Chlorine Oxides and Chlorine Oxygen Acids

HELMUT VOGT, Technische Fachhochschule Berlin, Berlin, Federal Republic of Germany (Chaps. 1, 4.2 – 4.6, 7, and 9)

JAN BALEJ, Ingenieurbüro für chemische Technik, Jülich, Federal Republic of Germany (Chap. 1)

JOHN E. BENNETT, Eltech Systems Corp., Fairport Harbor, Ohio 44077, United States (Chaps. 4.2 – 4.6)

PETER WINTZER, Cellulosefabrik Attisholz AG, Luterbach, Switzerland (Chaps. 7 and 9)

SAEED AKBAR SHEIKH, Davy McKee AG, Frankfurt, Federal Republic of Germany (Chaps. 2, 3, 4.1, 5, 6, and 9)

PATRIZIO GALLONE, Politecnico di Milano, Milano, Italy (Chaps. 8 and 9)

1. Introduction

Numerous chlorine oxides are known. However, only two anhydrides of chlorine oxygen acids, *dichlorine oxide,* Cl_2O, and *chlorine dioxide,* ClO_2, and two mixed anhydrides, *dichlorine hexoxide,* Cl_2O_6, and *dichlorine heptoxide,* Cl_2O_7, are fairly stable under certain condi-

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Table 1. Properties of chlorine oxides

	Dichlorine oxide [*7791-21-1*], Cl_2O	Chlorine dioxide [*10049-04-4*], ClO_2	Dichlorine hexoxide [*12442-63-6*], Cl_2O_6	Dichlorine heptoxide [*12015-53-1*], Cl_2O_7
Oxidation state	+ 1	+ 4	+ 6	+ 7
M_r	86.91	67.45	166.91	182.90
Melting point, °C	− 116	− 59	+ 3.5	− 90
Boiling point, °C	+ 2	+ 11	–	82
Appearance	yellow-brown gas, red-brown liquid	orange-yellow gas, red liquid	red liquid	oily, colorless liquid
Stability	decomposes at 100 °C, explodes on heating or shock	unstable at ambient temperature	decomposes at melting point	decomposes slowly at ambient temperature

tions. Table 1 shows some important properties of these chlorine oxides. Other chlorine oxides, such as *dichlorine dioxide* [*12292-23-8*], Cl_2O_2, *dichlorine trioxide* [*17496-59-2*], Cl_2O_3, or *dichlorine tetroxide* [*27218-16-2*], Cl_2O_4, are unstable.

The chlorine oxygen acids are formed by reaction of the corresponding chlorine oxides with water.

Hypochlorous acid [*7790-92-3*], HClO:

$$Cl_2O + H_2O \longrightarrow 2\,HClO$$

Chlorous acid [*13898-47-0*], $HClO_2$:

$$2\,ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$$

Chloric acid [*7790-93-4*], $HClO_3$:

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

Perchloric acid [*7601-90-3*], $HClO_4$:

$$Cl_2O_7 + H_2O \longrightarrow 2\,HClO_4$$

Table 2 lists the thermodynamic properties of chlorine oxides, chlorine oxygen acids, and their sodium salts [1].

The *oxidation power* of individual chlorine oxygen compounds is characterized by the changes in the standard enthalpy $\Delta H°$ and Gibbs free energy $\Delta G°$ of the decomposition reactions forming molecular oxygen (Table 3). As shown in Table 3, the thermodynamic stability of chlorine oxygen acids and chlorine oxides increases with increasing oxidation state of the chlorine atom. Therefore, concentrated perchloric acid can be isolated, whereas all other oxygen acids are stable only in diluted form. The instability of the chlorine oxides and their acids determines their industrial significance. All chlorine oxygen compounds are strong oxidants; the strongest are those with the lowest oxidation state of the chlorine atom.

Dichlorine oxide, Cl_2O, chlorine dioxide, ClO_2, all oxygen acids, and their salts, particularly those of sodium and potassium, are used industrially.

History. Soon after the discovery of chlorine in 1774, scientific and commercial interest was directed to the chlorine oxides, the chlorine oxygen acids, and their salts.

Hypochlorite was first prepared in 1787 by C. L. Berthollet by feeding chlorine into potash lye. This bleach liquor (eau de Javel) was soon applied in bleaching textiles and in papermaking. Labarraque replaced potash lye by the cheaper soda lye (eau de Labarraque).

Hypochlorite was prepared by electrolysis of sodium chloride as early as 1801. However, commercial electrochemical production did not start for a long time.

At the beginning of the 20th century, the traditional routes to form bleach liquors [2] fell out of use by the rapidly expanding chlorine – caustic industry that made large quantities of cheap waste chlorine available. Within the last 20 years, however, electrosynthesis has found a widespread revival and is today an alternative to chemical hypochlorite production wherever safety risks of small plants are decisive.

In 1799 C. Tennant and C. McIntosh developed a process for the production of *bleaching powder* by absorbing chlorine onto dry calcium hydroxide. This bleaching powder was much more stable than previously obtained bleaching products. In 1906, G. Pistor succeeded in producing highly concentrated bleach-

Table 2. Thermodynamic properties of chlorine oxides, chlorine oxygen acids, and their salts at 25 °C

Compound	Formula	CAS registry number	State*	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol
Dichlorine oxide	Cl_2O	[*7791-21-1*]	g	80.3	97.9
Chlorine dioxide	ClO_2	[*10049-04-4*]	g	102.5	120.5
Chlorine trioxide	ClO_3	[*13932-10-0*]	g	155	–
Dichlorine heptoxide	Cl_2O_7	[*12015-53-1*]	l	238.1	–
			g	272.0	–
Hydrochloric acid	HCl	[*7647-01-0*]	ao	– 167.2	– 131.2
Hypochlorous acid	HClO	[*7790-92-3*]	ao	– 120.9	– 79.9
Chlorous acid	$HClO_2$	[*13898-47-0*]	ao	– 51.9	+ 5.9
Chloric acid	$HClO_3$	[*7790-93-4*]	ai	– 104.0	– 7.95
Perchloric acid	$HClO_4$	[*7601-90-3*]	ai	– 129.3	– 8.52
Sodium chloride	NaCl	[*7647-14-5*]	ai	– 407.3	– 393.1
Sodium hypochlorite	NaClO	[*7681-52-9*]	ai	– 347.3	– 298.7
Sodium chlorite	$NaClO_2$	[*7758-19-2*]	ai	– 306.7	– 244.7
Sodium chlorate	$NaClO_3$	[*7775-09-9*]	ai	– 344.1	– 269.8
Sodium perchlorate	$NaClO_4$	[*7601-89-0*]	ai	– 369.5	– 270.4

* ao: undissociated solute in aqueous ideal solution at unit molality; ai: electrolyte in the hypothetical ideal solution at unit activity, dissociated into ions.

Table 3. Thermodynamic data of oxygen-forming decomposition reactions of chlorine oxygen compounds at 25 °C

Reaction	ΔH°, kJ/mol	ΔG°, kJ/mol
$Cl_2O\,(g) + H_2O \longrightarrow 2\,HCl\,(aq) + O_2\,(g)$	– 128.8	– 123.2
$4/5\,ClO_2\,(g) + 2/5\,H_2O \longrightarrow 4/5\,HCl\,(aq) + O_2\,(g)$	– 101.4	– 106.5
$4/7\,ClO_3\,(g) + 2/7\,H_2O \longrightarrow 4/7\,HCl\,(aq) + O_2\,(g)$	– 102.4	
$1/4\,Cl_2O_7\,(l) + 1/4\,H_2O \longrightarrow 1/4\,HCl\,(aq) + O_2\,(g)$	– 71.6	
$1/4\,Cl_2O_7\,(g) + 1/4\,H_2O \longrightarrow 1/4\,HCl\,(aq) + O_2\,(g)$	– 80.1	
$2\,HClO\,(aq) \longrightarrow 2\,HCl\,(aq) + O_2\,(g)$	– 92.5	– 102.7
$HClO_2\,(aq) \longrightarrow HCl\,(aq) + O_2\,(g)$	– 115.3	– 137.1
$2/3\,HClO_3\,(aq) \longrightarrow 2/3\,HCl\,(aq) + O_2\,(g)$	– 42.1	– 82.2
$1/2\,HClO_4\,(aq) \longrightarrow 1/2\,HCl\,(aq) + O_2\,(g)$	– 18.9	– 61.4

ing powder with more than 70 % available chlorine.

R. Chevenix first made *chlorine dioxide* in 1802 by the reaction of concentrated sulfuric acid and potassium chlorate, but the product was first identified by H. Davy and F. von Stadion in 1815/1816. Calvert and Davies used oxalic acid instead of sulfuric acid in 1859 and obtained chlorine dioxide together with carbon dioxide, thus eliminating the explosion risk. This and the investigations of E. Schmidt in 1921 – 1923 [3] laid the ground to today's extensive use of chlorine dioxide as a bleaching agent in the textile, pulp, and paper industry.

J. R. Glauber probably prepared *chlorate* for the first time, but C. L. Berthollet first made chlorate in 1787 by the reaction of chlorine with potassium hydroxide and identified it as the salt of chloric acid. The first electrochemical chlorate preparation was performed by W. von Hisinger and J. J. Berzelius in 1802. In 1851 a cell patent was granted to C. Watt that had the essential features of later cells, but industrial production did not start before 1886. Originally, all cells were operated with an alkaline electrolyte until J. Landin added chromic acid to the electrolyte and solved the problem of cathodic hypochlorite reduction [4], [5]. Within the few years before and after 1900, scientific research focused on the mechanism of chlorate formation [6–12]; this was supplemented by numerous investigations within the last 30 years. However, the detailed reaction mechanism is still a subject of scientific debate.

The most important technological improvements were (1) the separation of the electrochemical reactor from the chemical reactor in 1933 (A. Schumann-Leclercq) [13], (2) the utilization of the hydrogen formed at the cathode for "stirring" the electrolyte [14], and (3) the introduction of dimensionally stable titanium anodes 20 years ago [15].

F. VON STADION first made *perchlorates* by oxidation of chlorate at platinum anodes in 1816; he also obtained perchloric acid by the reaction of concentrated sulfuric acid with potassium perchlorate and by anodic oxidation of hydrochloric acid. Preparation of perchloric acid by electrolysis of dilute chloric acid was first carried out by J. J. BERZELIUS in 1835. Like all other electrochemical production methods, electrosynthesis of perchlorate and perchloric acid did not gain industrial significance before the end of the 19th century. In 1890, O. CARLSON was granted a patent for electrochemical perchlorate production, and in 1895 he operated the first commercial plant in Sweden. The first methodic studies of the reaction fundamentals were initiated by German researchers in 1898 [16–18].

General Significance. The importance of chlorine oxygen compounds is based predominantly on their oxidizing power. For 200 years, after the lawn bleaching of textiles became obsolete, the textile and paper industry has invariably been a main consumer of chlorine dioxide and hypochlorite. The importance of these products has steadily grown in accordance with the expansion of the pulp and paper industry. Traditional uses of chlorate as a herbicide or explosive became less important. On the other hand, the increasing demand for disinfection of process and drinking water and for sanitation in general has strongly favored the use of chlorine oxygen compounds. The importance of chlorinated lime as a disinfectant has declined. However, other chlorine oxygen compounds, above all hypochlorite, have grown. This trend was particularly favored by the danger of handling chlorine. Moreover, some of the chlorine oxygen compounds have found numerous novel uses that are reported in detail in the following chapters.

Today, chlorate production is one of the most important inorganic electrosyntheses. In addition, perchlorates are preferably made by electrochemical processes. On the basis of a deeper understanding of the chemical and electrochemical fundamentals and by introducing dimensionally stable anodes, design and operation of electrochemical plants have been revolutionized to such an extent that a modern electrochemical reactor has very little resemblance to a cell 20 years ago.

2. Hypochlorous Acid

Hypochlorous acid [*7790-92-3*], HOCl, M_r 52.5, is only moderately stable in aqueous solution. It is colorless when dilute and yellowish at higher concentrations. Hypochlorous acid is one of the most powerful oxidizing agents known.

Hypochlorous acid solution decomposes exothermically. The main decomposition products are hydrochloric acid and oxygen:

$$2\,\mathrm{HOCl} \longrightarrow 2\,\mathrm{HCl} + \mathrm{O_2}$$

Minor amounts of chlorine and chloric acid are also formed.

Production. Hypochlorous acid is produced by the reversible reaction of chlorine and water:

$$\mathrm{Cl_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{HOCl} + \mathrm{HCl}$$

For efficient conversion, hydrochloric acid must be removed from the equilibrium mixture. This is achieved by limestone, $CaCO_3$, soda ash, Na_2CO_3, or calcium hypochlorite, $Ca(OCl)_2$.

One of the common ways to produce hypochlorous acid is to pass chlorinated water through towers packed with powdered limestone [19]. The overall reaction is as follows:

$$\begin{aligned} &2\,\mathrm{Cl_2} + 2\,\mathrm{H_2O} + 2\,\mathrm{CaCO_3} \\ \longrightarrow\ &2\,\mathrm{HOCl} + \mathrm{CaCl_2} + \mathrm{Ca(HCO_3)_2} \end{aligned}$$

Calcium hydrogen carbonate present in the resulting solution provides the buffer needed to stabilize the product. Any hydrochloric acid still produced is removed by the reaction

$$\mathrm{Ca(HCO_3)_2} + 2\,\mathrm{HCl} \longrightarrow \mathrm{CaCl_2} + 2\,\mathrm{H_2O} + 2\,\mathrm{CO_2}$$

Hypochlorous acid can also be prepared by passing a mixture of dry chlorine and air through a column packed with yellow mercuric oxide, HgO. The resulting dichlorine oxide is dissolved in water to produce hypochlorous acid [20], [21].

Storage. Because of its limited stability, hypochlorous acid is best used soon after production. Its long-distance transport or intermediate storage should be avoided.

A solution containing less than 1 % hypochlorous acid can be stored in the dark over fairly long periods, provided that such metals as copper, nickel, or cobalt are absent. Solutions containing 30 % hypochlorous acid can also be stored, but at temperatures of −20 °C or lower.

Uses. Because of its instability, hypochlorous acid is not used extensively as an oxidizing or bleaching agent. It was used mainly in the water treatment industry for slime control, for treatment of drinking water, and for sterilization of swimming pools. These applications have now been taken over by the more stable hypochlorites.

3. Solid Hypochlorites

3.1. Properties

All solid hypochlorites are soft, white, dry powders. Some are almost odorless; others smell more or less strongly of chlorine or hydrochloric acid because of decomposition during storage (Eqs. 1 – 3). The stability of hypochlorites depends primarily on their water content, which is usually less than 1 %; tropical bleach contains even less than 0.3 %. They are stable up to 80 °C, tropical bleach even up to 100 °C. When heated to 180 °C, they decompose into chloride and oxygen. Such metals as iron, nickel, or cobalt decrease the stability of hypochlorites. Therefore, the raw materials used for the production of hypochlorites must be free of such metals. *Tropical bleach* (< 0.3 % water) free of heavy metals has a shelf life of more than 2 years, if properly stored.

If not properly stored in air-tight containers, hypochlorites suffer loss of available chlorine because of reaction with water:

$$Ca(OCl)_2 + CaCl_2 + 2\,H_2O \longrightarrow 2\,Ca(OH)_2 + 2\,Cl_2 \qquad (1)$$

or reaction with carbon dioxide:

$$Ca(OCl)_2 + CaCl_2 + 2\,CO_2 \longrightarrow 2\,CaCO_3 + 2\,Cl_2 \qquad (2)$$

or reaction with both:

$$Ca(OCl)_2 + CO_2 + H_2O \longrightarrow CaCO_3 + 2\,HOCl \qquad (3)$$

3.2. Production

Bleaching Powder. Standard bleaching powder is a mixture of calcium hypochlorite [*7778-54-3*], $Ca(OCl)_2$, calcium chloride, and calcium hydroxide containing varying amounts of water. It is made by passing chlorine over hydrated lime. The Rheinfelden bleaching powder process of Dynamit Nobel is a batch operation [22]. Dry, powdered lime hydrate is chlorinated at 45 °C and low pressure (5.3 kPa) in a horizontal reaction drum. Chlorine is injected as a liquid. The reaction mass is permanently mixed by a slowly rotating rake. The reaction of solid lime hydrate and chlorine leads to the formation of a mixture of dibasic calcium hypochlorite [*12394-14-8*], $Ca(OCl)_2 \cdot 2\,Ca(OH)_2$, and basic calcium chloride, corresponding to 40 % conversion of the available calcium hydroxide. The following equation characterizes the reaction [23], [24]:

$$5\,Ca(OH)_2 + 2\,Cl_2 \longrightarrow Ca(OCl)_2 \cdot 2\,Ca(OH)_2 + CaCl_2 \cdot Ca(OH)_2 \cdot H_2O + H_2O$$

On further chlorination, hemibasic calcium hypochlorite [*62974-42-9*], $Ca(OCl)_2 \cdot 1/2\,Ca(OH)_2$, and neutral calcium chloride hydrate are formed. After ca. 60 % of the available calcium hydroxide has been converted, the bleaching powder reaction stops; this can be represented by the following equation:

$$10\,Ca(OH)_2 + 6\,Cl_2 \longrightarrow Ca(OCl)_2 \cdot 2\,Ca(OH)_2 + 2\,Ca(OCl)_2 \cdot 1/2\,Ca(OH)_2 + CaCl_2 \cdot Ca(OH)_2 \cdot H_2O + 2\,CaCl_2 \cdot H_2O + 3\,H_2O$$

The reaction is strongly exothermic, generating 1100 kJ of heat per kg of chlorine converted. This heat and the low pressure cause the water formed during the reaction and the liquid chlorine to evaporate. Consequently, the reaction mass is dried completely under vacuum at a maximum temperature of 85 °C. The product is standard bleaching powder of 35 – 37 % available chlorine content (for definition, see Section 3.3).

