Manufacture of Chlorine Dioxide from Sodium Chlorite:  
Process Chemistry

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Abstract: Chlorine dioxide (ClO₂) has emerged as a highly efficient chemical agent for bleaching, oxidation, and disinfection. Various fundamental studies have been performed to investigate the reaction kinetics and the mechanism of ClO₂ production. These studies have led to improvements in the manufacturing processes and to the optimization of reaction conditions to provide a better yield and the rational utilization of raw materials. In this comprehensive review, various aspects of process chemistry in the manufacture of ClO₂ from sodium chlorite are reported. This knowledge will be useful for improving the current processes and for developing a more advanced process in the future.

Keywords: Chlorine dioxide, sodium chlorite, manufacture, processes, mechanism

Introduction to Chlorine Dioxide

Hypochlorite, chlorite, chlorate, and perchlorate are the most common oxychlorine species. All these compounds of chlorine are so closely related that the neglect of the chemistry of any one of the member of the series handicaps the chemistry of all of the others. Chlorine dioxide is another novel oxychlorine species that has attracted remarkable commercial attention not only because of environmental concerns but also because of its wide applications in the fields of bleaching, oxidation, and disinfection. Chlorine dioxide emerged as a powerful disinfectant at the beginning of the 20th century when it was first used at a spa in Ostend, Belgium.

Pure chlorine dioxide is an oily, dark amber-colored liquid that is extremely unstable at temperature above -40°C. It is also explosively unstable as a gas in concentrations higher than 10% by volume in air or at a partial pressure above 76 mm Hg (1.46 psig). It is a neutral compound of chlorine in a +4 oxidation state and exists as a free radical even in dilute aqueous solutions. Chlorine dioxide functions as a highly selective oxidant because of its unique, one-electron-transfer mechanism [1]. It is highly soluble in chilled water (~10 times more soluble than chlorine). In contrast to chlorine, it does not hydrolyze in water; rather, it remains as a dissolved gas in aqueous solution [2]. Chlorine dioxide is light sensitive; it spontaneously decomposes exothermally to produce chlorine and oxygen.

Chlorine dioxide is used commercially in such applications as textile, paper, fat, and pulp bleaching, wastewater treatment, water purification, removal of iron, manganese, H₂S, and phenols from industrial wastes, medical treatment, sanitation, food processing, fumigation, deodorization, and aquaculture. The chlorine dioxide-based bleaching process, the so-called ECF technology, has become more dominant in the production of bleached chemical pulps [3]. Wood pulp bleaching is the prime use of chlorine dioxide because it is a unique selective oxidizer for lignin. Unlike other oxidizing agents, chlorine dioxide does not attack cellulose and, thus, it preserves the mechanical properties of the bleached pulp. Furthermore, chlorine dioxide functions as an oxidant, rather than a chlorination agent, and, hence, it avoids the formation of chlorinated organic compounds.

In industrial and municipal wastewater treatment, chlorine dioxide is a quite effective biocide. It rapidly inactivates most microorganisms over a wide pH range and it helps to eliminate taste and odor problems from drinking waters because it does not react with organic matter to form trihalomethanes (THMs). Taste and odors resulting
from algae and decaying vegetation, as well as phenolic compounds, are controlled by chlorine dioxide. The odors from rotten food wastes can also be eliminated, in a process that is believed to be due to oxidation [4] of mercaptoethanol an (agent responsible for foul smells) by ClO₂. In 1988, the EPA registered chlorine dioxide as a sterilizing agent for equipment and tools. This present comprehensive review aims to highlight the various methods used to manufacture chlorine dioxide from sodium chlorite as the precursor and discusses their process chemistry.

Historical Background

The history of chlorine dioxide dates back to 1815 when its discovery was reported by Davy [5]. Chlorates had been treated with acids by several earlier chemists who expected to obtain chlorine, but the gaseous products had varying properties. Davy [6] suggested that chlorine was produced when hydrochloric acid reacted with chlorate in the presence of a manganese compound, whereas euclochlorine was formed in its absence. In modern terminology, euclochlorine is mixture of chlorine dioxide and chlorine in a 2:1 molar ratio. Millon [7] noticed that when using oxalic acid as the reducing agent, the gas produced was chlorine dioxide; it had the same formula as the gas produced from potassium chlorate upon the addition of sulfuric acid. These chemical pioneers laid the groundwork for discovering most of the reactions that take place between chlorates and acids. When concentrated sulfuric acid reacts with a solid chlorate, an explosion of chlorine dioxide may result, as follows:

\[ 3\text{KClO}_3 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + \text{HClO}_4 + \text{H}_2\text{O} + 3\text{KHSO}_4 \]  

(1)

Dilution of the acid with water or of the chlorate with an inert material [8] has been suggested as a means for controlling the above reaction. The major disadvantage of this reaction is that only two-thirds of the chlorine can be converted to chlorine dioxide, with the other third forming perchlorate. Calvert and Davies [9] experimented using different proportions of potassium chlorate and oxalic acid, but never obtained the theoretical yield suggested by equation (2):

\[ 2\text{KClO}_3 + 2(\text{COOH})_2 \rightarrow 2\text{ClO}_2 + 2\text{CO}_2 + (\text{COOK})_2 + 2\text{H}_2\text{O} \]  

(2)

Many more modifications have been suggested for this method, which became a common laboratory method for the production of chlorine dioxide. Here, oxalic acid serves as an acid as well as a reducing agent and the CO₂ that forms renders the ClO₂ less likely to explode. Schachterl [10] suggested the addition of sulfuric acid to the mixture of chlorate and oxalic acid. While this suggestion appears to be a logical development in accordance with equation (3), it has not been generally adopted:

\[ 2\text{KClO}_3 + (\text{COOH})_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + 2\text{CO}_2 + 2\text{KHSO}_4 + 2\text{H}_2\text{O} \]  

(3)

Manufacture of Chlorine Dioxide

An extensive amount of literature has been published on the manufacture of chlorine dioxide, especially in patents. There is a growing concern to develop a simpler, easier-to-operate, more-efficient, and economical process for the generation of chlorine dioxide. There is still plenty of room for improvement in the processes used to produce chlorine dioxide.

