, and 80 kg capacity drums in the United States. Sodium chlorite is not authorized for bulk transport as a solid.

Sodium chlorite solutions with more than 5% available chlorine have a U.S. Department of Transportation (DOT) shipping classification as a class 8 corrosive, identification number UN1908, with a group II packaging requirement. Sodium chlorite dry powder or flake is a class 5.1 oxidizer, identification number UN1496, also with a group II packaging requirement. The DOT HM-181 regulations on the containers, packaging, markings,

Table 3. 1991 Sodium Chlorite Production Capacity

Company	Country	Capacity, t[a,b]
North America		
Olin Corp.[c]	United States	7700
Albright & Wilson Americas, Inc.,[d] Div. of Tenneco Canada Inc.	Canada	4000[e]
Western Europe		
Energia e Industria Aragonesas, SA	Spain	1500
Atochem SA	France	7000
Degussa AG	Germany	5000
Hoechst AG	Germany	5000
Caffaro SpA	Italy	4000
East Asia		
Kuk-do Chemical Industry Co., Ltd.	South Korea	3000[e]
Nippon Carlit Co., Ltd.	Japan	2500
Daiso Chemical Co., Ltd.	Japan	1800
Hodogaya Soda Co., Ltd.	Japan	2500
Nippon Soda Co., Ltd.	Japan	1800

[a] Ref. 74.
[b] Estimated or actual production capacities for 80% assay basis sodium chlorite.
[c] Sale of chlorite business unit to Vulcan Chemicals (Birmingham, Ala.) announced in June 1992.
[d] Sale of chlorite business to Sterling Chemicals (Houston, Tex.) announced in March 1992.
[e] Information from public news releases and/or personal communication.

and transportation of sodium chlorite are published in the *Federal Register* under the *Hazardous Materials Regulations* (HMR), covering the transportation of hazardous materials in commerce (144, 145). In Canada, the regulations are under the *Transportation of Dangerous Goods Regulations*. The latest issue of the regulations should be consulted for any additions or changes.

2.5. Economic Aspects

The specific use applications of sodium chlorite varies from country to country. Important factors are the regulatory and environmental laws in effect for air and water quality standards. Sodium chlorite is generally priced at about four to six times the cost of sodium chlorate. The list price of 80% technical-grade $NaClO_2$ in January 1991 was $2.65/kg (146). In 1990, the estimated consumption of sodium chlorate for the production of sodium chlorite in Canada was about 2700 metric tons and about 9100 metric tons in the United States (74). In Western Europe, the 1990 chlorate consumption estimate was about 11,000 metric tons. A summary of 1991 U.S. and foreign sodium chlorite producer annual plant capacities in various world market areas is given in Table 3.

The principal U.S. manufacturers and/or water service companies that sold or leased chlorine dioxide generating equipment and services in 1991 were Aquatec, Capital Controls, Chemquip, Drew Chemical (Division of Ashland Chemical), Fischer & Porter, Prominent Fluid Controls, Rio Linda, and Wallace & Tiernan.

2.6. Specifications, Standards, and Quality Control

Technical-grade solid and solution sodium chlorite for use in potable water treatment has specifications listed by the American Water Works Association (AWWA) (147), the National Sanitization Foundation (NSF), and the American National Standard/NSF International (148).

In the AWWA specification standards, technical solid sodium chlorite should not contain less than 78.0 wt % $NaClO_2$. The impurity limits for 80% assay sodium chlorite should not be more than 17.0 wt % sodium chloride, 3.0 wt % sodium carbonate, 3.0 wt % sodium sulfate, and 0.0003 wt % arsenic. The AWWA standards also specify the analysis procedures for all of the chemical components in the sodium chlorite.

2.7. Toxicology

The toxic effects of sodium chlorite are directly related to its oxidant properties. Details of toxicological studies are summarized in reviews (149, 150). Sodium chlorite is toxic mainly from ingestion. The acute oral LD_{50} is approximately 180 mg/kg (rat) for the 79 wt % assay product. The dermal LD_{50} exposure is low, greater than 2 g/kg (rabbit). Sodium chlorite produces severe irritation or burns to the skin or eyes. Corneal damage and impairment of vision may occur if this material is not washed immediately from the eyes. Sodium chlorite is slightly toxic to most fish and other aquatic organisms. For bluegill (*Lepomis macrochirus*) the median tolerance limit, TL_{50}, is 208 mg/L and the lethal concentration fifty, LC_{50}, values are 265–310 mg/L. For rainbow trout (*Salmo gairdneri*), the TL_{50} is 50.6 mg/L and LC_{50} is 290 mg/L. Of the aquatic species tested, Daphnia is the most sensitive with an LC_{50} of 0.29 mg/L (150).