Gaseous chlorine can also be used for this reaction, but then the reaction takes 2 – 3 times longer, chlorine losses are higher, and the available chlorine content of the product is smaller.

Tropical Bleach. To reduce the water content further, finest ground quicklime, CaO, is added to the bleaching powder. It absorbs any water still present and is converted into calcium hydroxide. Although this operation decreases the available chlorine content by 1 – 2 %, the extra drying makes the resulting bleaching powder, known as tropical bleach, stable up to temperatures of 100 °C.

ICI has developed a continuous process for the production of bleaching powder, in which countercurrents of calcium hydroxide and chlorine react in a rotating drum [25]. The heat of reaction is removed by spraying the drum externally with water and by diluting the chlorine with cooled air; this gas stream also removes the water formed during the chemical reaction.

High-Percentage Hypochlorite. Solid hypochlorites with 70 % and higher available chlorine contents can be prepared by chlorinating slurries of such calcium compounds as calcium hydroxide, or bleaching powder. Initially, hemibasic calcium hypochlorite, $Ca(OCl)_2 \cdot 1/2\,Ca(OH)_2$, is formed. When further chlorinated, this gives neutral calcium hypochlorite dihydrate, $Ca(OCl)_2 \cdot 2\,H_2O$, which is then dried to the desired high-percentage hypochlorite. In all of these reactions, calcium chloride is formed as a byproduct [26–28]. Some processes recover the calcium values by adding sodium hypochlorite to the slurries:

$$2\,NaOCl + CaCl_2 \longrightarrow Ca(OCl)_2 + 2\,NaCl$$

In such cases, the product primarily consists of calcium hypochlorite, sodium chloride, and water, which is then removed [29].

Barium and Magnesium Hypochlorite. Barium hypochlorite [*13477-10-6*], $Ba(OCl)_2$, can be produced in large crystals with a maximum available chlorine content of 59 %. It is more stable than calcium hypochlorite but also more expensive because of the high cost of raw materials.

Magnesium hypochlorite [*10233-03-1*], $Mg(OCl)_2$, is extremely unstable and decomposes when dried.

3.3. Quality Specifications

The term *available chlorine content*, also called *active chlorine*, represents the mass fraction of liberated chlorine in bleaching powder when bleaching powder reacts with hydrochloric acid.

The following qualities of solid hypochlorites are available (content of available chlorine, wt %, in parentheses): tropical bleach (34 – 35), bleaching powder (35 – 37), and high-percentage hypochlorite (70).

3.4. Uses (→ Bleaching)

In the paper industry, calcium hypochlorite is used in single-stage bleaching. The more expensive sodium hypochlorite is used in the multistage process, which involves chlorination, caustic extraction, and hypochlorite oxidation. Kraft pulp is processed to higher brightness and greater strength when sodium hypochlorite is used instead of calcium hypochlorite.

For bleaching in laundry operations, bleaching powder is first suspended in water and then decanted. Only the solution is used because the insolubles could damage the fibers.

4. Hypochlorite Solutions

The reaction of gaseous chlorine with a slight excess of alkali produces highly concentrated hypochlorite solutions. Available chlorine concentrations of 170 – 220 g/L can be obtained, or even more if the residual chloride concentration is lowered extremely [30]. Hypochlorite solutions are relatively safe and are often chosen instead of chlorine for bleaching, disinfection, biofouling control, and odor control. Concern regarding the safety hazards associated with liquid chlorine has grown. Several major cities now restrict transportation of chlorine within their boundaries, and a great deal of attention has focused on accidents caused by the handling of liquid chlorine by unskilled labor [31]. This has increased the popularity of hypochlorite solutions in spite of their relatively high cost.

An attractive alternative to the chemical production of hypochlorite solutions described above is the on-site electrolysis of brine or seawater. Such processes are described in Section 4.2.

Stability. Hypochlorite solutions are more stable than solutions of hypochlorous acid, but they are active enough to be used as disinfectants or bleaching agents. The factors that affect the stability of the parent acid also affect the stability of hypochlorite solutions: concentration, presence of such metals as copper, nickel, or cobalt, pH, temperature, and exposure to light.

Available Chlorine. When chlorine reacts with caustic soda, half of the chlorine is lost because inert sodium chloride is formed:

$$Cl_2 + 2\,NaOH \longrightarrow NaOCl + NaCl + H_2O$$

However, as an oxidant, sodium hypochlorite decomposes to sodium chloride and oxygen:

$$NaOCl \longrightarrow NaCl + [O]$$

The oxidizing power of one oxygen atom is equivalent to that of two chlorine atoms. Therefore, the complete oxidizing power of the original chlorine is available in the hypochlorite solution; it is expressed in grams of available chlorine per liter of finished solution. Thus, the "available chlorine" of hypochlorite solutions compares the oxidizing power of the agent to that of the equivalent amount of elemental chlorine used to make the solution.

4.1. Chemical Production

A hypochlorite unit is attached to each chlor-alkali plant to render harmless the dilute chlorine that cannot be recovered economically. These units make most of the industrially produced hypochlorite solutions [32–34].

Beyond that, hypochlorite solutions with available chlorine contents higher than 5 g/L are made by passing chlorine gas through dilute solutions of sodium hydroxide or potassium hydroxide. Calcium hydroxide suspensions may also be used, from which, after filtration or decantation, clear calcium hypochlorite solutions are obtained [35].

4.1.1. From Chlorine

In the commercial production of hypochlorite solutions from chlorine gas and alkali solutions of various concentrations, the following conditions must be maintained.

1) The temperature must be controlled at 30 – 35 °C.
2) The solution must be alkaline at any stage.
3) The equipment must provide for thorough mixing and escape of inert gas.
4) Such heavy metals as manganese, iron, cobalt, nickel, or copper must be avoided in the system.
5) Available chlorine contents of more than 150 g/L should be avoided. The high decomposition rate of such concentrated solutions more than offsets any savings in transportation [36].

Sodium or Potassium Hypochlorites. Figure 1 shows a schematic diagram of a typical process for the commercial production of hypochlorite solutions. The continuous process can produce hypochlorite solutions of any available chlorine content between 0 and 150 g/L and any amount between zero and the designated capacity. The only parameters to be adjusted are the redox potential of the analyzer (b) and the desired dilutionof the caustic soda solution. For a given amount of chlorine coming in, the system automatically adjusts the caustic soda, process water, and hypochlorite solution flows into and out of the system.

Chlorine gas, diluted with air, is introduced into the chlorination column (a), packed with Raschig rings. Caustic soda is diluted to the desired concentration with water. Tank (d) provides for buffer capacity and homogenization. The pumps (e) circulate the mixture of caustic soda and sodium hypochlorite through the titanium heat exchanger (f), the chlorination column (a), and the tank (d).

Any amount of chlorine between zero and the designated capacity is absorbed in the circulating caustic, producing sodium hypochlorite. When the available chlorine concentration reaches the desired value, the analyzer (b) signals to open control valve (c) for the withdrawal of sodium hypochlorite to the storage tank (g). In this case, the liquid in tank (d) must be replenished by fresh caustic.

The storage tank (g) is equipped with a circulation pump and a heat exchanger to keep the temperature of the stored hypochlorite solution below 35 °C. If necessary, the inert gas leaving column (a) can be scrubbed before entering the atmosphere.

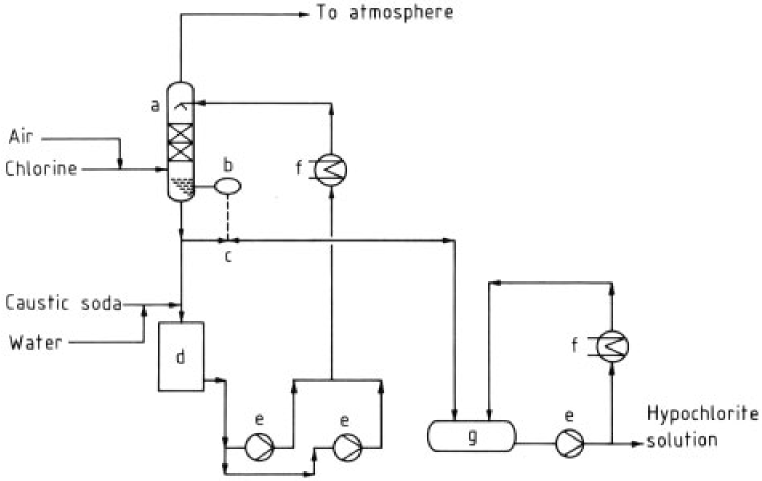

Figure 1. Production of hypochlorite solution from chlorine and caustic soda
a) Chlorination column; b) Analyzer; c) Control valve; d) Buffer tank; e) Pumps; f) Heat exchangers; g) Storage tank

Materials of Construction. All pumps have rubber-lined steel casings and titanium propellers. The heat exchangers are plated with titanium. The tanks (d) and (g) are made from fiberglass-reinforced plastic [37]. The same material is used for the chlorination column and the pipes; chlorinated poly(vinyl chloride) is an alternative material for the pipes.

Calcium Hypochlorite. If a solution of calcium hypochlorite is desired, milk of lime – a suspension of calcium hydroxide in water – is chlorinated. (The solubility of calcium hydroxide in water is 1.3 g/L at 20 °C.) In that case, the plant described in Figure 1 must be modified to handle the solid phase.

In addition to design changes in the equipment, no packing is needed in the chlorination column and the piping must be designed to ensure that pockets are avoided where solid particles can settle and block the pipes; a settler or filter is needed to remove all insoluble or suspended particles before a clear solution of calcium hypochlorite flows to the storage tank.

4.1.2. From Bleaching Powder

To avoid long-term storage of hypochlorite solutions, laundries prefer to store solid bleaching powder and then prepare the sodium hypochlorite solutions by using sodium carbonate, sodium sulfate, or caustic soda:

$$CaCl(OCl) + Na_2CO_3 \longrightarrow NaOCl + NaCl + CaCO_3$$

$$CaCl(OCl) + Na_2SO_4 \longrightarrow NaOCl + NaCl + CaSO_4$$

$$CaCl(OCl) + 2\,NaOH \longrightarrow NaOCl + NaCl + Ca(OH)_2$$

A disadvantage of this method is the precipitation of $CaCO_3$, $CaSO_4$, or $Ca(OH)_2$, which requires filtering or settling before the hypochlorite solution can be used.

4.2. Electrosynthesis

On-site, electrochemical production of dilute hypochlorite solution has long been recognized as an option wherever long-term storage of hypochlorite is unnecessary; it is now rapidly gaining popularity [38]. Hypochlorite solutions with an available chlorine content of up to 10 g/L are commonly produced on the site in electrochemical cells by using either prepared brine or natural seawater as feed.

4.2.1. Reaction Fundamentals

Electrolysis of sodium chloride yields chlorine at the anode:

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e$$

The final product depends on the operational conditions of the cell. In the production of chlorine gas, special care is taken to prevent mixing of anode and cathode products (→ Chlorine). Chlorine hydrolyzes and hypochlorous acid dissociates, forming hypochlorite and chloride in solution [39], [40]:

$$Cl_2 + H_2O \rightleftharpoons HClO + Cl^- + H^+$$

$$HClO \rightleftharpoons ClO^- + H^+$$

The formation of hypochlorous acid and hypochlorite ceases when the electrolyte is saturated with chlorine and chlorine gas evolves at pH 2 – 3.

However, in the electrosynthesis of hypochlorite, as well as of chlorate, anolyte and catholyte are vigorously mixed. The hydroxyl ions formed at the cathode

$$2\,H_2O + 2\,e \longrightarrow 2\,OH^- + H_2$$

maintain the electrolyte near neutrality (pH 7 – 9). Under this condition, the concentration of dissolved chlorine near the anode surface remains too low to permit evolution of gaseous chlorine, and hypochlorite is the main product.

There are four main loss reactions that complicate industrial operation; they have been studied to optimize the operating conditions [41], [42] and are described in the following paragraphs in more detail.

Cathodic Reduction. Hypochlorite is reduced at the cathode to form chloride:

$$ClO^- + H_2O + 2\,e \longrightarrow Cl^- + 2\,OH^-$$

The rate of this reaction is controlled by mass transfer and is, thus, linearly proportional to the overall hypochlorite concentration; it increases with flow rate and temperature [42–45].

Loss by cathodic reduction also occurs in chlorate production; in that case it is minimized by adding dichromate to the electrolyte (see Section 7.2.2). This remedy is not possible in the simple flow-through hypochlorite cells, and loss in commercial cells is considerable, as Figure 2 shows.

Several means are used to lower reduction loss. Smooth cathode surfaces are superior to rough surfaces [45]. Loss is also lowered by decreasing the active area of the cathodes, thereby increasing the cathode current density. Cathodic reduction was greatly suppressed by decreasing the active area to ca. 1 % with a synthetic resin coating [42]; however, the attendant voltage increase makes this approach industrially unattractive. Bubbles always cover a portion of the cathode surface and contribute to lower cathodic reduction. Hydrogen evolution increases cathodic reduction because its stirring action enhances the mass transfer coefficient. Efforts to lower the mass transfer coefficient by covering the cathode with a porous plastic have also been successful at suppressing cathodic reduction [47]. Similarly, the inhibitory action of calcium chloride was related to the formation of insoluble compounds on the cathode surface [48].

Anodic Oxidation. Anodic oxidation of hypochlorite to chlorate is used in industry and is described in detail in Section 7.3:

$$\begin{aligned} 3\,ClO^- + 1.5\,H_2O \longrightarrow\ & ClO_3^- + 3\,H^+ \\ & + 2\,Cl^- + 0.75\,O_2 + 3\,e \end{aligned}$$

This reaction is also controlled by mass transfer, and its rate increases with the hypochlorite concentration. Because hypochlorite is decomposed at the anode and cathode, commercial on-site production is restricted to a maximum concentration of available chlorine of ca. 10 g/L; this is usually sufficient for disinfecting and deodorizing water. The contribution of anodic oxidation to the overall loss can further be lowered by increasing the anodic current density; however, the anode lifetime may then decrease. The loss reaction may also depend on the anode material: dimensionally stable anodes based on RuO_2 were found to be more efficient than platinized titanium or graphite [42].

Anodic Water Electrolysis. This loss reaction competes with chlorine discharge, and its rate depends on the chloride concentration, various mass transfer coefficients, and the nature of the anode material.

$$H_2O \longrightarrow 1/2\,O_2 + 2\,H^+ + 2\,e$$

When NaCl concentrations are greater than 100 g/L, the loss is small. However, a typical NaCl concentration in a modern brine cell is ca.

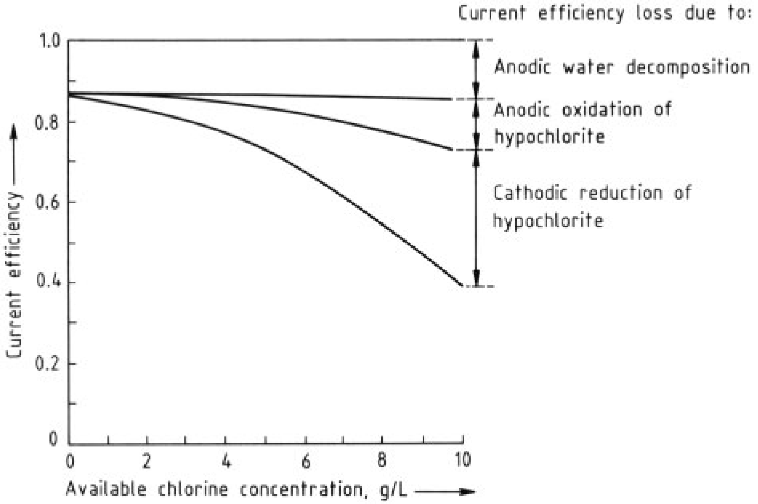

Figure 2. Current efficiency loss vs. available chlorine concentration (NaCl: 28 g/L, 25 °C, 1550 A/m^2) [46]

30 g/L, at which the rate of water decomposition is significant, as shown in Figure 2.