Chlorine dioxide is always generated on-site because of its unstable nature and risk of rapid decomposition. It is thermally unstable and sensitive to light and pressure. It may decompose explosively at partial pressures \( \geq 300 \) mm Hg. Pure solutions of chlorine dioxide may also detonate if exposed to bright light or an ignition source, such as heat, a spark, or an open flame. It can be stored only as a solution of approx. 1% in water. The upper safe limit for aqueous chlorine dioxide solutions is about 8 g/L at 30°C. It is a strong irritant that is as hazardous a gas as is NO₂; brief exposure at 1000 ppm can be fatal. The odor of ClO₂ can be detected even at 14 to 17 ppm, so adequate ventilation and proper care are needed in the workplace. The properties of ClO₂ do not bar its use, but a high degree of caution is desirable.

In all processes, it is produced from acid solutions of either sodium chlorite or sodium chlorate. Most of the small- and medium-scale generators use sodium chlorite as the precursor material, particularly for water treatment, chemical oxidation, and disinfection applications because they require high purity (i.e., Cl₂-free) water. The conditions for the production of ClO₂ from sodium chlorite can be controlled more easily than from sodium chlorate, but chlorite is the more expensive and unstable chemical. Chlorite is itself produced [11-13] by reduction of chlorine dioxide gas.

\[ 2\text{ClO}_2 + \text{H}_2\text{O}_2 + 2\text{NaOH} \rightarrow 2\text{NaClO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \]  

(4)

Other applications that do not require high-purity water utilize sodium chlorate [14-15]. This approach is typical of pulp bleaching where large quantities of chlorine dioxide are needed. Although chlorate-based processes have traditionally been used in the pulp and paper industries, these methods have recently also been tested in full-scale municipal water treatment plants, and so they are an emerging technology for the purification of drinking water.

From Sodium Chlorite

Chlorite is the intermediate member in the series of
oxycarbohydrate compounds; it has an oxidation state of chlorine of +3. It is more stable than hypochlorite, but less stable than chlorate and perchlorate. In many respects, its properties are intermediate between those systems. Sodium chlorite is a highly efficient bleacher and oxidative disinfectant, that is mainly applied in bleaching textiles, fibers, and paper pulp. The most important property of chlorite is its oxidizing power. In cold alkaline solutions, it has only a mild oxidizing action. Heating or acidification (or both) develops strong oxidizing conditions in chlorite solutions even at temperatures only slightly above normal and at pH values of 3 to 5; under such conditions, most materials that require bleaching resist deleterious attack. It is characteristic of lower scath to fiber. It is also used to whiten sugar, starch, grease, ointment, and wax. When used in purifying water, it leaves a negligible amount of chlorine in the water. It is also used in the sterilization and deodorization of sewage.

Sodium chlorite was first identified by Millon [7] over 100 years ago. It was obtained by alkaline absorption of the greenish yellow gas formed by the partial reduction of chlorate. This so-called Millon’s gas was indeed [16] a mixture of chlorate and chlorite dioxide. Commercially, chlorite can be formed by reduction of chlorine dioxide gas using H₂O₂ [11-13], Zn dust [17], or PbO [18] in an alkaline medium:

\[
2\text{ClO}_2^- + \text{Zn} + 2\text{NaOH} \rightarrow 2\text{NaClO}_2^- + \text{Zn(OH)}_2^- (5)
\]

\[
2\text{ClO}_2^- + \text{PbO} + 2\text{NaOH} \rightarrow 2\text{NaClO}_2^- + \text{PbO}_2 + \text{H}_2\text{O} (6)
\]

Chlorite is a convenient source of chlorine dioxide, which is formed by the oxidation of chlorite as follows:

\[
\text{ClO}_2^- \rightarrow \text{ClO}_2^- + e^- (7)
\]

In aqueous solution, its standard redox potential, \(E^o\), is -0.954 V [19], but in alkaline solution, Latimer [20] determined the standard redox potential to be -1.15 V. There are several methods to generate chlorine dioxide from sodium chlorite. Some of them are listed as follows:

- Chlorite-acid process:
  \[
  4\text{ClO}_2^- + 2\text{H}^+ \rightarrow 2\text{ClO}_2 + \text{ClO}_2^- + \text{Cl}^- + \text{H}_2\text{O} (8)
  \]
  (In the absence of chlorite)
  \[
  5\text{ClO}_2^- + 4\text{H}^+ \rightarrow 4\text{ClO}_2 + \text{Cl}^- + 2\text{H}_2\text{O} (9)
  \]
  (In the presence of chlorite)

- Chlorite-chlorine process:

- Chlorite-hypochlorite process:

- Chlorite-persulfate process:

- Chlorite-acetic anhydride process:

\[
4\text{ClO}_2^- + (\text{CH}_3\text{CO}_2\text{O})_2 \rightarrow 2\text{ClO}_2 + \text{ClO}_2^- + \text{Cl}^- + 2\text{CH}_3\text{COO}^- (10)
\]