Sodium chlorite is not listed by the USEPA or any regulatory authority as a carcinogen. Studies conducted in mice and rats did not show an increase in tumors in animals exposed to sodium chlorite in their drinking water. Sodium chlorite has been found to have mutagenic activity in some *in vitro* test systems such as the Ames Salmonella reverse mutation assay without the presence of metabolic activators. The significance of these test results in regard to human health is not clear because of the oxidizing effects of the chlorite ion (149).

Controlled animal and human clinical studies on the effects of sodium chlorite and/or chlorine dioxide have been conducted in a 1–1000 mg/L concentration range. Metabolically, both ClO_2 and ClO_2^- are rapidly reduced following ingestion. Most of the chlorine is excreted from the urine in the form of Cl^- ion with a small amount of ClO_2^-. The no observed effect level, NOEL, from animal studies involving ClO_2 and ClO_2^- generally ranges between 10 and 100 ppm. Exposure of laboratory animals to ClO_2 above 100 mg/L in drinking water have shown a decrease in blood cell glutathione, red blood cell counts, and hemoglobin. Some mild effects on the thyroid and anemia were noted in younger laboratory animals. Human volunteers in one study with doses up to 24 mg/L of ClO_2 or ClO_2^- showed no adverse health effects (149).

Dry sodium chlorite decomposes at temperatures above about 175°C, forming sodium chloride, sodium chlorate, and oxygen as by-products. The reaction is extremely exothermic and therefore self-sustaining. Sodium chlorite should be kept away from heat or flames. Contact or mixing of sodium chlorite with acids can produce poisonous and possibly explosive mixtures of chlorine dioxide and chlorine gas. Sodium chlorite is incompatible with all combustibles, reducing agents, and oxidizers. Mixtures or contamination of sodium chlorite with oxidizable, combustible, or organic materials can be easily ignited by heat or friction and may spontaneously burn or explode. Examples of these materials are cloth, wood, paper, greases, oils and solvents, rubber, leather, and plastics. Sodium chlorite is especially incompatible with sulfur, sulfur compounds, powdered metals, and phosphorous and ammonium compounds (150).

Protective personal equipment for handling sodium chlorite includes splash-proof goggles, neoprene gloves and boots, waterproof or washable outer clothing, and a dust mask for powder handling. All chlorite contaminated clothing should be washed quickly and thoroughly with water to prevent fires. Spills should be contained and dampened with water before collecting into clean metal or high density polyethylene containers to reduce fire hazards. Contaminated materials should be washed or incinerated in an environmentally acceptable manner. Material Safety Data Sheets (MSDS) issued by the sodium chlorite manufacturer should be consulted before handling and use.

2.8. Uses

More than 80% of all the sodium chlorite produced is used for the generation of chlorine dioxide. Sodium chlorite or the chlorine dioxide generated from it or from sodium chlorate must be registered with the USEPA for each specific application use as a biocide for microbial growth control or disinfection. These regulations are covered under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).

2.8.1. Municipal/Industrial Water Treatment

The principal consumption of sodium chlorite is as the precursor in chlorine dioxide generation for use as an effective disinfectant alternative in municipal and wastewater treatment. Chlorine dioxide is used for taste and odor control as well as for iron and manganese removal. An estimated 300–400 utilities in the United States have chlorine dioxide treatment equipment (151). One role for chlorine dioxide is in the control of total trihalomethanes (TTHMs) in potable drinking water to meet the USEPA drinking water regulations under the Safe Drinking Water Act Amendment of 1986. The regulation is a 0.10 mg/L maximum contamination level for water systems serving populations of over 10,000 people. Pilot-plant studies have proven chlorine dioxide useful in oxidizing the organic precursors in the water before the final chlorine residual disinfectant is added for controlling TTHMs (152). The present regulations have a recommendation for limiting the amount of total combined residual oxidant levels of chlorine, chlorine dioxide, chlorite, and chlorate to a 1.0 mg/L maximum for chlorine dioxide treated drinking water (153, 154). Methods for the removal/reduction of the ClO_2 and/or $ClO_2{}^-$ residuals in drinking water treatment process are being evaluated using ferrous iron compounds (155), sulfur reducing compounds (155–157), anion exchange (158), and carbon adsorption (159, 160) as well as by membrane separation methods. Revised USEPA drinking water regulations covering disinfectants and by-products are expected by 1995.