When salt must be purchased, the conversion of chloride into hypochlorite must be maximized. A typical on-site electrosynthesis from prepared brine consumes 3 – 5 kg of salt per kg of available chlorine produced. The question of chloride consumption is meaningless where natural seawater is used as a feed. However, in cases of low salinity or very cold seawater, oxygen evolution caused by anodic water electrolysis may decrease current efficiency by as much as 40 % [49].

As in the case of chlorate synthesis, the nature of the anode material strongly influences the amount of water decomposition. Platinized titanium and dimensionally stable anodes based on RuO_2 are more selective for chlorine evolution, whereas PbO_2 and graphite anodes have a greater tendency to evolve oxygen.

Chemical Chlorate Formation. Autoxidation of hypochlorite to chlorate is the preferred route of commercial chlorate production (Section 7.3). The rate of this reaction depends on pH and temperature; in industrial hypochlorite production, it is minimized by keeping the temperature below 40 °C and the pH above 7 [41].

4.2.2. Industrial Cells

The number of companies offering hypochlorite cells has grown quickly in the past few years. Over 20 suppliers offer a wide variety of cell designs. They can all be classified into three basic types: (1) tube cells, (2) parallel-plate cells, and (3) rotating or mechanical scraper-type cells. Of the modern hypochlorite cells, the tube cells were developed first. They generally consist of two concentric pipes, one being the anode and the other the cathode, with the annular space serving as the electrode gap. This type of cell may be operated under pressure and is well-suited for small applications. Parallel-plate cells achieve a much better packing of electrode area, and most large industrial installations use cells of this type. Only two of the manufacturers offer rotating or mechanical scraper-type cells. In theory, such cells should be able to operate indefinitely without deposit buildup, and would therefore result in low maintenance cost. In practice, however, their extra mechanical action is difficult to maintain, and such cells have not yet captured a significant market share.

Seawater Cells. Cells designed to operate by using natural seawater are different from those using prepared brince. Cells using seawater tend to operate at a higher electrolyte flow rate and a wider electrode gap than brine cells to minimize problems arising from cathode deposits. Seawater cells also produce a lower product concentration, typically solutions with an available chlorine content of 0.5 – 4.0 g/L. Hypochlorite concentration is kept low to maximize current efficiency whenever high salt usage is not a concern (see also Table 4).

Table 4. Typical operational data of electrolytic cells for hypochlorite generation

Parameter	Brine feed	Seawater feed
Current density, A/m^2	1500	1500
Current efficiency, %	65	90
Temperature, °C	25	5 – 25
Concentration		
NaCl (cell entrance), g/L	30	15 – 30
Available chlorine (cell exit), g/L	8 – 10	1.0 – 3.0
Energy consumption, kW/h/kg of available chlorine	4.5 – 5.0	3.3 – 4.1
Sodium chloride consumption, kg of NaCl per kg of available chlorine	3 – 3.5	

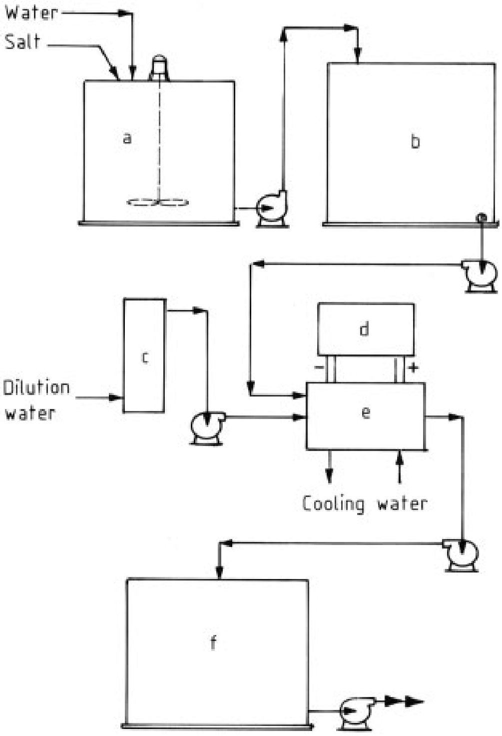

Figure 3. Typical layout for a brine hypochlorite cell system
a) Automatic brine makeup; b) Brine storage tank; c) Water softener; d) Rectifier; e) Hypochlorite cell; f) Hypochlorite storage tank

Brine Cells. Brine cells usually produce solutions with an available chlorine content of 7 – 10 g/L to keep salt cost low. Most manufacturers offer brine cells of the same design as their seawater cells, but electrolyte flow rate is lowered to maximize current efficiency at the higher concentration of available chlorine. Figure 3 shows a flow diagram for a typical system designed for electrolysis using prepared brine. Although brine cells were developed first, they now have only a small share of the total on-site hypochlorite cell market.

Table 4 shows typical operational data of seawater and brine feed cells.

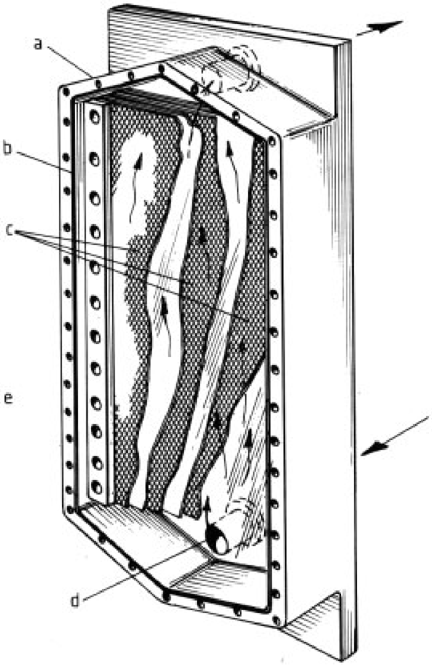

Figure 4. Sanilec seawater electrolysis cell
a) Molded polypropylene cell body; b) O-ring seal; c) Dimensionally stable anodes; d) Seawater inlet; e) Clear acrylic cover (not shown)

Sanilec System. Eltech System Corp. first offered the Sanilec system for seawater electrolysis in 1973. The cells are of a parallel-plate design (Fig. 4) and feature once-through operation without recycle [31]. Cells producing 30, 70, 140, or 155 kg/d can be banked in series to produce hypochlorite solutions of available chlorine concentrations up to 3.0 g/L. Full-load a.c. power consumption is as low as 4.1 kWh per kg of chlorine, partly because dimensionally stable anodes are used. These cells use cathodes made of nickel alloys and remove hydrogen pe-

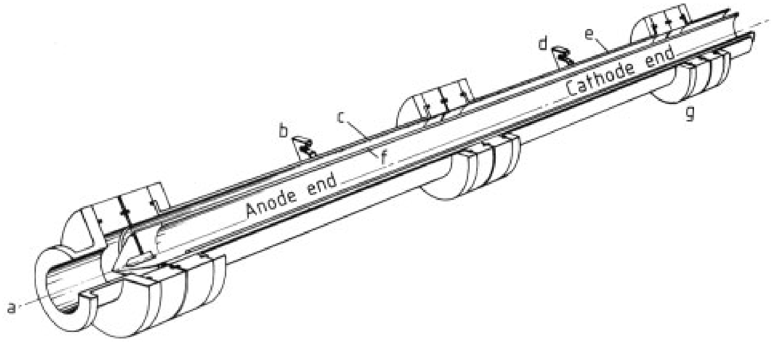

Figure 5. Chloropac seawater cell
a) Inlet; b) Cathode connector; c) Cathode; d) Anode connector; e) Anode; f) Bipolar electrode; g) Insulating flange

riodically to lower power consumption. Typical operational data are shown in Table 4.

Chloropac System. Englehard Minerals & Chemical Corp. produces tube cells with concentric titanium pipes as anode and cathode under the trade name of Chloropac System [50]. These cells are designed for an operating pressure of 1000 kPa. They utilize a high seawater flow rate to minimize deposit formation.

As shown in Figure 5, the electrodes are assembled in a bipolar arrangement, which is particularly suited for smaller capacities. The platinized titanium anodes are coated with 5 µm of platinum and have good current efficiency for chlorine evolution. The power consumption is claimed to be 3.5 – 5.0 kW h per kg of chlorine.

M. G. P. S. System. Mitsubishi Heavy Industries offers monopolar plate-type cells arranged in series under the name of the M. G. P. S. system. The cell body is made from mild steel lined with rubber, and the system is well-suited for large industrial applications. Cathodes are made from titanium and anodes from platinized titanium; precious metal oxide anodes are also used. The available chlorine concentration ranges from 0.2 to 1.0 g/L, and the power consumption is reported to be 5.8 kW h per kg of chlorine.

Seaclor System. The Oronzio de Nora Seaclor system features a bipolar parallel plate-type seawater cell [51] shown in Figure 6. Cathodes are made from titanium and anodes are based on RuO_2. Hypochlorite solutions with an available chlorine content of up to 2.5 g/L are produced; power consumption is cited to be 3.4 – 4.5 kW h per kg of chlorine. The most notable feature of the Seaclor system is the size of the individual cells, which may be large enough to produce nearly 1000 kg/d.

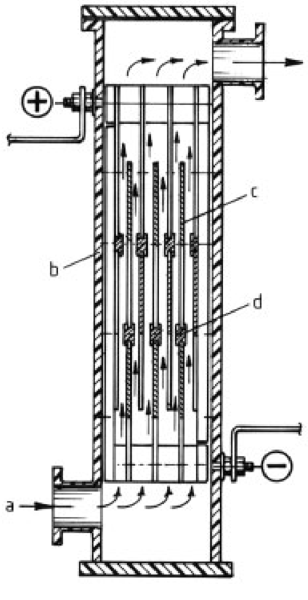

Figure 6. Seaclor hypochlorite cell
a) Inlet; b) PVC cell body with overlay; c) Bipolar electrode; d) Insulator

Pepcon System. The Pepcon system made by Pacific Engineering & Production Co. of Nevada is distinctly different from other commercial cells because it employs less expensive PbO_2 anodes. Pacific Engineering uses a tube-type design, with a steel or titanium pipe forming the outside of the cell and a PbO_2-plated graphite rod at the center. Steel has a small overpotential for hydrogen evolution, but it requires careful protection to prevent corrosion during shutdown.

Maintenance. The major problem of on-site hypochlorite cells, especially those using natural seawater as feed, is that of deposit formation. Because the electrolyte adjacent to the cathode is strongly alkaline, magnesium hydroxide and calcium hydroxide deposit at the cathode surface. If allowed to build up, these deposits may bridge the electrode gap, reducing cell efficiency and ultimately causing anode failure [52].

Most manufacturers of industrial hypochlorite cells will tolerate deposit formation, but simultaneously attempt to minimize the problem by controlling the current density, turbulence, and cathode surface. In the case of seawater the deposit – chiefly $Mg(OH)_2$ – is soft and can generally be scoured from the cathode surface and flushed from the cell by using a high flow rate. Although at least two suppliers suggest that acid cleaning of deposits is never necessary, it seems likely that occasional removal of deposits is required on a cycle that varies from a few days to a few months. Usually, the deposit is removed by flushing the cell with hydrochloric acid. This dissolves the deposit quickly and consumes very little acid. Large industrial installations usually provide for convenient acid washing.

Brine cells may also form deposits as a result of hardness ions introduced from either feed water or from impurities in the salt. In this case, the deposit will usually consist of a hard calcium carbonate, which is also easily removed with acid. Unlike in seawater cells, however, it is often practical to soften the cell feed; brine cells can then be designed to operate with very little deposit formation.

A second major maintenance item is occasional replacement of anodes. The lifetime of both precious metal oxide and platinized titanium anodes is adversely affected by high current density, low salinity, low electrolyte temperature, and severe deposit formation. Manufacturers should be consulted on the expected anode lifetime and cost of replacement. Typically, anodes must be replaced or recoated after 2 – 5 years from startup.

4.3. Storage

Hypochlorite solutions slowly decompose if catalytic amounts of cobalt, nickel, or copper are present; iron and magnesium do not act catalytically [53]. Therefore, long-term storage and transport over long distances must be avoided. Hypochlorite solutions prepared from seawater are especially unstable and should be consumed directly after on-site preparation.

Hypochlorite solutions for household use have an available chlorine concentration of ca. 40 g/L. Special attention must be paid to minimize oxygen evolution. Improper storage of hypochlorite bottles may cause stoppers to be blown out and bottles to explode. Vented stoppers are used to avoid pressure buildup in the bottles.

4.4. Uses

Concentrated hypochlorite solutions are used primarily in the paper and textile industries for bleaching. Since chlorine dioxide (Chap. 5) produces a brighter product and is less harmful to fibers, the use of a hypochlorite solution as bleaching agent in these industries has declined.

On the other hand, the use of electrochemically produced dilute hypochlorite solutions has increased largely over the past several years. Electrolytic generators can be used whenever hypochlorite is needed for disinfection or for bleaching; their advantages are economy, safety, and convenience.

Currently, the broad area of biofouling control accounts for over half of the market for such equipment, especially at locations remote from chlor-alkali plants. The largest seawater electrolysis plants for the production of hypochlorite in the world, a 60 000-kg/d plant in Kuwait and a 48 000-kg/d plant in Saudi Arabia, were commissioned in 1980 as parts of large desalination projects. The hypochlorite is used to control slime and algae in piping and tubes and to eliminate odor in the desalted water.

Another important and quickly growing use for hypochlorite cells is disinfection of seawater for secondary oil recovery; otherwise, slime growth would clog the oil-bearing strata.

The largest plant for this purpose is a 5400-kg/d plant at Qurayyah, Saudi Arabia, where disinfected seawater is filtered, deaerated, and pumped 100 km inland for injection.

Shipboard applications account for many seawater electrolysis installations worldwide. In this case, smaller units are used to inhibit marine growth in seawater systems for sanitary services and for distilled water treatment. Fishing fleets also use hypochlorite as a disinfectant for storage.

Coastal utilities and industrial plants use hypochlorite from seawater electrolysis to control mollusks, algae, and slime, which may block seawater intakes, clog piping, and reduce heat transfer efficiency. Inland utility and industrial plants use brine hypochlorite cells when handling and safety are of primary concern. Nuclear power plants are particularly sensitive to the hazards of liquid chlorine.

Both coastal and inland wastewater treatment plants are major users of chlorine for disinfection before discharge. This was first started on the island of Guernsey in 1966 and was operated for 6 years [54].

On-site hypochlorite production from brine is also used for drinking water treatment, but it is only economical at remote locations or where safety is a major concern.

A number of companies have introduced on-site generators to supply chlorine demand for swimming pools. Many of these have been small chlor-alkali cells with separated anolyte and catholyte; but unseparated hypochlorite generators have gained acceptance and now represent an important portion of that market.

On-site hypochlorite generators are sometimes selected for other less common applications, such as textile manufacturing, industrial and laundry bleaching, cyanide destruction, odor control, ocean aquariums, and food processing [41], [55].

4.5. Economic Aspects

The Middle East now represents about half of the total market for electrolytic hypochlorite generation. The rest of the market is roughly balanced between East Asia, South America, and the United States. The total installed capacity has grown from ca. 200 t/d in 1979 to estimated 700 t/d in 1984. This probably represents total system sales approaching U.S. $ 200×10^6 through 1984.

On-site hypochlorite generation is difficult to compare with purchased chlorine or hypochlorite because chemical costs vary widely from nation to nation. Bulk liquid chlorine prices vary from ca. $ 150/t in the United States to well over $ 1000/t in remote locations, and hypochlorite prices vary from $1500/t of available chlorine content in the United States to over $ 2500/t where transportation cost is high. Therefore, a direct economic comparison with purchased chemicals can only be made for each location individually. There are many cases in which the selection of on-site generation is motivated primarily by economics, rather than by safety or convenience.

4.6. Plant Safety

Dilute sodium hypochlorite solution is much safer than liquid or gaseous chlorine. Sodium hypochlorite solution, as produced by on-site electrolytic generators (with an available chlorine content of 0.5 – 10.0 g/L), is regarded as corrosive and as an irritant when ingested or inhaled. It is also a mild skin irritant, and prolonged exposure may result in a burn or rash [56].

The primary safety concern associated with the electrolysis equipment is the explosion and fire hazard from byproduct hydrogen. This hazard is increased if oxygen is present in the cell gas. Oxygen content ranges from 3 % to 9 % in efficiently operating cells, but it varies widely in practice. Cells with anodes having poor selectivity for chlorine evolution or with poor design for operation at low temperature and low salinity may result in an oxygen concentration of 40 % or more in the cell gas.