Chlorite-Acid Process

The chlorite-acid process is the simplest and easiest process to operate. The theoretical yield of chlorine dioxide from acidification of chlorite is only 80%. In contrast to alkaline or neutral solutions, acidic solutions of chlorite decompose at measurable rates, with the rate generally increasing with decreasing pH [21-30] and increasing temperature [22-24,26,29-31]. The products of this decomposition reaction are chlorate, chlorine dioxide, and chlorite. The most common acids used for the decomposition of chlorite are hydrochloric acid, sulfuric acid, acetic acid, phosphoric acid, and citric acid. In the absence of an added chloride ion, which catalyzes the reaction and also alters the stoichiometry, the decomposition of acidic chlorite or self-disproportionation of chlorous acid can be approximated by [21-24,28,30,31-35]:

\[
4\text{ClO}_2^- + 2\text{H}^+ \rightarrow 2\text{ClO}_2 + \text{ClO}_2^- + \text{Cl}^- + \text{H}_2\text{O} (8)
\]

Barnett [36] studied the decomposition of chlorous acid at the boiling point and reported the gradual transition from equation (8) to (9) as the concentration of chlorous acid decreased:

\[
5\text{HClO}_2 \rightarrow 4\text{ClO}_2^- + \text{HCl} + 2\text{H}_2\text{O} (9)
\]

This reaction predominates when using a weak acid and a high chloride concentration. Kieffer and Gordon [23] used a variety of conditions to study the stoichiometry of the disproportionation of chlorous acid as a function of time at an ionic strength of 2.0. They reported that at the beginning of the reaction, less chlorine dioxide than the amount predicted from equation (8) is formed in 0.7 to 2.0 M acids and that as the reaction proceeds, the relative amount of chlorine dioxide increases and that of chlorate decreases. They showed that if the reaction proceeds for a sufficiently long time and the acidity is relatively high, the ratio of ClO₂⁺ to ClO₂⁻ is generally > 2. Deviations from equation (8) are expected because the product, chloride ion, not only accelerates the rate of decomposition but also alters the stoichiometry [23,24,28,31] to approximate equation (9).

Hong [31] proposed that the presence of chloride ion initiates the two reactions represented by equations (9) and (10), which occur in parallel with equation (8).

\[
3\text{ClO}_2^- \rightarrow \text{Cl}^- + 2\text{ClO}_2^- (10)
\]

Equation (10) occurs only to a minor extent. The reactions of equations (8) and (9) both appear to be independent of the primary salt effect, but the contribution of equation (9) increases upon increasing the chloride concentration. A number of authors [23,30,31] have observed that the reaction order, with respect to chloride ion at high chloride concentration, is one. The order is also one with respect to chlorite, as well as acid. Hong [31] found
that chloride ion could have both an inhibiting as well as accelerating effect on the formation of chlorine dioxide from chlorite. The inhibiting effect only predominates when using a weak acid and a low chloride concentration. The rate of formation of ClO₂ goes through a maximum at pH of ca. 2 [22-24,31]. The rate law for the self disproportionation of chlorous acid at low pH was reported by Kieffer and Gordon as follows:

\[
- \frac{d[\text{HClO}_2]}{dt} = k_1[\text{HClO}_2]^2 + \frac{k_2[\text{HClO}_2][\text{Cl}^-]^2}{K + [\text{Cl}^-]} \quad (11)
\]

Here, the parameters \( k_1 \) and \( K \) are independent of the acid concentration, but \( k_2 \) is directly proportional to the \( \text{H}^- \) ion concentration. The rate law above is applicable for the kinetic data both in the presence and in the absence of chloride ion. This rate law is consistent with the following mechanism:

Path A:- In the absence of added chloride:

- **Step 8a.** \( \text{HClO}_2 + \text{HClO}_2 \xrightarrow{k_1} \text{HOCl} + \text{H}^- + \text{ClO}_3^- \) (rate-determining)
- **Step 8b.** \( \text{HOCl} + \text{HClO}_2 \rightarrow \text{Cl}_2\text{ClO}_2 + \text{H}_2\text{O} \)
- **Step 8c.** \( \text{HClO}_2 + \text{H}^- + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \)
- **Step 8d.** \( \text{Cl}_2 + \text{HClO}_2 \rightarrow \text{Cl}_2\text{ClO}_2 + \text{H}^- + \text{Cl}^- \)
- **Step 8e.** \( \text{Cl}_2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{ClO}_3^- + 2\text{H}^+ \)
- **Step 8f.** \( 2\text{Cl}_2\text{ClO}_2 \rightarrow \text{Cl}_2 + 2\text{ClO}_2 \)

Path B:- In the presence of added chloride:

- **Step 9a.** \( \text{HClO}_2 + \text{Cl}^- \xrightarrow{k} \text{HClO}_2^- \)
- **Step 9b.** \( \text{HClO}_2^- + \text{Cl}^- \xrightarrow{k} \text{Products} \) (rate-controlling)

Although some authors [29,37,38] have reported the formation of Cl₂ gas when chlorite is reacted with concentrated HCl solution, most evidence appears to be against the formation of Cl₂. If any chlorine is formed, it would react immediately with chlorite because the chlorine-chlorite reaction is known to be rapid in acidic solution [39]. A typical conventional ClO₂ generator using the above process is shown in Figure 1.