Sodium chlorite generated ClO_2 is also finding increasing use for microbiological control in industrial cooling systems and towers. It is especially useful in replacing chlorine in industrial ammonia plants because of its nonreactivity with ammonia. In many areas of the United States, chlorine dioxide is beginning to replace chlorine because of the concern for handling chlorine in populated areas.

2.8.2. Food Industry Disinfection

ClO_2 solution generated from sodium chlorite is used in the washing of fruits and vegetables as a fungicide and for flume water disinfection. Chlorine dioxide does not react with the large quantity of ammonia compounds present to form chloramines as does chlorine (see Chloramines and bromamines; Food processing). Other applications using chlorine dioxide for meat and poultry washing and sanitizing food process equipment have been previously approved, but as of this writing are under review by the United States Federal Drug Administration (USFDA).

2.8.3. Industrial Processes

The use of sodium chlorite as an oxidizer in NO_x and SO_x combustion flue gas scrubber systems has been described (161–163). Sodium chlorite has also been used for treatment and removal of toxic and odorous gases such as hydrogen sulfide and mercaptans. Chlorine dioxide from chlorite is also useful for microbial and slime control in paper mills and alkaline paper machine systems (164, 165). The use of sodium chlorite in textile bleaching and stripping is well known. Cotton is not degraded by sodium chlorite because the oxidation reactions are specific for the hemicellulose and lignin components of the fibers.

2.8.4. Disinfectant Formulations and Sterilization

Hundreds of applications covering disinfectant compositions using sodium chlorite have been described in U.S. and foreign patents. Some examples of these are as antimicrobial additives for latexes (166), marine antifouling agents (see Coatings, marine) (167, 168), antimildew detergent compositions (169), toothpaste and solution compositions for prevention and treatment of periodontal oral disease (see Dentifrices) (170–172)), and compositions for the disinfection of contact lenses(qv) (173).

In many patent or literature descriptions, a stabilized chlorine dioxide solution or component is used or described. These stabilized chlorine dioxide solutions are in actuality a near neutral pH solution of sodium chlorite that may contain buffer salts or additives to obtain chlorite stability in the pH 6–10 range. The uv spectra of these solutions is identical to that of sodium chlorite. These pH adjusted chlorite solutions can produce the active chlorine dioxide disinfectant from a number of possible organic or inorganic chemical and microbiological reactions that react, acidify, or catalyze the chlorite ion.

Chlorine dioxide gas generated from chlorite has been used as a chemosterilizing agent substitute for ethylene oxide in medical applications (174, 175). Aqueous foam compositions containing chlorine dioxide have also been developed for the sanitization of hard surfaces (176).

2.8.5. Metallurgical and Ore Processing

Sodium chlorite is used in solution formulations to oxidize the copper surfaces in multilayer circuit boards for better adhesion as well as in other electronic applications (177–179). The use of oxidant gases including chlorine dioxide and chlorine generated in an electrochemical cell has been proposed for the desulfurization of coal (see Coal conversion processes, cleaning and desulfurization) (180). Chlorine dioxide is also described for lowering the viscosity of coal–water slurries by reacting with sulfides in the coal (181). Processes using chlorine dioxide generated from sodium chlorite have also been described for the recovery of precious metals from carbonaceous ores (182) and by ore leaching (183).

2.8.6. Oil Field and Petroleum Processing

Sodium chlorite is finding increasing use as the choice precursor for generating chlorine dioxide for biocidal control in the production of crude oil (see Petroleum). The use of water in the oil field pumping and processing systems presents significant corrosion problems related to the growth of sulfate-reducing bacteria. Chlorine dioxide does not react with most of the aromatic components present in the crude oil and also has the advantage of not forming chlorinated hydrocarbon by-products as in the case of chlorine. Chlorine dioxide also helps in the separation of the crude oil from the water by breaking up emulsions and by reacting with the sulfides and phenolic compounds present (184–190). Sodium chlorite is used in drilling muds as a biocide for protecting the organic additives from degradation (191). In addition, sodium chlorite is used in combination with inorganic acids, such as hydrochloric or sulfuric acid, in generating chlorine dioxide for hydraulic fracturing or restoring the permeability of the underground formations around wellbores by direct injection or stimulation into wells (192–196).

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