The explosion limit for hydrogen – oxygen mixtures is 6.0 % O_2. Explosive impact will be soft at this point, but will increase quickly in severity as oxygen content increases. Two measures are taken in commercial cells against this: (1) dilute the byproduct hydrogen with sufficient air to less than 4.0 %, the explosion limit for hydrogen in air, or (2) allow the cell gas to vent with proper precaution, e.g., the installation of rupture disks.

A special hazard arises when cell deposits are washed with dilute hydrochloric acid. In addition to the hazards of handling hydrochloric acid, chlorine gas evolves when HCl is accidentally mixed with stored hypochlorite solution, or when the cells are started without first flushing out the acid.

5. Chlorine Dioxide

5.1. Properties

Chlorine dioxide [*10049-04-4*], ClO_2, M_r 67.45, is a yellowish-green to orange gas. It can be condensed to a reddish-brown liquid at 11 °C and solidified to orange red crystals at − 59 °C. The density of liquid ClO_2 is as follows [57]:

t, °C	− 33	− 21	− 17	5
ϱ, g/cm^3	1.907	1.788	1.735	1.635

Chlorine dioxide has an irritant, pungent odor that resembles that of a mixture of chlorine and ozone. Chlorine dioxide is an extremely unstable gas, readily decomposing into chlorine and oxygen even on mild heating. It is explosive as a gas or liquid at high concentration [58], [59]. However, it can be handled easily when it is diluted with air to less than 15 vol%.

Chlorine dioxide is easily soluble in water (heat of solution: − 26.8 kJ/mol); at 10 °C its solubility in water is 5 times that of chlorine (Table 5).

Chlorine dioxide can be easily driven out of aqueous solutions with a strong stream of air. When an aqueous solution is cooled, $ClO_2 \cdot 8\,H_2O$ crystals precipitate. Chlorine dioxide is also soluble in carbon tetrachloride, sulfuric acid, or acetic acid [61].

Other important properties of chlorine dioxide are its photochemical [62] and thermal [63] decomposition. Solutions of chlorine dioxide are relatively stable in the dark, but they decompose into chlorine and oxygen when exposed to light. Therefore, these solutions are very strong oxidants and extremely reactive and corrosive. They attack all metals except platinum, tantalum, and titanium.

In dilute aqueous solutions, chlorine dioxide oxidizes hydrocarbons to ketones and alcohols [64]. In the absence of water, chlorine dioxide loses its bleaching power.

5.2. Production

Because of the explosion risk, chlorine dioxide is manufactured on site. Its industrial production is based on the reduction of chlorate [65–67]. Undesirable byproducts are chlorine and chloride. For analysis of chlorine dioxide, see [68–71].

Reaction Mechanism [72], [73]. The basic reaction mechanism of chlorine dioxide formation is the same for all known processes. All processes use chlorate as the raw material; in all processes chlorine dioxide formation takes place in strong acidic solutions; and byproduct chloride is found in all generator solutions.

The presence of chloride ions is essential for the formation of chlorine dioxide [74], [75]; this is evident from the following facts:

1) No significant amount of chlorine dioxide is formed in acidified chlorate solutions with various reducing agents when chloride has previously been removed from the reaction system by adding silver sulfate.
2) If chlorine dioxide generators are allowed to stand overnight, minor ClO_2 formation consumes all of the chloride present in the reaction mass. When the supply of fresh raw materials is started the next morning, a specific chloride level must build up before chlorine dioxide can be produced at the desired rate. This chloride buildup phase can be eliminated by deliberately adding fresh chloride to the generator in the beginning.

Independent on the choice of reducing agent, the primary reaction for chlorine dioxide production is the reaction between chloric acid and hydrochloric acid to form chlorine dioxide and chlorine. Traces of Mn^{2+} and Ag^{+} ions catalyze the reaction [76].

$$\begin{array}{ll}
HClO_3 + HCl & \longrightarrow HClO_2 + HClO \\
HClO_3 + HClO_2 & \longrightarrow 2\,ClO_2 + H_2O \\
HClO + HCl & \longrightarrow Cl_2 + H_2O \\
\hline
2\,HClO_3 + 2\,HCl & \longrightarrow 2\,ClO_2 + Cl_2 + 2\,H_2O
\end{array}$$

In industrial chlorine dioxide production, sulfur dioxide, hydrochloric acid, or methanol are

Table 5. Solubility of chlorine dioxide in water [60]

25 °C		40 °C		60 °C	
p, mbar	c, g/L	p, mbar	c, g/L	p, mbar	c, g/L
46	3.01	74.9	2.63	141.2	2.65
29.5	1.82	45.7	1.6	71.6	1.18
17.9	1.13	25.2	0.83	28.4	0.58
11.2	0.69	13.2	0.47	16.0	0.26

used as reducing agents. Other reducing agents are not economical.

5.2.1. Day – Kesting Process [74], [77], [78]

This process combines the production of chlorine dioxide from sodium chlorate, with hydrochloric acid as reducing agent, and electrochemical sodium chlorate production from sodium chloride:

$$2\,NaCl + 6\,H_2O \xrightarrow{\text{Electrolysis}} 2\,NaClO_3 + 6\,H_2$$

$$2\,NaClO_3 + 4\,HCl \longrightarrow 2\,NaCl + 2\,ClO_2 + Cl_2 + 2\,H_2O$$

The efficiency of chlorine dioxide production depends on how far the rate of the competing chlorine production can be decreased:

$$NaClO_3 + 6\,HCl \longrightarrow 3\,Cl_2 + NaCl + 3\,H_2O$$

This can be achieved by maintaining a high chlorate concentration and a low hydrochloric acid concentration in the reaction system.

Chlorate solution is rapidly circulated from a large storage tank through the electrolytic cells, which oxidize chloride to chlorate. From the same tank the chlorate solution is also circulated slowly through the chlorine dioxide generator. The reaction takes place in a heated multicompartment column. The reactant solutions, chlorate and hydrochloric acid, are added from the top and air is introduced from the bottom of the column [79]. Chlorate is reduced with hydrochloric acid to chlorine dioxide and chlorine. Both gases are stripped from the system with air; at the same time, chlorine dioxide is diluted below the explosion limit [80]. The depleted chlorate solution is then returned to the storage tank and recycled to the chlorate electrolysis. The mixture of chlorine dioxide and chlorine is stripped with water to give a solution rich in chlorine dioxide [80], [81] and a gas phase rich in chlorine. Chlorine can then be recycled to the process as hydrochloric acid by reduction with hydrogen produced in the electrolytic cells or neutralized with NaOH solution to produce hypochlorite.

Although it has always been cheaper to produce chlorine dioxide by this process, it never gained momentum because of the high initial capital expenditure involved.

Lurgi [79], [82–86], Chemetics [87], [88], and others [89–91] have developed integrated systems that combine this process with the production of chlorine, caustic soda, and hydrochloric acid. Such combined systems use sodium chloride and electric power as the raw materials and produce chlorine dioxide solution and caustic soda (Fig. 7).

5.2.2. R2 Process [92–100]

Hooker Chemical Corporation, together with Electric Reduction Company, developed the R2 process, starting from the single-vessel process [101–103], and Electric Reduction Company further improved the details. Chlorine dioxide is produced according to the following overall reaction:

$$\begin{aligned}&2\,NaClO_3 + 2\,NaCl + 2\,H_2SO_4\\ &\longrightarrow 2\,ClO_2 + Cl_2 + 2\,Na_2SO_4 + 2\,H_2O\end{aligned}$$

An undesirable side reaction produces additional chlorine:

$$\begin{aligned}&NaClO_3 + 5\,NaCl + 3\,H_2SO_4\\ &\longrightarrow 3\,Cl_2 + 3\,Na_2SO_4 + 3\,H_2O\end{aligned}$$

In continuous industrial processes, the molar ratio of chlorine dioxide to chlorine is nearly 2 : 1, indicating that the ClO_2 production efficiency is almost 100 % (based on chlorate).

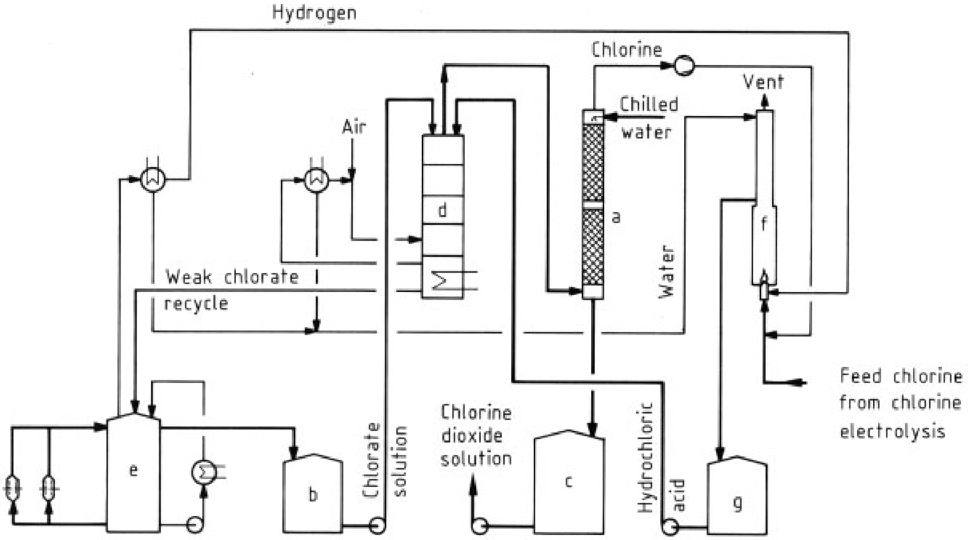

Figure 7. Schematic diagram of the integrated Day – Kesting process [82]
a) Chlorine stripper; b) Sodium chlorate solution; c) Chlorine dioxide solution storage; d) Chlorine dioxide generator; e) Chlorate electrolysis; f) Hydrochloric acid furnace; g) Hydrochloric acid storage

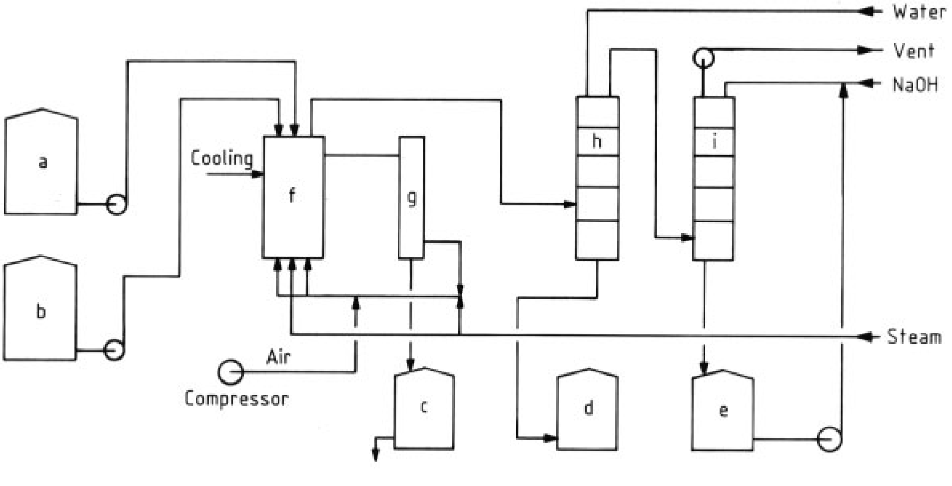

Figure 8. Schematic diagram of the R2 process [104]
a) $NaCl + NaClO_3$ storage; b) Acid storage; c) Spent acid; d) ClO_2 solution storage; e) NaOCl solution storage; f) ClO_2 generator; g) Stripper; h) ClO_2 absorption tower; i) Cl_2 absorption tower

Figure 8 shows a schematic diagram of the R2 process. Concentrated solutions of sodium chlorate, sodium chloride, and sulfuric acid (equimolar ratio) are metered to a vigorously agitated reaction vessel. Air is blown into the reactor through porous plates. Under optimum conditions, the reaction mass contains 0.1 – 0.2 mol/L of sodium chlorate, 4.5 – 5 mol/L of sulfuric adic and 0.02 – 0.08 mol/L of sodium chloride. Chlorine dioxide is absorbed from the gas phase in packed towers in cold water, and chlorine leaves the system as byproduct. The liquid effluent from the reactor is a mixture of sodium sulfate and sulfuric acid. The process can also be operated in such a way that sodium hydrogen sulfate crystallizes from the effluent solution [105], [106]. It provides sulfate for kraft pulping; the sulfuric acid is recovered for reuse.

The R2 process has been modified [106] and optimized [103], [107], [112] to suit the requirements of the industry. Currently, it is probably the most extensively used process for the production of chlorine dioxide.

5.2.3. Mathieson Process [67], [74], [96], [98], [104]

Sulfur dioxide is the reducing agent in the Mathieson process. The main overall reaction is as follows:

$$2\,NaClO_3 + H_2SO_4 + SO_2 \longrightarrow 2\,ClO_2 + 2\,NaHSO_4$$

Solutions of sodium chlorate and sulfuric acid are added continuously to a relatively large, cylindrical, lead-lined tank (primary reactor) from the top. Sulfur dioxide, diluted with air, is introduced through gas diffusion plates at four points in the bottom of the tank. The reaction mass overflows to a smaller secondary reactor of similar construction. The generated chlorine dioxide still contains some unreacted sulfur dioxide; it is stripped from the reaction mass by air and then washed in a scrubber packed with Raschig rings. The scrubber is installed on top of the primary generator, and the fresh sodium chlorate solution serves as a washing liquid on its way down to the primary generator. The mixture of chlorine dioxide, air, and chlorine coming out of the scrubber goes to the absorption tower.

5.2.4. Solvay Process [67], [74], [96], [98], [113]

The Solvay process uses methanol as reducing agent. The main overall reaction is as follows:

$$\begin{aligned} &2\,NaClO_3 + CH_3OH + H_2SO_4 \\ &\longrightarrow 2\,ClO_2 + HCHO + Na_2SO_4 + 2\,H_2O \end{aligned}$$

The reaction between sodium chlorate, methanol, and sulfuric acid takes place in two jacketed, lead-lined steel reactors. The chemicals are added to the bottom of the first vessel and flow by gravity from one reactor to the other. Each vessel has its own supply of methanol and air. The two reactors are operated at different temperatures and chlorate concentrations. Up to 70 % of the reaction is completed in the first reactor. Additional methanol and up to 10 % of the total acid requirement is fed to the second reactor; the conversion of chlorate is then more than 95 %.

5.2.5. Other Processes

The *Holst process* [114–116] is a batch version of the Mathieson process and has not been exploited because of its low chlorine dioxide yield. When solid sodium chlorate is successively added, the unreacted sulfuric acid from the previous operating period can be utilized and the conversion efficiency of chlorate increases to 83 %.

The *Persson process* [74], [117] has only historical value. The main raw materials were sodium chlorate and sulfur dioxide, but the latter was used to reduce chromic acid to chromic sulfate, and this in turn reduced chlorate to chlorine dioxide.

The *CIP process* [118], [119] was in operation long before it was published, maintaining secrecy for several years. Concentrated sodium chlorate solution is carefully metered and distributed to a packed reaction tower. Sulfur dioxide gas, diluted with air or nitrogen, enters from the bottom, reacts with the chlorate, and is oxidized to sulfuric acid. Chlorate is reduced to chlorine dioxide. The additional inert gas dilutes the ClO_2 formed to a safe concentration, and the mixture is led to the absorption tower.

Small-Scale Production from Sodium Chlorite [120–123]. Small-scale consumers produce chlorine dioxide by passing chlorine gas through a sodium chlorite solution:

$$2\,NaClO_2 + Cl_2 \longrightarrow 2\,NaCl + 2\,ClO_2$$

The reaction is almost quantitative.

The alternative acidification of sodium chlorite solution with hydrochloric acid is also commonly used:

$$5\,NaClO_2 + 4\,HCl \longrightarrow 4\,ClO_2 + 2\,H_2O + 5\,NaC$$

5.3. Economic Aspects

The economy of chlorine dioxide production depends on the efficient utilization of the byproducts of the process [97], [105]. When the chlorine dioxide production is combined with chloralkali membrane cells and hydrochloric acid synthesis (Lurgi concept), chlorate cells work most efficiently [82–90]. Byproducts from one unit can then be used as raw materials or make-up chemicals for the others. In this way, high initial capital cost is paid back in the long run by a far lower operating cost. The R2 process offers similar possibilities if it is combined with a paper mill [95], [107], [111].