In this typical acid-chlorite generator, sodium chlorite (~25% w/v) and commercial hydrochloric acid (30~38% w/v) are pre-diluted in an aspirator-type injector. Vacuum control valves are installed at the suction inlets of the injector, which will open only when the appropriate operating vacuum has been reached. This design ensures that the two basic chemicals can not be mixed unless a minimum quantity of injector operating water is available and in no case can only one of the basic chemicals be aspirated because, in the absence of the second chemical, no sufficient operating vacuum can be achieved. The feed rates of sodium chlorite, HCl, and the dilution water are regulated by ball control valves and are indicated on flow meters. Dilution water is added to the chloride dioxide at the outlet of the reaction vessel, before it is passed into the chlorine dioxide storage tank, which is fitted with level probes for controlling of the batch cycle. The high level probe stops the generating cycle by closing the solenoid valves and the low level probe restarts the system. Adjustable alarm switches are installed on the flow meters to monitor the preset flow rates. All electrical functions and controls are grouped together in a control panel.

For the purpose of deodorization and microbial suppression, this process was utilized by Khanna and coworkers [4], wherein chlorite-impregnated expanded amorphous
aluminum silicate (EAAS) was mixed with acid-impregnated EAAS in a specific ratio to release a desired concentration of chlorine dioxide. EAAS can be synthesized by heating the naturally occurring siliceous volcanic rock known as Perlite. Perlite is chemically inert and has the ability to expand in volume when heated to certain temperatures.

**Chlorine-Chlorite Process**

The chlorine-chlorite process is most flexible and efficient method for ClO₂ generation. Chlorine reacts rapidly with acidified or neutral solutions of chlorite [28,29,31,35,39-44]. Several authors [18,29,35,42,45] have observed that chlorine reacts quantitatively with chlorite and produces chlorine dioxide as follows:

$$2\text{NaClO}_2 + \text{Cl}_2 \rightarrow 2\text{ClO}_2 + 2\text{NaCl} \quad (12)$$

The stoichiometry of the reaction varies with the pH and the initial concentration of the reactants. The major products are chloride, chlorate, and chlorine dioxide. Chlorate is formed by a slow side reaction as follows:

$$\text{NaClO}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{NaClO}_3 + 2\text{HCl} \quad (13)$$

The reaction shown in equation (12) is rapid and the rate of generation of ClO₂ can be controlled by regulating the flow of gaseous chlorine. Logan [46] designed an apparatus that prevents injected chlorine from contaminating the chlorine dioxide that is generated, wherein chlorine is absorbed in the generator completely filled with chlorite solution. This solution is transferred to an aerator, and the chlorine dioxide is removed for use by aspirating with an inert gas. However, if ClO₂ is not removed as it is formed, it will dissolve in the generating solution to such an extent that it will produce a dark-red solution. Under these conditions, chlorate may be formed in an amount equivalent to as much as 30% of the chlorite decomposed in case of concentrated solutions. It is evident [28,29] that acidic conditions will favor the formation of chlorine dioxide and alkaline conditions tend to produce chlorate.

Taube and Dodgen [28] studied the above reaction with tagged chlorine and proposed that the intermediate Cl₂O₅ must be unsymmetrical (Cl—Cl ≪ Cl—O—Cl—O) rather than symmetrical (O—Cl—Cl—O). The proposed mechanism [28] of the chlorine-chlorite reaction can be expressed in the following steps:

**Step12a.** $\text{Cl}_2 + \text{ClO}_2 \rightarrow \text{Cl} — \text{ClO}_3 + \text{Cl}$

**Step12b.** $2\text{Cl} — \text{Cl} ≪ \text{Cl}_2 + 2\text{ClO}_2$

**Step12c.** $\text{Cl} — \text{Cl} ≪ \text{H}_2\text{O} \rightarrow \text{Cl} + \text{ClO}_3 + 2\text{H}^+$

The formation of the intermediate is the rate-determining step. The intermediate can decompose either by a second-order reaction (step 12b) into chlorine and chlorine dioxide or by a first-order reaction (step 12c) into chlorite and chlorate.

Subsequently, Emmenegger and Gordon [39] found that more-dilute solutions having constant chlorine-to-chlorite ratios favor the production of chlorate. The more-dilute solutions produce a lower concentration of the intermediate, and thus, favor the first-order reaction (step 12c) over the second-order reaction (step 12b). The authors [39] also expanded the above mechanism as follows:

$$\text{Cl}_2 + \text{ClO}_2 \rightarrow \text{Cl} — \text{Cl} — \text{ClO}_3 \rightarrow \text{Cl} — \text{Cl} ≪ \text{ClO}_3 + \text{Cl}$$

A typical ClO₂ generator [47] using the chlorine-chlorite process is shown in Figure 2. The conventional generator
using the aqueous chlorine-chlorite process generates chlorine dioxide in a two-step process. First, chlorine gas is reacted with water to form hypochlorous and hydrochloric acid. These acids then react with sodium chlorite to form ClO₂ as follows:

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCI} + \text{HCl} \quad (14)
\]

\[
2\text{NaClO}_2 + \text{HOCI} + \text{HCl} \rightarrow 2\text{ClO}_2 + \text{H}_2\text{O} + 2\text{NaCl} \quad (15)
\]

An insufficient feed of chlorine will result in a large amount of unreacted chlorite, whereas an excess chlorine feed leads to the formation of chlorate. A highly acidic (pH < 3) reaction mixture, a dilute solution of chlorite, and an excess of hypochlorous acid will also favor the formation of chlorate. In addition, sodium hydroxide is one of the products of the reaction between HOCI and chlorite:

\[
2\text{HOCI} + 2\text{NaClO}_2 \rightarrow 2\text{ClO}_2 + \text{Cl}_2 + 2\text{NaOH} \quad (16)
\]

The resulting pH will be high, which retards the formation of ClO₂ and accelerates the formation of chlorate.