5.4. Uses

Chlorine dioxide is the most widely used bleaching agent, in particular for high-quality cellulose. It destroys lignin without attacking cellulose, yielding a characteristically white cellulose. The general trend is to eliminate chlorine and hypochlorite as bleaching agents altogether [124], [125] and replace them with chlorine dioxide [81], [126], [127].

Chlorine dioxide is used in the pulp and paper, textile, and food industries. In the pulp and paper industry, a unique whiteness can be achieved in kraft pulp, sulfite pulp, and soda pulp [96]. In the textile industry, chlorine dioxide produces high-quality fibers with additional special advantages. Shrinkproof wool owes its quality to the reaction of chlorine dioxide with the cross-linking sulfur atoms of the wool.

Chlorine dioxide is also used in sanitization, e.g., of industrial and municipal waters, sewage, algae, or decomposed vegetables. Waterworks use chlorine dioxide to handle taste and odor problems of household water [68], [122], [123], [128].

6. Sodium Chlorite

6.1. Properties

Sodium chlorite [*7758-19-2*], $NaClO_2$, M_r 90.45, is the sodium salt of the unstable chlorous acid; it exists as an anhydrous and a trihydrated form (transition point 38 °C). Very pure $NaClO_2$ crystals are white, but they usually have a greenish tint because traces of chlorine dioxide are present.

The stability of sodium chlorite lies between that of hypochlorite and chlorate. For further information, see [129]. Sodium chlorite is not sensitive to impact if organic matter is excluded. It can be struck with a clean metal surface without detonation. However, in the presence of organic matter – the film usually occurring on a hammer suffices – the impact may result in a spontaneous puffing. As a strong oxidizing agent, solid sodium chlorite forms explosive mixtures with such oxidizable materials as sulfur, powdered coal, metal powders, or organic compounds. Sodium chlorite solutions should never be allowed to dry on fabrics because this would result in a flammable combination.

Sodium chlorite is soluble in water: [129]

t, °C	5	17	20	30	40	45	50	60
Solubility, wt %	34	39	40.5	46	50.7	53	53.7	55

More important is its solubility in the presence of caustic soda (Table 6), sodium chlorate [130], sodium chloride, [131], and sodium carbonate [132]. For the system $NaClO_2-NaCl-NaClO_3-H_2O$, see [133], [134].

Aqueous solutions of sodium chlorite must be protected from light. At low pH (approximately 2), chlorite solutions contain chlorous acid that decomposes to form chlorine dioxide and chlorate:

$$4\,HClO_2 \longrightarrow 2\,ClO_2 + HClO_3 + HCl + H_2O$$

At pH 3 – 4, decomposition slows down. Alkaline solutions are stable, and dilute solutions can even be boiled without decomposition. Concentrated alkaline solutions of sodium chlorite slowly decompose when heated [135–137]:

$$3\,NaClO_2 \longrightarrow 2\,NaClO_3 + NaCl$$

The reaction of sodium chlorite with hypochlorite depends on pH [137]. At low pH, the reaction produces chlorine dioxide, whereas at high pH, chlorate is formed. The reaction with chlorine produces chlorine dioxide and sodium chloride:

$$2\,NaClO_2 + Cl_2 \longrightarrow 2\,ClO_2 + 2\,NaCl$$

Crystalline sodium chlorite is slightly hygroscopic without caking; it is stabilized with alkali for long-term storage. When heated to 180 – 200 °C, it decomposes partially to sodium chlorate and sodium chloride or completely to sodium chloride and oxygen [129]. For the analysis of sodium chlorite, see [69], [70], [138–140].

Table 6. Solubility in the $NaOH-NaClO_2-H_2O$ system at 30°C

d_4^{30}	c_{NaOH}		c_{NaClO_2}		Solid phase
	wt %	g/L	wt %	g/L	
–	55.3	–	0	–	
–	51.1	–	1.5	–	$NaOH-H_2O$
1.568	51.2	802.8	1.7	26.7	
1.575	50.6	797.0	2.45	38.6	$NaOH+NaClO_2$
1.546	48.9	756.0	2.5	38.7	
1.519	42.3	627.3	5.1	77.5	
1.496	35.9	537.1	7.65	114.4	
1.474	31.5	464.3	10.5	154.8	
1.453	26.8	389.4	14.9	216.5	$NaClO_2$
1.457	23.6	343.9	18.7	272.5	
1.447	20.3	293.7	22.4	322.7	
1.451	16.0	232.2	28.2	409.7	
1.457	15.4	224.4	29.2	425.4	
1.469	10.3	151.3	36.8	540.6	
1.469	9.5	139.6	38.0	558.2	
1.471	9.0	132.4	38.8	570.7	
1.473	7.86	115.7	40.5	596.6	
1.473	6.2	91.3	42.9	631.9	unstable
1.468	5.8	85.1	43.1	632.7	unstable
1.476	6.1	90.0	42.6	628.8	
1.441∗	3.55	51.2	43.5	626.8	$NaClO_2 \cdot 3\,H_2O$
1.410∗∗	0.0	–	45.7	644.7	

∗ The solid phase was analyzed.

∗∗ The solutions contain traces of NaCl (0.06 wt %).

6.2. Production

Sodium chlorite is produced by treating chlorine dioxide with caustic soda [141–143]:

$$2\,ClO_2 + 2\,NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

The reaction products, sodium chlorite and sodium chlorate, have nearly the same solubility in water and are difficult to separate. Industrial sodium chlorite production uses the following procedure [144]. The absorption of chlorine dioxide in caustic soda solution and the simultaneous reduction of chlorate to chlorite are achieved by a suitable reducing agent, such as hydrogen peroxide [145]:

$$2\,ClO_2 + 2\,NaOH + H_2O_2 \longrightarrow 2\,NaClO_2 + 2\,H_2O + O_2$$

The product is a 33 wt % solution of sodium chlorite, which is then converted to a dry solid containing ca. 80 wt % of sodium chlorite, the rest being stabilizers.

Numerous complex chlorites have been prepared [146], but only sodium chlorite has proven to be of any commercial value.

Efforts to produce sodium chlorite by electrolysis, similar to hypochlorite or chlorate, have not yet been successful. Its synthesis from chlorine dioxide and sodium amalgam [147] could not be realized because redox potential [148] and pH [149] were difficult to control. Other processes for the direct reduction of chlorine dioxide were not efficient [150], [151].

6.3. Uses

Sodium chlorite is a very efficient bleaching agent. Its oxidation potential allows a controlled bleaching that is not attainable with other bleaching agents. Therefore, it is widely used as a bleaching agent in the textile industry [135–137], [152–155].

Another important use of sodium chlorite is the small-scale production of chlorine dioxide; see Section 5.2.5 [120–123].

7. Chloric Acid and Chlorates

Chloric acid is not being produced on an industrial scale. However, sodium chlorate and potassium chlorate have outstanding industrial significance. Sodium chlorate is produced on a very large scale by one of the most important inorganic electrosyntheses. All other chlorates are produced in much smaller amounts for special purposes, usually from sodium chlorate.

Table 7. Physical properties of sodium chlorate and potassium chlorate

	$NaClO_3$ [*7775-09-9*]	$KClO_3$ [*3811-04-9*]
M_r	106.44	122.55
Crystal system	cubic	monoclinic
mp, °C	260	356
Enthalpy of fusion, kJ/mol	21.3	
Density, g/cm^3	2.487 (25 °C) 2.385 (252 °C)	2.338 (20 °C)
Molar heat capacity, $J\,mol^{-1}\,K^{-1}$	$54.7 + 0.155\,T$ * (298 – 533 K)	99.8 (20 °C)
Standard enthalpy of formation, kJ/mol	– 365.8 (cryst.) – 344.1 (ai)**	– 391 (cryst.)
Standard entropy, $J\,mol^{-1}\,K^{-1}$	123.4 (cryst.) 221.3 (ai)**	143 (cryst.)
Enthalpy of dissolution (200 mol of H_2O/mol of chlorate, 25 °C), kJ/mol	+ 21.6	+ 40.9

* T = temperature, K.

** ai = ideal solution of unit activity.

7.1. Properties

Physical Properties. Anhydrous *chloric acid* [*7790-93-4*], $HClO_3$, M_r 84.46, is unstable and explosive. Dilute aqueous solutions are colorless and odorless; they are stable at low temperature if catalytically active contaminants are excluded. In the presence of such catalysts, the solutions may decompose vehemently, particularly at elevated temperature. Addition of polyphosphates or hydrogen peroxide lowers the decomposition tendency. Above 95 °C, pure chloric acid solutions decompose to form chlorine dioxide, chlorine, oxygen, and perchloric acid, but in the presence of hydrochloric acid, the products are chlorine and chlorine dioxide.

Concentrated chloric acid is a strong oxidant. In addition to the noble metals, only Hastelloy C exhibits satisfactory resistance against corrosion. At low temperature, dilute chloric acid may be kept in containers made of poly(vinyl chloride). At 18 °C, the density of an aqueous 13 % $HClO_3$ solution is 1.080 g/cm^3 while that of a 25 % solution is 1.166 g/cm^3.

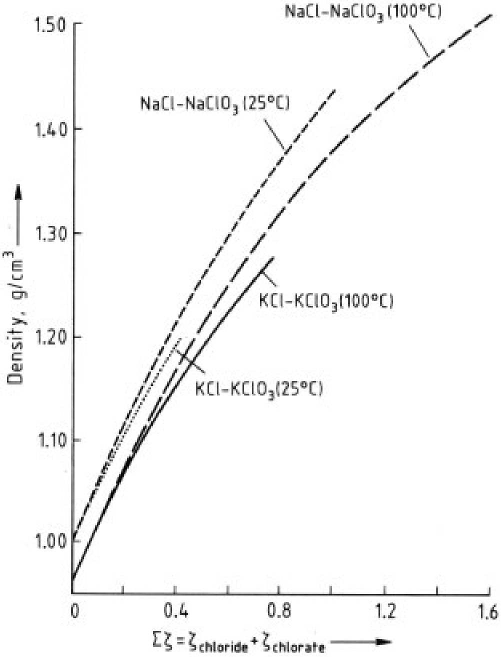

Figure 9. Densities of aqueous solutions of $NaCl - NaClO_3$ and $KCl - KClO_3$ [156]
$\Sigma\,\zeta$ is the sum of mass ratios ζ_{chloride} (kg of chloride/kg of H_2O) and ζ_{chlorate} (kg of chlorate/kg of H_2O)

Physical properties of *sodium chlorate* and *potassium chlorate* are shown in Table 7. Figure 9 shows the densities of aqueous chloride – chlorate solutions. Figure 10 shows the relative vapor pressure depression of aqueous solutions of chloride and chlorate. The electric conductivity of pure chlorate solutions is given in Table 8; for further data, see [158]. Solubility data of the aqueous chloride – chlorate system are shown in Figures 11 and 12 and in Table 9. The mass fraction of saturated sodium chlorate solutions in the range from 0 to 100 °C can be calculated from

$$w = 0.445 + 0.00226t$$

where

t = temperature, °C
w = mass fraction, kg of $NaClO_3$/kg of solution

The freezing point depression ΔT (in K) of aqueous solutions of sodium chlorate is given by

$\Delta T = 33.64\zeta - 115.1\zeta^2$

where ζ = mass ratio, kg of $NaClO_3$/kg of H_2O

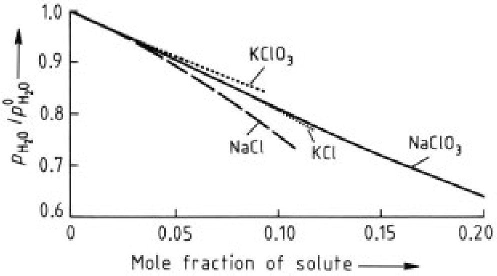

Figure 10. Vapor pressure depression of aqueous chloride and chlorate solutions

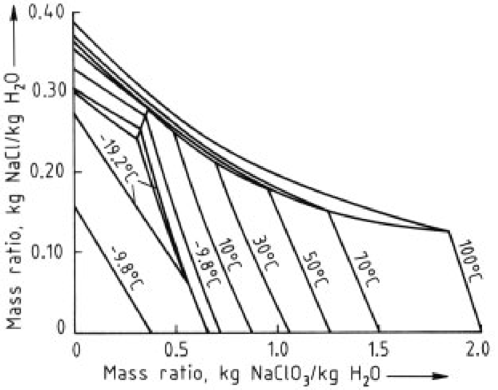

Figure 11. Solubility of aqueous solutions of NaCl and $NaClO_3$ [159]

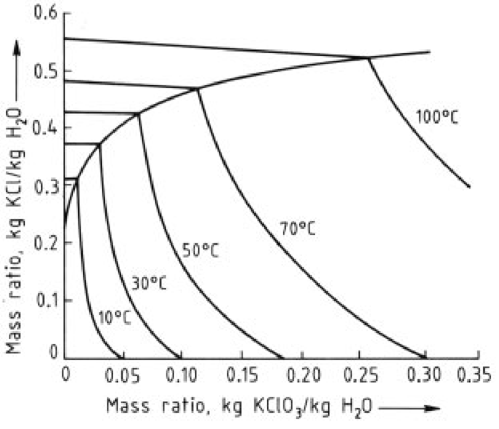

Figure 12. Solubility of aqueous solutions of KCl and $KClO_3$ [159]

Chemical Properties. Chlorates decompose to yield oxygen. They form flammable and explosive mixtures with organic substances, phosphorus, ammonium compounds, some sulfur compounds, and some metal salts, oxidizable solvents, or other oxidizable substances. Potassium chlorate decomposes below the melting temperature. Alkaline chlorate solutions do not exhibit strong oxidizing properties. With decreasing pH, however, the oxidizing activity of chlorate solutions increases. Concentrated acidic solutions are vigorous oxidants as a result of chloric acid formation.

Solutions containing more than 30 % $HClO_3$ decompose spontaneously. In the presence of organic matter or reducing agents the reaction may be violent, especially at elevated temperature.

7.2. Production Fundamentals

Sodium chlorate (and to a minor extent potassium chlorate) is produced by electrolysis of an aqueous sodium chloride (potassium chloride) solution. Hypochlorite forms as an intermediate that is further oxidized to chlorate along two competing reaction paths. The concentrated chlorate solution is either submitted to crystallization (see Section 7.4) or it is used directly, particularly in the production of chlorine dioxide.

An aqueous solution containing 450 – 550 g/L of sodium chlorate and 90 – 100 g/L of sodium chloride is generated directly by electrosynthesis; it can be used as feed in the Kesting process (Section 5.2.1) [160]. The spent solution from that process, containing 140 g/L of sodium chlorate and 220 g/L of sodium chloride, is then fed back to the electrolysis system.

The other, less common chlorates are chemically formed by conversion of sodium chlorate with the corresponding chloride. Other production methods, such as the chemical formation of chlorates by introducing gaseous chlorine into a warm hydroxide solution, are now obsolete.

7.2.1. Chlorate-Generating Reactions

An aqueous solution of sodium chloride is electrolyzed, usually in cells without a diaphragm.

Table 8. Electric conductivity of pure sodium chlorate solutions [157]

Concentration,	Conductivity, Ω^{-1} m^{-1}		
g/L	20 °C	40 °C	60 °C
100	6.2	8.9	11.8
200	10.4	14.9	19.7
300	13.4	18.9	25.0
400	15.0	21.5	28.5
500	15.7	22.7	30.3
600	15.5	23.1	30.8
750		21.7	29.7

Table 9. Mass ratio (kg of salt/kg of H_2O) of the solution in equilibrium with crystalline chloride and chlorate [158]

t, °C	$NaCl-NaClO_3$ solution		$KCl-KClO_3$ solution	
	NaCl	$NaClO_3$	KCl	$KClO_3$
− 9.8	0.270	0.360	0.2466	0.0056
+ 10	0.249	0.499	0.3123	0.0144
30	0.2125	0.706	0.3703	0.0321
50	0.1785	0.958	0.4226	0.0635
70	0.1495	1.238	0.4651	0.1162
100	0.1245	1.85	0.518	0.2588

Hydrogen and sodium hydroxide are formed at the cathode, while chloride is discharged at the anode. Chlorine does not evolve as a gas, but undergoes hydrolysis (Fig. 13):

$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^- \quad (4)$$

Chlorate then forms simultaneously by two competing reactions: (1) predominantly by autoxidation of hypochlorite in the bulk electrolyte, and (2) to a small extent (ca. 20 %) by anodic chlorate formation. The detailed mechanism of the reaction was essentially clarified at the turn of the century, but continues to be the subject of intense studies [39, b].

Autoxidation. Autoxidation of hypochlorous acid, also called chemical chlorate formation, is a homogeneous reaction that proceeds according to the following overall equation, which gives no information on the individual steps:

$$3\,HClO \longrightarrow ClO_3^- + 2\,Cl^- + 3\,H^+ \quad (5)$$

Autoxidation is preceded by dissociation of a part of the total hypochlorous acid involved in autoxidation:

$$HClO \longrightarrow ClO^- + H^+ \quad (6)$$

This dissociation can occur to a significant degree only at some distance from the anode, where the electrolyte is sufficiently buffered by hydroxyl formed by the cathode reaction. The hypochlorite formed then reacts with the complementary amount of hypochlorous acid:

$$2\,HClO + ClO^- \longrightarrow ClO_3^- + 2\,Cl^- + 2\,H^+ \quad (7)$$

Equation (7) shows the classical form of Foerster [161], [162], which was attacked [163] but has since been confirmed [164], [165].

Anodic Chlorate Formation. The mechanism of anodic chlorate formation was established by Landolt and Ibl [166]. Hydrolysis of chlorine (Eq. 4) is considered to be fast. Because of the formation of H^+ ions, one might expect the electrolyte in the anodic boundary layer to be strongly acidic. However, this is the case only at low chloride concentration. Large chloride concentrations, as they occur in industrial processes, shift the hydrolysis equilibrium (Eq. 4) to the left. In the electrolyte layer adjacent to the anode, the H^+ concentration is too small to permit noticeable diffusion of H^+ into the inner electrolyte. Therefore, hydrogen is transported away from the anode as hypochlorous acid rather than H^+. In the bulk electrolyte where the pH is high, hypochlorous acid is largely dissociated. The hypochlorite ion diffuses back to the anode

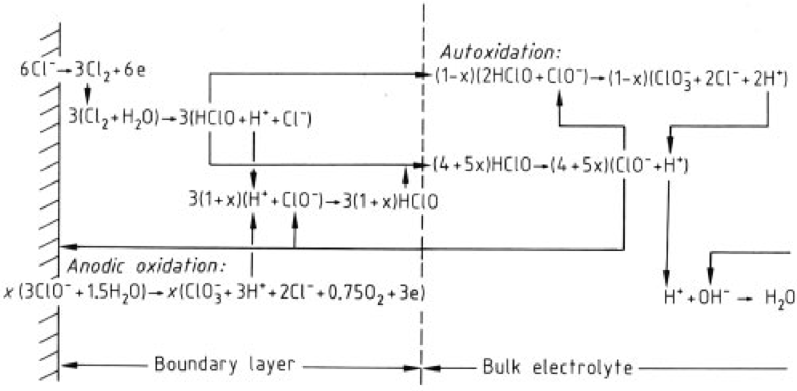

Figure 13. Chlorate formation by autoxidation in bulk electrolyte and by anodic oxidation

and more than two-thirds of it is consumed by buffering before reaching the anode. However, less than one-third of that hypochlorite is discharged at the anode to form chlorate and oxygen [166–168]:

$$3\,ClO^- + 1.5\,H_2O \longrightarrow ClO_3^- + 3\,H^+ + 2\,Cl^- + 0.75\,O_2 + 3\,e \qquad (8)$$

The stoichiometry of the anodic chlorate formation (Eq. 8) was recently reviewed [39, b].

As shown in Figure 13 the discharge of 6 mol of chloride yields 1 mol of chlorate; this is independent of the reaction route, either autoxidation or anodic discharge of hypochlorite. However, the anodic oxidation (Eq. 8) requires 50 % additional electric energy. Therefore, industrial processes endeavour to suppress the anodic oxidation in favor of the autoxidation. The effective means is a short residence time of the electrolyte solution inside the electrochemical reactor by applying large flow rates using rather short electrode lengths. Thereby the average bulk concentration of hypochlorite ($ClO^- + HClO$) is lowered and the undesired anodic chlorate formation controlled by mass transfer is minimized. However, increasing flow rates increase the mass transfer coefficient, thus counteracting the beneficial effect of short residence time. The optimum is at elevated values of the flow rate; this method to suppress anodic oxidation is used in all modern industrial chlorate systems. Under these conditions, chlorate is formed predominantly outside the interelectrode space, e.g., in a separate chemical reactor where the route is necessarily restricted to autoxidation (Fig. 14).

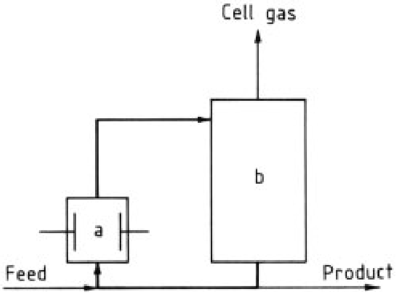

Figure 14. Concept of separate electrochemical reactor (a) and chemical reactor (b) for chlorate electrosynthesis

7.2.2. Loss Reactions

In addition to anodic chlorate formation, further loss reactions decrease current efficiency and must be suppressed in industrial systems.

Cathodic Reduction of Hypochlorite. The main loss occurs by cathodic reduction of hypochlorite, as described in Section 4.2.1:

$$ClO^- + H_2O + 2\,e \longrightarrow Cl^- + 2\,OH^-$$

The reaction competes with hydrogen generation. Without special precautions, its rate is controlled by mass transfer and, therefore, linearly proportional to the hypochlorite concentration in the bulk electrolyte. The reaction can widely be suppressed by adding a small amount of dichromate (1 – 5 g/L) to the electrolyte solution. By cathodic deposition a porous surface film of chromium hydroxide forms [169]. Inside the pores of this film, the effective current density increases, and the resulting potential gradient across the film impedes the diffusion of any kind of anions to the cathode, whereas the access of cations to the cathode and their reduction are facilitated. The protective film ceases to grow after a certain thickness is reached; the increase in cell voltage caused by the ohmic resistance of the film is more than compensated by the gain in current efficiency [165], [170]. Increasing the electrolyte temperature favors mass transfer of hypochlorite to the cathode and, therefore, requires more dichromate. When the current is interrupted, the surface layer dissolves. It takes some time to reestablish a new film after the current is switched on, but cathodic reduction immediately takes place. Therefore, cells should be operated continuously, and a minimum cathodic current density is recommended to prevent dissolution of the film [171]; from industrial experience, a current density of 20 A/m^2 is considered satisfactory.

Cathodic Reduction of Chlorate. Chlorate is also reduced at the cathode, but this reaction is less significant than the reduction of hypochlorite described in the preceding paragraph:

$$ClO_3^- + 3\,H_2O + 6\,e \longrightarrow Cl^- + 6\,OH^-$$

The rate of reduction is strongly affected by the cathode material; reduction at iron is much faster than at nickel and platinum. Chlorate reduction is also restrained by the chromium hydroxide layer on the cathode [16], [171–174]. In closed-loop electrolyte systems (e.g., Fig. 14), the presence of residual dichromate in the solution has a beneficial effect because its additional buffering capacity stabilizes the various reaction equilibria [165], [175], [176].

Catalytic Decomposition of Hypochlorite. Hypochlorite solutions decompo e in the presence of catalytically active contaminants:

$$2\,ClO^- \longrightarrow 2\,Cl^- + O_2$$

Oxides of nickel, cobalt, and copper are very effective; their catalytic activity decreases in that order. The catalytic action of manganese, iron, lead, and tin has been demonstrated, but is at least one order of magnitude smaller [53], [177]. Autocatalytic decomposition is also possible, but its extent is negligible at ambient temperature [177], [178].

Chlorine Desorption. Hydrogen and oxygen gas bubbles evolved at the cathode and anode, respectively, tend to desorb some chlorine from the solution. This amount of chlorine is lost for chlorate production unless it is recovered from the cell gas by absorption outside the cell. Water vapor contained in the gas bubbles increases their volume and, thus, the desorption loss. Therefore, the operation temperature is limited to a maximum of 80 – 90 °C. Chlorine loss results not only in a corresponding loss in current efficiency, but also in a steady increase in pH. Therefore, chlorine gas or, more usually, hydrochloric acid must be permanently added to maintain the pH.

Further loss reactions are of minor importance: *perchlorate* may be formed by anodic oxidation of chlorate, particularly at low chloride concentration, provided the oxygen overvoltage is large enough (see Section 8.2.2). With the industrial anodes used in chlorate electrosynthesis, perchlorate formation is negligible. The *anodic decomposition of water,* which plays a major role in hypochlorite production, is negligible as long as the chloride concentration is larger than 100 g/L.

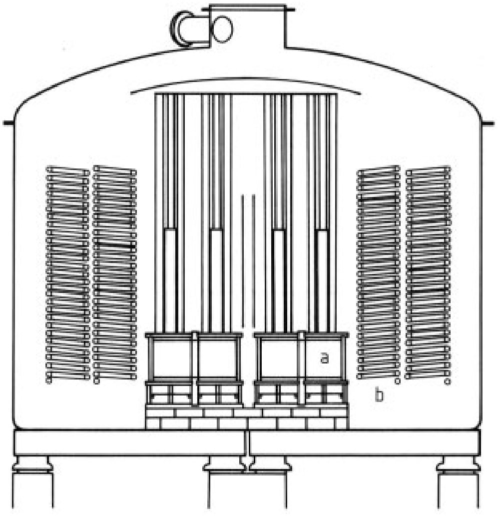

Figure 15. Huron electrosynthesis system with integrated electrolysis cells
a) Chemical reactor; b) Cooling coils

7.3. Industrial Electrosynthesis Systems

Chlorate cell design has changed much within the last 25 years by the introduction of coated titanium anodes [179] and by the systematic application of the results of chlorate formation theory. Hypochlorite autoxidation occurs at high temperature outside the interelectrode gap or even outside the electrochemical reactor to decrease the hypochlorite concentration before the electrolyte reenters the cell. The first industrial plant of this type was started in 1969 in Finland.

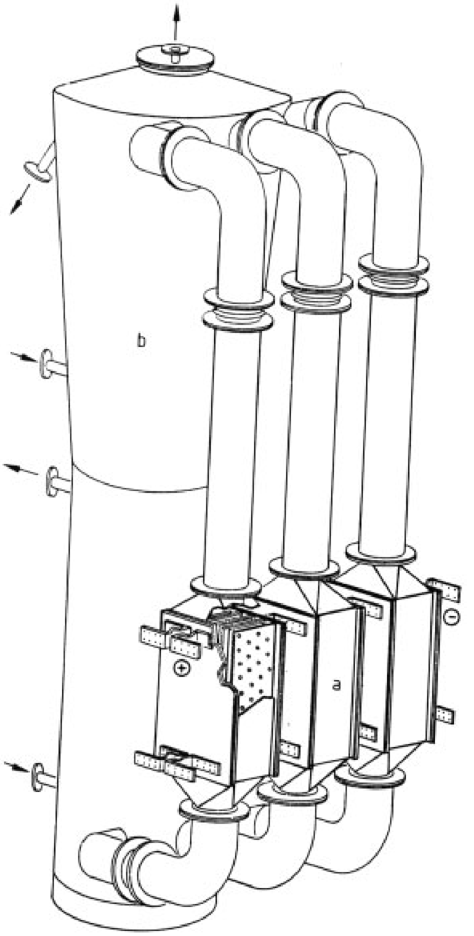

Figure 16. Electrosynthesis system with natural convection of electrolyte (Krebs, Paris)
a) Electrolysis cell; b) Chemical reactor; c) Cooler

The requirement for large electrolyte flow rate resulting from the considerations of Section 7.2 is taken into account in all modern cells. Hydrogen evolved at the cathode provides for a natural flow of the electrolyte and is used for its recirculation through the cell compartment and the chemical reactor without requiring additional pumping. Other systems use a mechanical pump to provide the required circulation rate. Hydrogen gas is released at the top of the unit. For safety reasons, the gas volume in the equipment must be minimized. To stabilize the pH value, the solution is continuously acidified (cf. Section 7.2.2.).

Some electrosynthesis systems combine the cell and the chemical reactor in a single unit (Huron, Fig. 15, and Atochem). Other industrial systems are composed of an electrochemical reactor and a separate chemical reactor [180] interconnected by electrolyte circulation pipes with integrated heat exchangers for the removal of excess heat (Krebs, Fig. 16, and Pennwalt, Fig. 17) or separate heat exchangers (Krebskosmo, Chemetics, and Fröhler – Lurgi – Uhde). None of these electrosynthesis systems is clearly superior from an engineering point of view.

7.3.1. Electrolysis Cell Types

Most cells are equipped with coated titanium anodes [181], and only some 5 – 10 % of all chlorate cells still use graphite anodes. Older cells have also been operated with anodes of magnetite (Fe_3O_4) [182], [183], platinum [184], graphite [185–188], or lead dioxide [189], [190]; reviews on these older anodes can be found in [39] and [191–193]. The following survey is restricted to modern cells with coated titanium anodes. Typical operational data are shown in Table 10.

Modern electrochemical reactors [194–196] cover the complete spectrum of unipolar and bipolar electrodes, including direct coupling of cells with unipolar electrodes, an arrangement sometimes called multipolar (Fig. 18).

Cells with *unipolar* electrodes (Krebs, Pennwalt, Fröhler – Lurgi – Uhde, and Atochem) are suitable for large currents up to 100 kA. Repair of one cell does not necessitate shutdown of the entire electrolyzer. Parasitic currents [197], corrosion, and malfunction of a cell unit are easy to locate. Pennwalt and Atochem use two cathodes per anode. This design allows circulation within the cell [194], [195]. Cells with *bipolar* elec-

Table 10. Typical operational data of sodium chlorate cells

Parameters	Krebs, Paris	Chemetics, Vancouver	Fröhler – Lurgi – Uhde	Pennwalt, Philadelphia	Atochem, Paris	Huron Chemicals, Kingston	Krebs, Zürich	Krebskosmo, Berlin
Current per cell, kA	75	15 – 85	6 – 50	30	30 – 75	480	30	17.5
Cell type	NC	DC	TDK	P8-3	TA2	cell-in-tank	ZMA	CZB 50 – 150
Cell connection	unipolar	multipolar	unipolar	unipolar	unipolar	multipolar	unipolar	bipolar
Anode surface, m^2	30	7 – 25	7.1 – 17.8	8.92	20/30	proprietary	10	30.6/91.8
Current density, kA/m^2	2.5	1.8 – 3.5	2.8	3.36	1.5 – 2.5	1.5 – 4	3.0	3.0
Operating voltage,								
min., V	2.85	2.70	2.9	3.4	2.92	3.1 at 3 kA/m^2	3.1	3.1
max., V	3.00	3.00	3.0	3.7	3.10	3.4 at 3 kA/m^2	3.3	3.4
Energy consumption (d.c.), kW h/t of $NaClO_3$	4500 – 4750	4250 – 4750	4610 – 4770	5650	4600 – 4900	5000 – 5500	5100	5000 – 5500
Current efficiency, %	95.5	96	95	96	96	> 93.5	95	94 – 96
Current concentration, A/L	30	25 – 30	22	20	13 – 22	6 – 20	20	25
Operating temperature, °C	80	80	75	90	70 – 80	65	80	80
pH of cell liquor	6.2	6 – 7	6.4	5.5 – 6.5	6.2 – 6.4	6.3 – 6.9	6.5	6.5
Interpolar distance, mm	4	–	3.5	4	6	proprietary	5	4
Kind of coating	$Pt/Ir/RuO_2$	IMI	platinate	Pt/Ir	RuO_2	Pt/Ir or RuO_2	$Pt/Ir/RuO_2$	noble metal oxide
Anode coating life, years	6 8 – 10	> 10	8 – 10	7 – 10	7 – 10	dep. on coating	> 6	4
Cathode material	spec. carbon steel	steel	mild steel	carbon steel	spec. steel	titanium	steel	steel
Cell liquor composition:								
Min. NaCl concentration, g/L	100	100	90	70 – 110	100	50	100	80
Max. $NaClO_3$ concentration, g/L	600	640	550	500 – 650	625	700	600	650
NaOCl concentration, g/L	1.3 – 1.8	–	3	1 – 2	1	–	2	2 – 3
$Na_2Cr_2O_7$ concentration, g/L	3 – 4	3 – 4	3	3 – 5	5	1.1	5	3
Cell gas composition:								
H_2, vol%	97.7 – 98.2	97.5	97.5	97.5	> 98	97 – 99	97.5	97.5
O_2, vol%	1.5 – 2	2	2	1.5	1 – 2	1.0 – 2.5	2	2
Cl_2, vol%	0.3	0.5	0.5	1.0	0.1 – 0.2	0.1 – 0.2	0.5	0.3
Requirements per t of $NaClO_3$ (100 %):								
NaCl, kg	560	560	–	560	550	–	550	570
HCl (33 %), kg	35	–	–	Cl_2	30	–	33	50
NaOH (30 %), kg	24	–	–	–	10	–	–	60
$Na_2Cr_2O_7 \cdot 2H_2O$, kg	0.05 – 0.1	–	–	5	0.3	–	neglig.	0.3
Production:								
$NaClO_3$ (100 %), kg/d	1137	–	–	446	–	7628	453	1370/4110
H_2, m^3 (STP)/d	753	–	–	291	–	4760	300	910/2730