In recycled aqueous chlorine or a “French Loop” type of generator [48], chlorine is injected into a continuously circulating water loop, which eliminates the need for a great excess of Cl₂ gas to be fed into generator, because molecular chlorine will dissolve into water and, thus, maintain the low pH of the feed water. Loop-based generators keep the chlorite concentration at or above saturation levels. The low pH will favor a high yield of ClO₂. The “French Loop”-type of generator is more difficult to operate and so a newer design and more modifications are needed. In yet another gaseous chlorite-chlorite process, sodium chlorite can be vaporized and reacted under vacuum with molecular chlorine [49]; this process is very rapid because it uses undiluted reactants.

Chlorite-Hypochlorite Process

The reaction between hypochlorite and chlorite has been studied extensively by various authors [28,31,35,39, 50-52]. It is known to generate ClO₂ gas as follows:

\[
\text{HOCI} + \text{ClO}_2^- + \text{H}^+ \rightarrow 2\text{ClO}_2 + \text{Cl}^- + \text{H}_2\text{O} \quad (17)
\]

Meanwhile, it is always accompanied by another side reaction; it leads to the formation of chlorate:

\[
\text{HOCI} + \text{ClO}_2^- \rightarrow \text{H}^+ + \text{ClO}_3^- + \text{Cl}^- \quad (18)
\]

The ratio of ClO₂ to chlorate formed depends on the reaction conditions, such as the pH, presence of chloride, and the proportions of chlorite and hypochlorite [35,39]. Compared to the chlorine-chlorite reaction, the reaction between chlorite and hypochlorite is slower and produces less chlorine dioxide and more chlorate. An increase in the chlorite concentration favors chlorite dioxide formation [26,39], but an increase in the hypochlorite concentration favors chlorate formation [31,35]. White and coworkers [35] suggested that this is consistent with the occurrence of the reaction:

\[
2\text{ClO}_2 + \text{HOCI} + \text{H}_2\text{O} \rightarrow 2\text{HClO}_3 + \text{HCl} \quad (19)
\]

The authors [35] found that in experiments in which the ratio of chlorite to hypochlorite was 2, the chlorine dioxide formed immediately and did not disappear with time because there was no excess of hypochlorite remaining to react. However, in another series of experiments, where the ratio of chlorite to hypochlorite was 1:2 and 1:4, the chlorine dioxide formed immediately, but then decreased, and the chlorate concentration increased. This finding confirms the predictions of equation (19).

Subsequently, Emmenegger and Gordon [39] reported that the generated chlorine dioxide did not disappear with time in an acidic solution, even when hypochlorite was present in excess. Because the formation of the intermediate (ClO₂) in the hypochlorite-chlorite reaction is a slow step, the lower concentration of this intermediate will favor its first-order decomposition to produce chlorate, rather than the second-order process that forms ClO₂. Furthermore, because the reaction between hypochlorite and chlorite is quite rapid, the reaction between ClO₂ and hypochlorite is too slow [53] to be an important path in the mechanism. Granstrom and coworkers [54] observed that the ratio of hypochlorous acid consumed to chlorite consumed remains constant and it varies with the experimental conditions. This finding provides further evidence against the idea that equation (19) contributes significantly to the mechanism. If hypochlorous acid and ClO₂ reacted, then the ratio of hypochlorous acid consumed to chlorite consumed would not be a constant during the course of the reaction.

The chlorite-hypochlorite reaction also follows the same mechanism as suggested by Taube and Dodgen [28] and later extended by Emmenegger and Gordon [39] for the chlorite-chlorine reaction. The formation of the intermediate, Cl₂O₃, follows the equation:

\[
\text{HOCI} + \text{ClO}_2^- \xrightarrow{k_b} \{ \text{Cl}^- + \text{ClO}_3^- \} \quad \xrightarrow{k_b} \{ \text{Cl}^- + \text{ClO}_3^- \} + \text{OH}^{-}
\]

This intermediate \( \{ \text{Cl}^- + \text{ClO}_3^- \} \) can be decomposed by a second-order reaction to give ClO₂ or by a first-order reaction to yield chlorate in the same way. Chlorine produces the intermediate \( \text{Cl}_2\text{O}_3^- \) more rapidly than does hypochlorous acid. A high H⁺ ion concentration will favor the formation of the intermediate by means of \( k_b \).

Yin and Ni [55] provided a quantitative description of the chlorite effect on ClO₂ generation from the hypochlorite-chlorite reaction under slightly acidic conditions.
(pH 3.86 to 4.91). In that study, the authors used mercuric oxide to capture any chloride that was introduced as a contaminant or as a product and found that ClO₂ is generated from the HOCI-ClO₂ reaction even in the absence of chloride. It is postulated that there are two routes for the ClO₂ generation: one is chloride-promoted and the other is chloride-independent on the ClO₂ generation pathway. The rate equation of the chloride-independent pathway is

\[
\frac{d[ClO_2]}{dt} = k_1[ClO_2][HOCI][H^+] \quad (20)
\]

and that of the chloride-promoted pathway is

\[
\frac{d[ClO_2]}{dt} = k_2[ClO_2][HOCI][H^+][C^\Gamma] \quad (21)
\]

where \(k_1\) and \(k_2\) are \(5.9 \times 10^5\) (mol/L)²·s⁻¹ and \(8 \times 10^6\) (mol/L)²·s⁻¹, the activation energies are 20.9 and 10.1 kJ/mol, and the pre-exponential factors are \(5.77 \times 10^5\) (mol/L)²·s⁻¹ and \(6.75 \times 10^{10}\) (mol/L)³·s⁻¹ for the chloride-independent and chloride-promoted pathways, respectively.