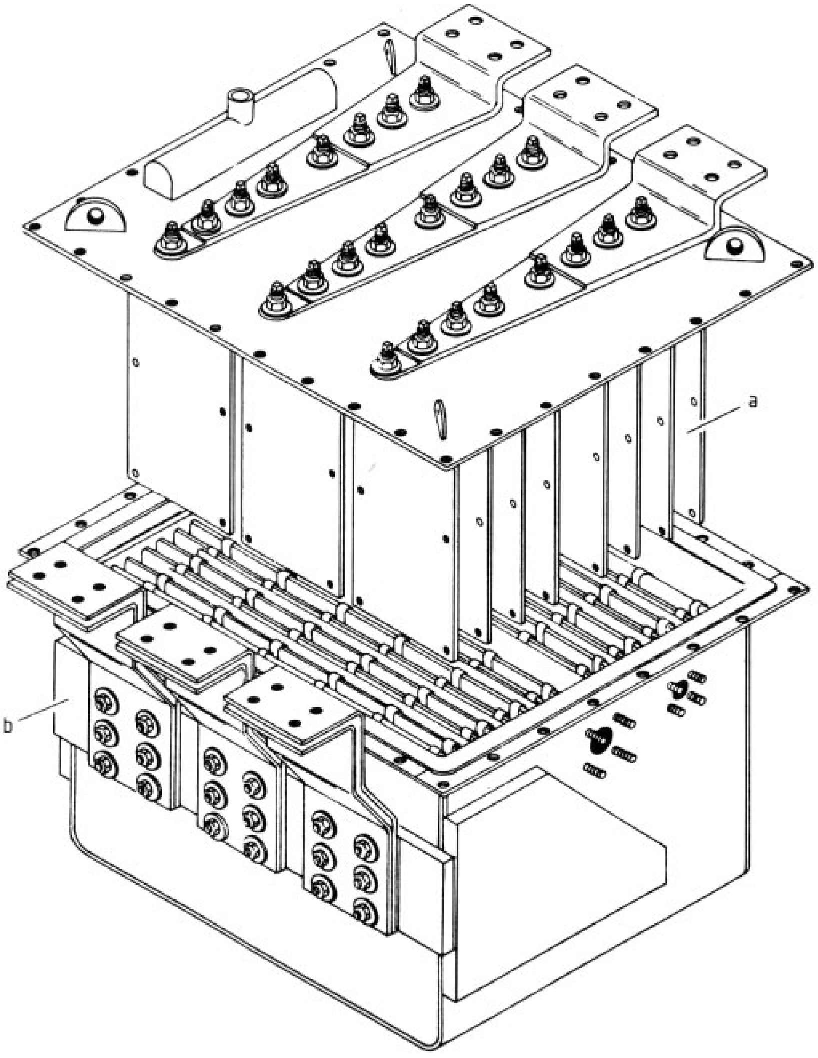

Figure 17. Pennwalt electrochemical reactor
a) Anodes; b) Cathodes

trodes (Krebskosmo) seldom exceed 30 kA (in charge of the voltage), thus lowering the rectifier cost. *Multipolar cells* (Chemetics and Huron) combine some of the advantages of cells with unipolar and bipolar electrodes and require a minimum of bus bars, resulting not only in savings in investment cost, but also in cell voltage. However, the entire electrolyzer system must be shut down for repair of a single unit.

7.3.2. Electrodes

Anodes. N. B. Beer made a decisive breakthrough in anode technology in the mid-1960s by introducing anode coatings based on ruthenium dioxide, RuO_2 [15], [198–201]. In fact, the anode surface is composed of a mixture of RuO_2 with other metal oxides, primarily titanium dioxide. These anodes maintain a low overvoltage for chlorine formation at high current densities for long periods without being consumed and changing their mechanical dimensions. Independent of the detailed nature of the mate-

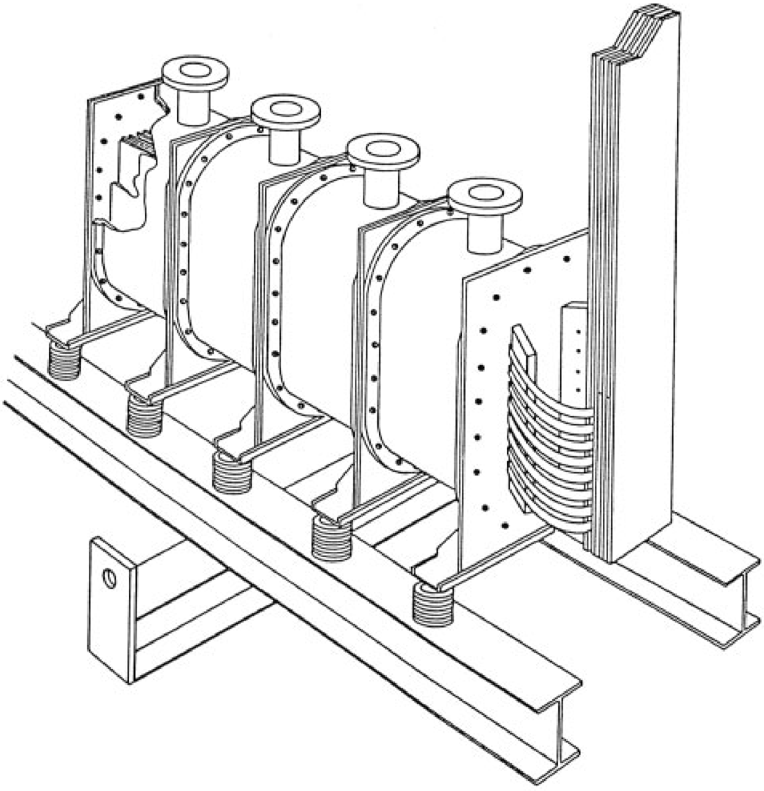

Figure 18. Directly connected electrochemical reactors (multipolar arrangement, Chemetics)

rial, they are called *dimensionally stable anodes* (DSA) (→ Chlorine) [202–204]. In the chlorate field, dimensionally stable anodes have been selected for 80 % of the total capacity installed since 1978.

Sintered titanium anodes (STA) have been developed by Sigri. In these electrodes, an intermediate layer of sintered titanium suboxide is applied between the titanium substrate and the coating, which gives improved mechanical stability, excellent adhesion to sintered titanium structures, and increased active surface area [205], [206]. Imperial Chemical Industries (ICI) has used these anodes in large-scale production since 1971. Other novel anodes have been developed by Imperial Metal Industries (IMI) and Marston Excelsior (Marex Electrode).

Titanium anodes normally consist of 1.5 – 4-mm sheets or of expanded mesh, activated by platinum group metal oxides. In troublefree operation, the durability of the coating based on ruthenium dioxide [207] is between 6 and 10 years. The literature on coated titanium anodes for chlorate electrosynthesis is reviewed in [193].

Cathodes. Mild steel has been the industrial standard for many years. It has a low hydrogen overvoltage and is cheap and stable under the operating conditions. However, steel corrodes when the cells are shut down, and it absorbs hydrogen, which tends to make the metal brittle and to form fissures in the welding areas and blisters [208]. The cathodes are usually 3 – 8 mm thick. The sheets are often perforated with holes of 3 – 6 mm diameter or they are slotted, which facilitates the release of hydrogen bubbles from the interelectrode gap. Mild steel cathodes tend to collect carbonate deposits, which increase the potential of the cathodes. This requires periodic acid washing unless the process water is deionized to contain less than 0.05 mg/kg of impurities.

The application of steel cathodes in bipolar cells is complicated because dissimilar metals must be joined. However, no connection problems arise by explosion bonding of titanium and steel [209].

Attempts to coat the steel cathodes or to replace them by other metals have not brought satisfactory results. Titanium has not been generally accepted because of its tendency to form titanium hydride, TiH_2, which gradually makes the cathode break off and limits the lifetime to 2 years. Attempts to lower the overvoltage by coating the cathodes with nickel, molybdenum, or their oxides [210] have not yet been successful because these materials catalyze the decomposition of hypochlorite during shutdown. Cathodes made from titanium alloys, e.g., Ti – 0.2 % Pd , remain stable for 2 years at a temperature of 95 °C, whereas the durability is much longer at 75 °C.

7.3.3. Operational Parameters

Temperature. The operation of electrochemical reactors benefits from temperature increase in two ways: (1) the cell potential decreases by lowering the resistivity of the electrolyte, and (2) autoxidation of hypochlorite to chlorate is more strongly favored than anodic oxidation. Consequently, the current efficiency increases with temperature. On the other hand, the temperature should not be near the boiling temperature of the electrolyte because then the rate of chlorine and water desorption increases. The introduction of dimensionally stable metal anodes has permitted raising the operating temperature from 40 – 45 °C (previously with graphite anodes) to 80 – 90 °C.

Pressure. Increasing the electrolyte pressure lowers not only the rate of chlorine desorption, but also the volume of the gas bubbles released from the electrolyte; thus, it acts favorably on the interelectrode resistivity. However, serious engineering problems arise when the pressure is increased. Industrial electrochemical reactors are usually operated at a gage pressure of less than 0.1 MPa (1 bar).

Interelectrode Distance. The electric interelectrode resistance strongly depends on the quantity of gas bubbles dispersed in the electrolyte [211]. When the electrolyte flow rate is increased and the electrode distance decreased, the resistance decreases. However, a very small electrode distance leads to a large frictional pressure drop in the reactor. Therefore, the minimum spacing of industrial reactors is ca. 3 mm, which roughly agrees with the results of optimizations [212]; distances of 3 – 5 mm are generally used between metal electrodes.

pH Value. According to Equation (7) (see Autoxidation, page 24), autoxidation of hypochlorite requires the simultaneous presence of hypochlorous acid and hypochlorite. The concentration of both species is very dependent on pH. A carefully controlled pH value, therefore, is a prerequisite of an industrially acceptable current efficiency. The optimum pH depends on the temperature and is maintained in the range of 6.1 – 6.4 in modern industrial electrochemical reactors operated at 80 – 90 °C.

Chloride Concentration. The brine feed to the cells is always close to being saturated to obtain a large final chlorate concentration of the product solution. The chloride concentration should not fall below 80 – 100 g/L because water decomposition is favored at low chloride concentration [213]. If necessary, the brine is resaturated with salt, but solubility limits must be observed (Figs. 11 and 12).

Current Density. High current density increases the acidity near the anode, thus depressing anodic hypochlorite oxidation. In addition, cathodic hypochlorite reduction is hampered. However, current density of industrial cells is limited by the concurrent increase in cell potential. Current densities of industrial cells are optimized on the basis of these considerations and thus permit operation at higher current efficiencies.

Current Efficiency. If x is the fraction of the hypochlorous acid (or chlorine) involved in the anodic oxidation and $(1 - x)$ is the fraction that produces chlorate along the autoxidation reaction, the current efficiency ε is (cf. Fig. 13)

$$\varepsilon = \frac{1}{1 + 0.5x} \qquad (9)$$

Exclusive anodic chlorate formation would result in a current efficiency of $\varepsilon = 66.7$ %, provided the contribution of loss reactions is negligible. The short survey of the operational parameters given in the previous sections highlights the complex system that governs current efficiency in chlorate electrosynthesis. The problem has been dealt with in detail in [39] and is the object of methodical investigations [215], [216]. Mathematical models have been established to provide means to theoretically predict current efficiency. A model assuming ideal stirred-tank-reactor conditions for both the electrochemical and the chemical reactor [214] was compared with industrial results [180]. A more recent model combines a plug flow electrolyzer with either a stirred tank or a plug flow chemical reactor [217]. The results show satisfactory agreement with data from two industrial systems [218].

The current efficiency of operating industrial cells with external recirculation of the electrolyte (Fig. 14) can be assessed by measuring the difference Δc of total hypochlorite concentration (mol/L) at the cell outlet and inlet. Because the difference of total hypochlorite concentration represents the amount of hypochlorite converted to chlorate by autoxidation outside the cell, the current efficiency is calculated to be

$$\varepsilon = \frac{2}{3}\left[1 + \frac{\dot{V}_L \cdot \Delta c \cdot F}{I}\right] \tag{10}$$

where

F = Faraday constant (96 487 A s/mol)
$\dot{V}_L$ = volume flow rate, m^3/s
I = total current, A

Equation (10) does not take account of the autoxidation in the interelectrode gap, and it neglects all loss reactions; both factors tend to balance.

In all electrosynthesis systems, including those without external electrolyte recirculation, the current efficiency may be estimated by analyzing the gas mixture leaving the electrochemical reactor. The amount of anodic chlorate formation (together with the catalytic decomposition) can be assessed from the volume fraction of oxygen (φ_{O_2}). The loss caused by chlorine desorption is represented by the volume fraction of chlorine (φ_{Cl_2}). Moreover, the ratio of the true hydrogen flow rate N_{H_2} to the flow rate N'_{H_2} as calculated from Faraday's law indicates the loss through cathodic reduction of hypochlorite and chlorate [219]:

$$\varepsilon = \frac{1 - 3\varphi_{O_2} - 2\varphi_{Cl_2}}{1 - \varphi_{O_2} - \varphi_{Cl_2}} \cdot \frac{N_{H_2}}{N'_{H_2}} \tag{11}$$

In industrial operation, the current efficiency is predominantly lowered by anodic chlorate formation; when neglecting any other loss reaction, one obtains a very simple approximation equation:

$$\varepsilon \approx 1 - 2\varphi_{O_2} \tag{12}$$

The error of Equation (12) as compared to Equation (11) is within the accuracy of gas analysis in the current efficiency range of modern cells. Automatic measurement of the oxygen concentration in the cell gas, therefore, serves as a simple and reliable means to control cell operation.

7.3.4. Brine Purification

Solar salt from seawater, rock salt, or very pure "vacuum salt" are used as raw material. The brine must not contain large amounts of magnesium and calcium, which could form deposits on the cathodes. Sodium carbonate and sodium hydroxide are added to the brine to raise its pH to at least 10. The sulfate concentration must be lower than 10 – 20 g/L. The brine must be free of heavy metals that favor the decomposition of hypochlorite (see Section 7.2.2). Maximum impurity concentrations are listed below:

SO_4^{2-}	10 g/L
SiO_2	10 mg/kg
Al, $P_2O_7^{4-}$, Ca	5 mg/kg
Fe, Mn, Sn	1 – 5 mg/kg
Cu, Mg, Pb, Ti	1 mg/kg
Cr, Mo	0.5 mg/kg
Ir, Co	0.2 mg/kg
Ni	0.05 mg/kg

7.4. Crystallization

For the crystallization of chlorate, a solution of 560 – 630 g/L of sodium chlorate and 90 – 120 g/L of sodium chloride is produced at 70 – 90 °C. The temperature at the cell outlets is first raised to 85 – 95 °C to convert the remaining 1.5 g/L of hypochlorite into chlorate. Urea, ammonia, hydrogen peroxide, or sodium formate is added to complete the hypochlorite decomposition. The solution is then rendered slightly alkaline with NaOH; this reduces corrosion in the crystallizer. The $NaClO_3$ solution is subsequently fed to a vacuum crystallizer, based on flash cooling with subsequent crystallization.

Crystalline chlorate is separated from sodium chloride solution by cooling or evaporation [220]. Crystallization conditions depend on the concentration of NaCl and $NaClO_3$, on solution temperature, and on mixing intensity. The cooling rate has little influence on the crystal size; ca. 90 % of the crystals have 120 – 260 µm diameter. The solution temperature, initially raised to 90 – 95 °C, drops to 48 °C in the separator and to 35 °C in the vacuum crystallizer at 2.9 kPa. The concentrated slurry contains 15 – 20 wt % of crystals; it is passed through a hydrocyclone and then a pusher centrifuge. Energy consumption, efficiency and economic optimization of the overall process were studied [221]; an energy flow diagram is given in [222].

Potassium chlorate is generally made from potassium chloride and sodium chlorate:

$$NaClO_3 + KCl \longrightarrow KClO_3 + NaCl$$

Solid KCl is added to the sodium chlorate cell liquor in stoichiometric amounts. The mixture is then transferred to a crystallizer and the potassium chlorate slurry is removed as described in the preceding paragraph. The mother liquor is recycled to the cells, where the salt is converted to chlorate and the process is repeated. Quality requirements for solid KCl are high, because no purification is possible after it is added to the solution.

7.5. Construction Materials

Chlorate solutions are kept slightly alkaline except during electrolysis, where a specific acidity must be maintained.