Yin and Ni [56] also investigated the effect of chloride on the HOCI-HOC₂O reaction in 4.5 M sulfuric acid solution, i.e., conditions under which most of the commercial ClO₂ generators in the pulp and paper industries operate. The authors [56] explained that in the absence of chloride, the following two reactions are dominant, leading to the formation of chloric acid:

\[
2\text{HClO}_3 \rightarrow \text{HOCI} + \text{HClO}_2 \quad (22)
\]

\[
\text{HClO}_2 + 2\text{HOCl} \rightarrow \text{Cl}_2 + \text{HClO}_3 + \text{H}_2\text{O} \quad (23)
\]

In contrast, ClO₂ is generated in the presence of chloride by the following mechanism:

\[
\begin{align*}
\text{Cl}_2 & \xrightarrow{\text{O}} \text{Cl}^- + \text{Cl}^- + \text{H}^+ + \text{Cl}^\Gamma \\
\rightarrow & \text{Cl}^- + \text{Cl}^- + \text{H}^+ + \text{Cl}^\Gamma \\
\end{align*}
\]

This process demonstrates the dramatic catalytic effect of chloride in the HOCI-HOC₂O reaction under high acid strength. In strongly acidic solution, the presence of chloride ion in the solution is negligible, because all the chloride ions are undissociated (in the form of chlorous acid); thus, the reaction between HOCI and HClO₂, as suggested in the E & G mechanism [39], is not possible, because HClO₂ is no longer a strong nucleophile. Therefore, in the absence of chloride, chlorate is the major product. However, in the presence of chloride, Cl⁻ ions attack HClO₂ to give a strong nucleophile, which then reacts with HOCI to yield the intermediate \{Cl₂O₂\}, leading to the formation of ClO₂.

**Other Processes**

Various researchers have speculated the possibility of a reaction between chlorous acid and chloric acid, leading to the production of ClO₂:

\[
\text{HClO}_2 + \text{HClO}_3 \rightarrow 2\text{ClO}_2 + \text{H}_2\text{O} \quad (24)
\]

This idea seems to have originated from Oechsli [57] without any experimental verification. White and coworkers [35] added chlorate to chlorite in acid solution (pH 1.7 to 4), but no evidence of enhanced production of ClO₂ was reported. Subsequently, Hong [31] found that 0.324 M sodium chlorate increased the rate of initial decomposition only by 6.7% when using 0.0207 M sodium chlorite and 0.0375 M sulfuric acid. Recently it has been observed [58] that high acidity and a high [ClO₂]/[ClO₃⁻] ratio may favor the chlorite-chlorate process. We [58] have performed several experiments by injecting chlorite solution slowly into an acid solution of sodium chlorate. Although 100%-pure chlorine dioxide is obtained in this case, this process is accompanied by the simultaneous decomposition of chlorite in the acidic medium, which in turn reduces the efficiency of the ClO₂ generation.

Several other compounds are also known to be responsible for ClO₂ generation from chlorous acid, such as aldehydes (especially formaldehyde) and anhydrides (such as acetic anhydride). Many authors [59-61] have reported the chlorite-acetic anhydride reaction:

\[
4\text{NaClO}_2 + (\text{CH}_2\text{CO}_2)\text{O} \rightarrow 2\text{ClO}_2 + \text{NaCl} + \text{NaClO}_3 + 2\text{CH}_3\text{COONa} \quad (25)
\]

White and coworkers [35] reported the production of ClO₂ upon the addition of formaldehyde to a solution of sodium chlorite. At a pH of ca. 7, a pure chlorite solution hardly decomposes, even after 6 hrs at room temperature, but upon the addition of formaldehyde, the same concentration of chloride is almost completely consumed within 30 min with the formation of ClO₂ and CO₂. The invariable existence of CO₂ indicates that formaldehyde is oxidized. The beauty of this reaction is that it permits ClO₂ generation at pH of 7, where the rate of corrosion will be lowest. Acetaldehyde and benzaldehyde also bring about the evolution of ClO₂ from chlorite solution:

\[
\text{R-CHO} + 3\text{ClO}_2 + 2\text{H}^+ \rightarrow 2\text{ClO}_2 + \text{R-CO}_2\text{H} \quad (26)
\]

This aldehyde-chlorite reaction is supposed to involve the following steps:

**Step 26a.**

\[
\begin{align*}
\text{R-CHO} & \xrightarrow{\text{n}} (\text{R-CO}_2\text{H}) \xrightarrow{\text{ClO}_2} \xrightarrow{\text{n}} \text{R-CO}_2\text{H} \quad \text{R-CO}_2\text{H} \xrightarrow{\text{H}_2\text{O}} \text{HOCl} + \text{R-CO}_2\text{H}
\end{align*}
\]
Step 26b. $H^+ + HOCl + 2ClO_2 → 2ClO_2 + Cl^- + H_2O$

Chlorine-dioxide may be generated by oxidation [62, 63] of chlorite, as shown in equation (7). The oxidation of chlorite by sodium peroxidisulfate [64,65] is also reported to generate chlorine-dioxide:

$$2NaClO_2 + Na_2S_2O_8 → 2ClO_2 + 2Na_2SO_4$$ (27)

This process yields a chlorine-dioxide solution free not only from residual chlorite but also from chlorate and other undesirable byproducts, and it can be used directly in water treatment. The oxidation of chlorite by sodium peroxidisulfate is possible at room temperature in the pH range from 6 to 9. The reaction rate can be enhanced by adding a catalyst, such as silver, iron, or manganese salts.

All these conventional processes are reliable and efficient, but for continuous high efficiency, low Cl₂ contamination, and the maximum utilization of raw materials, they need care and attention. The processes need an excess of acid or chlorine or hypochlorite to maximize the conversion of sodium chlorite. This excess amount depends on the generator design and can be 10～15% of the stoichiometric amount. The control and feeding of two or three chemicals in the desired proportions is difficult, and if not monitored carefully, can lead to untreated chlorite, an unwanted side reaction forming chlorate, or an excessive amount of chlorine leaving the system.

**Recent Developments: Electrochemical Method**

It has been reported that chlorine dioxide can be generated by electrochemical oxidation [66-69] of sodium chlorite. Logan [66] described an electrochemical ClO₂ generating process in which a mixture of sodium chlorite and sodium chloride was electrolyzed in an electrolytic cell equipped with a porous diaphragm separating the anode and cathode compartment. In another study [67], ClO₂ was generated and separated using gas membranes, i.e., microporous hydrophobic membranes that permit gas or chlorine dioxide vapor to pass through, but resist the passage of liquids and ions.

The electrochemical ClO₂ generation system consists of an electrolytic cell and a hydrophobic microporous gas pore membrane. The membrane can withstand a chlorine dioxide environment and only allows the passage of ClO₂ and other gases (O₂ and water vapors) to the acceptor solution. The system consists of a circulation loop (anolyte loop) where the sodium chlorite solution (anolyte) is recirculated by a sealless pump through the anode compartments of an integrated cell comprising the chlorine dioxide generating and anolyte pH control cells. An excess of sodium chlorite is maintained in the reaction mixture, which is recycled and cannot leave the system in any form except as ClO₂. The electrolytic cell is divided by an ion-permeable separator into anode and cathode compartments. Schematic diagrams of the ClO₂ generation system, gas pore membrane, and electrolytic cell are shown in Figures 3, 4, and 5, respectively.

In this system, sodium chlorite is electrochemically oxidized into ClO₂ in the solution:

$$2NaClO_2 + 2H_2O → 2ClO_2 + 2NaOH + H_2$$ (28)
The analyte solution containing dissolved ClO₂ gas flows into the perstraction module, where ClO₂ and water vapors are transferred to the acceptor solution. The depleted solution is returned back to the cell and is further fortified with chlorite feed. The pH of the cell is kept in the range from 5 to 5.5 using an auto-pH control system. The weakly caustic solution is separated from the hydrogen gas, which is evolved at the cathode. The generator is operated via a computer-controlled system, with safety interlocks that allow it to operate autonomously. Once started, it will operate unattended at its preset parameters with very little intervention or monitoring. The whole system has a single set point adjustment for modulation capacity and can be controlled from a distant position. The electrochemical conversion efficiency of chlorite to ClO₂ in this newly developed system is very high when compared to conventional processes.

**Chlorite-Carbon Dioxide Process**

Recently, a novel method [70] has been reported where CO₂ is injected into 10% sodium chlorite solution having its initial pH and temperature at 11.7 and 21°C, respectively. CO₂ injection leads to the formation of carbonic acid and lowers the pH of the reaction solution, which in turn initiates the decomposition of sodium chlorite. The overall process can be summarized as follows:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^- \quad (29)
\]

\[
5\text{ClO}_2^- + 5\text{H}^+ \rightarrow 4\text{ClO}_2 + \text{HCl} + 2\text{H}_2\text{O} \quad (30)
\]

This process needs a very simple design. It was observed that a constant gas flow is not necessary; rather, the optimal production of chlorine dioxide can be achieved by injecting carbon dioxide into the chlorite solution for some time, followed by an incubation period.

Some more patents present a rapid, new means to generate and store pure solutions of high concentrations of chlorine dioxide for subsequent use. When an aqueous solution of chlorite is mixed with a non-aqueous, water-immiscible liquid, it yields two phases [71]. If an acid is then added in the mixture and vigorously agitated, chlorine dioxide can be extracted from the non-aqueous medium. Because chlorine dioxide does not react with several hydrocarbons, such as hexane, cyclohexane, octane, benzene, xylene, and toluene, and, furthermore, the unreacted chlorite, the acid, and the chloride byproduct are insoluble in the non-polar organic phase and remain in the water phase, this process leads to the preparation of contaminant-free chlorine dioxide. A block diagram showing the acid-chlorite process of generating and storing ClO₂ in a non-aqueous liquid is presented in Figure 6.

The same procedure can be extended also to the chlorine-chlorite process. Chlorine can be dissolved in a non-polar organic liquid and then this organic solution is mixed and vigorously agitated with an aqueous solution of chlorite. Separation of the aqueous and non-aqueous phases provides a pure solution of chlorine dioxide in the non-aqueous phase. This non-aqueous solution of highly purified ClO₂ may be further used to obtain a pure aqueous solution of chlorine-dioxide, when it is mixed and vigorously agitated with water.

In recent years, Klatte and coworkers [72-74] have employed chemically impregnated zeolite crystals to generate chlorine dioxide, for the purpose of disinfection, and then subsequently absorb the chlorine dioxide. Zeolites are hydrated metal aluminosilicates that have well-defined tetrahedral crystalline structures. Because of their porous structures and extensively connected channels, they have been employed as molecular sieves for selective absorption. Klatte [74] first passed oxygen through a bed of zeolite crystals impregnated with sodium chlorite and then through another bed of zeolite crystals impregnated with acid. The acids used for the purpose were phosphoric acid, acetic acid, and citric acid. The generation of chlorine dioxide occurred as follows:
Table 1. Brief Summary of Chlorite-Based Chlorine Dioxide Generation Processes

- **Chlorite-Acid Process:**
  \[ 5\text{NaClO}_2(\text{aq}) + 4\text{HCl} \rightarrow 4\text{ClO}_2 \text{(g)} + \text{NaCl} + 2\text{H}_2\text{O} \]

  Attributes: Low pH, corrosive effluent, formation of chlorate possible, slow reaction rate, chemical feed pump interlocks needed, maximum yield ~ 80%, chloride-catalyzed, HCl may be replaced by HSO_4, phosphoric acid, acetic acid, or others.

- **Aqueous Chlorine-Chlorite Process:**
  \[ \text{Cl}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} \]
  \[ \text{HOCl} + \text{HCl} + 2\text{NaClO}_2(\text{aq}) \rightarrow 2\text{ClO}_2(\text{g}) + \text{H}_2\text{O} + 2\text{NaCl} \]

  Attributes: Low pH, formation of chlorate possible, slow reaction rate, NaOH is formed, yield 80 ~ 92%, more corrosive effluent due to low pH, three chemical pump system.

- **Recycled Aqueous Chlorine or "French Loop" Process:**
  \[ 2\text{HOCl} + 2\text{NaClO}_2(\text{aq}) \rightarrow 2\text{ClO}_2(\text{g}) + \text{Cl}_2(\text{g}) + 2\text{NaOH} \]

  Attributes: Excess Cl₂ or acid needed because of NaOH formed, yield 92 ~ 98% with ~10% excess Cl₂, corrosive, no need for excess chlorine, difficult to operate, maturation tank required after mixing.

- **Gaseous Chlorine-Chlorite Process:**
  \[ \text{Cl}_2(\text{g}) + \text{NaClO}_2(\text{aq}) \rightarrow 2\text{ClO}_2(\text{g}) + 2\text{NaCl} \]

  Attributes: Neutral pH, rapid reaction, ejector-based with no pumps, motive water is dilution water, no excess Cl₂, non-corrosive effluent, highly calibrated flow meters needed, yield 95 ~ 99%.

- **Gaseous Chlorine-Solid Chlorite Matrix Process:**
  \[ \text{Cl}_2(\text{g}) + \text{NaClO}_2(\text{g}) \rightarrow 2\text{ClO}_2(\text{g}) + 2\text{NaCl} \]

  Attributes: Humidified Cl₂ is pulled or pumped through a stable solid NaClO₂ matrix. Rapid reaction rate, infinite turndown is possible with yield > 99%, Cl₂ contamination.

- **Chlorite-Hypochlorite Process:**
  \[ 2\text{ClO}_2 + \text{ClO}^- + 2\text{H}^+ \rightarrow 2\text{ClO}_2^- + \text{Cl}_2 + \text{H}_2\text{O} \]

  Attributes: Slow reaction kinetics, less ClO₂ but more chlorite than chlorine-chlorite process.

- **Chlorite-Aldehyde Process:**
  \[ \text{R-CHO} + 3\text{ClO}_2^- + 2\text{H}^+ \rightarrow 2\text{ClO}_2^- + \text{R-COOH} + \text{Cl}_2 + \text{H}_2\text{O} \]

  Attributes: Neutral pH (~7), high yield, corrosion of reaction vessel is low, formation of volatile carboxylic acid.

- **Electrochemical Process:**
  \[ \text{ClO}_2(\text{aq}) \rightarrow \text{ClO}_2(\text{g}) + e^- \]

  Attributes: Recent process, integrated continuous process, 25% NaClO₂ solution recycled in electrolytic cells, gas pore membrane is used to separate ClO₂ gas, computer-controlled, pH 5 to 5.5, high yield relative to conventional processes, expensive.

O₂ + 2H₃PO₄ + 2NaClO₂ → 2ClO₂ + 2NaHPO₄ + 2H₂O
O₂ + 4CH₃COOH + 4NaClO₂ → 4ClO₂ + 4CH₃COONa + 2H₂O
O₂ + citric acid + NaClO₂ → ClO₂ + sodium citrate + H₂O

Zeolite crystals are impregnated by immersing in or spraying with the respective aqueous solution of sodium chlorite or acid. If it is desirable to remove the chlorine dioxide from the fluid stream, then the fluid is moved through a bed of zeolite crystals impregnated with potassium hydroxide, sodium sulfite, or ferrous sulfate. The removal of chlorine dioxide takes place as follows:

2ClO₂ + 2KOH → KClO₂ + KClO₂ + H₂O
2ClO₂ + 2NaOH + Na₂SO₃ → 2NaClO₂ + Na₂SO₄ + H₂O

The rapid growth in the applications of chlorine dioxide over the last twenty years is primarily due to its proven effectiveness as an environmentally friendly bleacher, disinfectant, antiseptic, sanitizer, algicide, fungicide, germicidal, and oxidizer. Chlorite-based processes have generally been used for the purpose of disinfection, water treatment, and oxidation, but recently they have been used for fumigation, sterilization, and deodorization. The primary aim is to develop a process that possesses the following attributes:

- Single chemical feed
- High ClO₂ generation efficiency
- Low operating cost
- High purity of chlorine dioxide
- Minimal chlorine contamination
- Maximum utilization of raw material
- Ease of operation and control

Although much work has been performed in this direction, there is still plenty of room available to improve or develop a process that can satisfy all of these attributes.
References