Mild steel and cast iron are suitable for equipment if the liquor is alkaline and free of active chlorine. In acidic media, poly(vinyl chloride) (PVC) tubes and tanks made from fiber-reinforced PVC are used up to 50 °C. Poly(vinyl chloride) stabilized with Ba or Cd (PVC-C) is much better suited, but the consumption rate is nevertheless 1 mm per year at 60 °C [223].

Titanium, polytetrafluoroethylene (PTFE), glass, and poly(vinylidene fluoride) (PVDF) have excellent resistance at all temperatures and under all conditions. Evaporators are made from yellow brass, rubber-lined steel, monel, stainless steel (AISI: 316; DIN: 1.4401) with cathodic protection, or titanium. Stainless steel should be used for the dryer because it is imperative to avoid Fe_2O_3 contamination of the chlorate, which would act as an explosion catalyst. Pump seals must be of the noncombustible type. Titanium is increasingly used in all equipment as the material for anodes, heat exchangers, reaction vessels, pumps, and tubes.

7.6. Environmental Protection

The gas released from the electrochemical reactor always contains some chlorine in addition to hydrogen and oxygen. The mixture passes a cooler, where the major amount of chlorine condenses. Residual amounts of chlorine (0.3 %) are lowered to $(1-3)\times10^{-4}$ % by absorption in alkaline solution (15 % NaOH) and to $(1-10)\times10^{-7}$ % by subsequent adsorption on activated carbon. The resulting gas mixture of hydrogen and some oxygen can either be vented to the atmosphere or used as a fuel. The oxygen concentration (1.5 – 2.5 %) depends on the reaction conditions of the cell (see Section 7.2). In trouble-free operation, environmental pollution problems do not arise. Pure hydrogen can be produced by passing the residual gas mixture over a noble metal catalyzing combustion and subsequently purified by selective permeation in palladium at elevated temperature (350 °C).

Wastewater from cleaning tanks and building floors requires appropriate treatment to avoid damage of the water flora by chlorates acting as herbicides. A process to remove almost 100 % of dichromate from chlorate solutions by use of a fixed bed of standard ion-exchange resin has been operated for several years in a pilot plant and is about to be commercially exploited [224].

Table 11. Quality specifications for chlorates of sodium and potassium

	Sodium chlorate			
	"White crystals", wt %	Crystalline, wt %	Powder, wt %	Solution at 20 °C, g/L
$NaClO_3$	96.5 – 97.5	99.75 – 99.95	99.4 – 99.75	500
NaCl, max.	0.05	0.03	0.06	0.16
Na_2SO_4, max.	0.04	traces	0.04	0.11
CaO, max.	nil	nil	nil	0.11
$NaBrO_3$, max.	0.02	traces	0.02	0.004
Fe, max.	traces	nil	traces	traces
$Na_2Cr_2O_7$, max.	nil	nil	nil	0.004
Insolubles, max.	0.02	0.02	0.02	0.02
Humidity, max.	2.00	0.02	0.02	–
Bulk density, g/cm^3				
not vibrated	1.15	1.31	1.49	1.317
vibrated	1.55	1.58	1.65	

	Potassium chlorate	
	Typical specification, wt %	Aragonesas S.A., for matches, wt %
$KClO_3$, min.	99.7	99.8
KCl, max.	0.032	0.05
NaCl, max.	0.2	
$KClO_4$, max.	0.1	
K_2CrO_4	nil	
$KBrO_3$, max.	0.07	0.04
Fe, max.	0.01	nil
Insolubles, max.	0.01	0.02
Humidity, max.	0.05	0.02

7.7. Quality Specifications

The purity requirements of chlorate depend on the intended purpose and are usually negotiated between producer and user. Various products differ considerably in quality. Standard values for white and yellowish sodium chlorate and potassium chlorate are shown in Table 11. The given potassium chlorate quality is satifactory for many purposes, but may be recrystallized for special requirements (Table 11).

7.8. Storage, Transportation, and Safety

Chlorates should be stored in a cool, dry, fireproof building. Preferably, a separate storage building should be provided with cement floors and metal catwalks.

Wooden construction must be avoided because of the combustibility of chlorate-impregnated wood. Crystalline chlorate may be stored in concrete, lined steel bins, or glazed tile silos. Dried air should be supplied to prevent caking from atmospheric moisture. Drums and packages containing chlorates should not be stored where such noncompatible chemicals as acids, solvents, oils, organic substances, sulfur, or powdered metals could be spilled [225]. Ventilation must be provided for operations where fine chlorate dust arises. The ventilation system should discharge to a water scrubber and be designed for easy cleaning. Pumps handling chlorate solutions should be of the "packless" type. Electrical supply and distribution points are to be inspected periodically for dust. Motors and switches must not be housed in the plant or store and must conform to the National Electrical Code (United States). Metal or plastic pallets are recommended for handling containers.

Safety showers and water supply should be available to workers. The containers (barrels) must be kept closed and not be stored on top of each other. Chlorates are handled in polyethylene bags, in metal drums, or metal-lined fiberboard or plywood drums (25 – 170 kg). Bulk chlorates can be delivered by tank trucks or railroad tank cars either in the dry or wet state. They are usually unloaded as a slurry by recirculation of hot water (60 °C) between the car and the dissolver tank. The recommended material for storage tank construction is stainless steel (AISI

316). Tanks lined with rubber or plastics are not recommended because of possible fire or explosion hazards. For more details, see references [226–237].

7.9. Uses

Sodium Chlorate. The rapid growth of sodium chlorate production is mainly due to the widespread use of the chlorate-derived chlorine dioxide bleach by the pulp and paper industry. The once predominant use of sodium chlorate as a nonselective herbicide has strongly declined. Second in importance is its use as an intermediate in the production of other chlorates, mainly potassium chlorate, and of sodium perchlorate for conversion to ammonium perchlorate, which is used as an oxidizer in solid propellants. Sodium chlorate is further used as oxidizing agent in uranium refining and other metallurgical operations, as an additive to agricultural products and dyes, in textile and fur dyeing, metal etching, and in chemical laboratories and throughout the chemical industry as an oxidizing agent.

Potassium Chlorate. Potassium chlorate is used mainly in the manufacture of matches and in the pyrotechnics, explosives, cosmetics, and pharmaceutical industry; it is superior to sodium chlorate because of its smaller hygroscopicity.

Barium Chlorate. Barium chlorate is prepared by reaction of barium chloride with sodium chlorate solution. It is precipitated by cooling, purified by recrystallization, and used in pyrotechnics.

Calcium Chlorate. Solutions of calcium chlorate are used as herbicide.

7.10. Economic Aspects

Because of the steadily increasing demand for chlorine dioxide in the pulp industry, production of sodium chlorate has doubled in the past 10 years. Figure 19 shows annual production data. Canada is the world's leading producer with 0.5 Mt $NaClO_3$ in 1984, closely followed by the United States with 0.41 Mt $NaClO_3$.

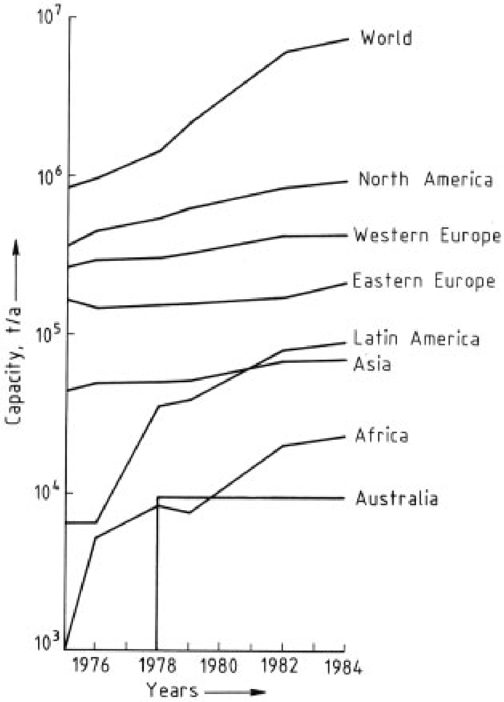

Figure 19. Chlorate production capacities

Since electric power cost amounts to ca. one-third of the total production cost of sodium chlorate, cheap energy is the key economic factor.

8. Perchloric Acid and Perchlorates

Perchloric acid [*7601-90-3*] and its salts, particularly ammonium perchlorate [*7790-98-9*], NH_4ClO_4, sodium perchlorate [*7601-89-0*], $NaClO_4$, and potassium perchlorate [*7778-74-7*], $KClO_4$, find many applications because of their strong oxidizing power; their chemical stability is sufficient to permit high-energy oxidation under controlled conditions. Perchloric acid is used on a limited scale mainly as a reagent for analytical purposes; its production has increased because of its use as a starting material for pure ammonium perchlorate, a basic ingredient of explosives and solid propellants for rockets and missiles. Minor amounts of potassium perchlorate occur in Chile, in natural deposits of sodium nitrate.

Table 12. Density, ϱ, and vapor pressure, p, of anhydrous perchloric acid

	t, °C			
	0	10	20	25
ϱ, g/cm^3	1.808	1.789	1.770	1.761
p, kPa	1.546	2.506	3.913	4.826

8.1. Physical and Chemical Properties

8.1.1. Perchloric Acid

Anhydrous perchloric acid, M_r 100.5, can be obtained by distilling at reduced pressure a mixture containing 1 part of 20 % $HClO_4$ and 4 parts of 20 % oleum. It is a colorless, strongly hygroscopic liquid, melting at − 102 °C. At atmospheric pressure, it decomposes at 75 °C. Its density and vapor pressure vs. temperature are given in Table 12.

Perchloric acid is miscible with water in all ratios and forms a series of hydrates as shown in Table 13. Boiling points and densities vs. concentration are given in Table 14. For other physical properties, see [239], [240].

Anhydrous perchloric acid is a very strong oxidizing agent. Some metals like nickel, copper, silver, and gold are only slightly oxidized at ambient temperature. Platinum is not attacked, but it decomposes the acid by catalytic action. In contact with combustible materials, the perchloric acid reacts violently, forming explosive mixtures with paper, charcoal, ethanol, acetic anhydride, and gelatin.

Perchloric acid is more stable in aqueous solution than in anhydrous form. The azeotropic mixture (72.5 wt % $HClO_4$) decomposes in the absence of oxidizable matter only above the boiling point. Concentrated perchloric acid is a strong oxidizing agent, especially at high temperature; it forms explosive mixtures with organic compounds, which can detonate on heating, percussion, or exposure to sparks or a flame.

Perchloric acid is a strong acid and reacts in aqueous solution with metals, metal oxides, and hydroxides, as well as with salts of volatile acids, forming the corresponding perchlorates. Some oxides, e.g., CuO, catalyze the decomposition of perchloric acid. This occurs through a chain of reactions that give chlorine, oxygen, and water as ultimate products.

8.1.2. Perchlorates

At least one element in each group of the periodic table, except the noble gases, forms perchlorates; this includes not only metals, but also nonmetallic elements, such as nitrogen in hydrazine perchlorate [*13762-80-6*] or fluorine in fluorine perchlorate [*37366-48-6*]. Organic ammonium, diazonium, and sulfonium perchlorates form another large class. Perchlorates are generally colorless and well (or fairly) soluble in water and such organic solvents as alcohols, ketones, or esters. Table 15 lists the solubilities of some metal perchlorates. Other physical properties can be found in [227], [241], and [242].

When heated, alkali metal and alkaline-earth metal perchlorates decompose before reaching the melting point, with the exception of $LiClO_4$ (*mp* 247 °C). The hydrates of the perchlorates generally have definite melting points, but they decompose on further heating, after liberation of water.

The outstanding chemical property of the perchlorates is their strong oxidizing power. This is exploited either in mixtures of perchlorates with combustible materials or by using organic perchlorates as explosives or propellants. On the other hand, all perchlorates, also in the pure state, are liable to undergo explosive decomposition if they are heated above a critical temperature, with liberation of chlorides and oxygen; ammonium perchlorate has been investigated extensively in this respect in view of its importance for jet propulsion [243–248].

8.2. Production

8.2.1. Perchloric Acid

Perchloric acid is made from sodium perchlorate and hydrogen chloride [239], [249]. A saturated $NaClO_4$ solution reacts with an excess of HCl,

Table 13. Perchloric acid and its hydrates, $HClO_4 \cdot n\,H_2O$

	n					
	0	1	2	2.5	3	3.5
CAS registry no.	[*7601-90-3*]	[*60477-26-1*]	[*13445-00-6*]	[*34099-94-0*]	[*35468-32-7*]	[*41371-23-1*]
M_r	100.46	118.47	136.49	145.5	154.51	163.5
c_{HClO_4}, wt %	100	84.8	73.6	69.1	65.0	61.5
mp, °C	− 112	+ 50	− 17.5	− 29.8	− 37 (α) − 43.2 (β)	− 41.4

Table 14. Boiling points and densities of aqueous perchloric acid solutions

	c_{HClO_4}, wt %							
	24.34	38.9	50.67	56.65	61.2	65.20	70.06	72.5
bp, °C	105.8	114.8	132.4	148.0	162.3	189.2	198.7	203
ϱ^{25}, g/cm^3	1.154	1.280	1.4058	1.4799	1.5413	1.5993	1.6748	1.7150

Table 15. Solubility of some perchlorates in water at 25°C (grams in 100 g of water)

NH_4ClO_4	24.922	$Sr(ClO_4)_2$	309.67
$LiClO_4$	59.71	$Ba(ClO_4)_2$	198.33
$NaClO_4$	209.6	$Cu(ClO_4)_2 \cdot 2\,H_2O$	259
$KClO_4$	2.062	$AgClO_4$	540
$RbClO_4$	1.338	$Cd(ClO_4)_2 \cdot 6\,H_2O$	478
$CsClO_4$	2.000	$Mn(ClO_4)_2 \cdot 6\,H_2O$	268
$Mg(ClO_4)_2$	99.601	$Co(ClO_4)_2 \cdot 6\,H_2O$	292
$Ca(ClO_4)_2$	188.60	$Ni(ClO_4)_2 \cdot 6\,H_2O$	267

and NaCl precipitates. The dilute per-chloric acid produced after filtration (32 % $HClO_4$) is concentrated in three stages up to 70 – 71 % $HClO_4$; the last stage is vacuum distillation.

A continuous, electrochemical process for the production of perchloric acid has been developed in the Federal Republic of Germany. It involves the anodic oxidation of gaseous chlorine dissolved in chilled 40 % $HClO_4$ [250], [251]:

$$Cl_2 + 8\,H_2O - 14\,e \longrightarrow 2\,HClO_4 + 14\,H^+$$

The electrolyzer is of the filter press type; it is composed of poly(vinyl chloride) (PVC) frames and the electrodes are separated by a diaphragm of PVC fabric. The anodes are made from platinum foil, spot-welded to tantalum rods. The cathodes are horizontally slitted silver plates. A 40 % $HClO_4$ solution is circulated from the electrolyzer to an external cooler, which keeps the temperature within − 5 to + 3 °C. The operating conditions are as follows: current 5000 A; current density 2.5 – 5 kA/m^2; voltage 4.4 V; current efficiency 0.60; and chlorine concentration at inlet 3 g/L. The outflowing solution is distilled to remove residual chlorine and byproduct hydrogen chloride and to obtain high-purity perchloric acid. Platinum consumption is 0.025 g/t of 70 % $HClO_4$; it dissolves at the anode, but partly redeposits at the cathode and can thus be recovered. Per ton of 70 % $HClO_4$, 9600 kWh of electricity (d.c.) is used. The high purity of the product, directly obtained by a continuous process not requiring separation stages, is an advantageous tradeoff versus the relatively low current efficiency. The process further allows unusual perchlorates to be prepared by direct conversion with perchloric acid, thus avoiding the route via sodium chlorate.

8.2.2. Perchlorates

Various methods for the production of perchlorates are described in [239]. In practice, commercial production is based on the following steps:

1) Electrochemical production of sodium chlorate from sodium chloride (Chap. 7)
2) Electrochemical oxidation of sodium chlorate in aqueous solution to sodium perchlorate
3) Conversion of sodium perchlorate into another perchlorate, e.g.:

$$NaClO_4 + KCl \longrightarrow KClO_4 + NaCl$$

$$NaClO_4 + NH_4Cl \longrightarrow NH_4ClO_4 + NaCl$$

In the last step, the corresponding sulfate, which causes fewer corrosion problems, can be used instead of the chloride.

This indirect method for the production of perchlorates other than $NaClO_4$ is advantageous over their direct electrosynthesis from the corresponding chlorates, because of their relatively small solubility in water (Table 15). Attempts have been made to make sodium perchlorate directly from sodium chloride, by a single electrolysis [252–254]. The advantage, however, seems debatable, because the resulting current efficiency is only slightly better than 50 % under optimum conditions.

Anodic Oxidation. The anodic oxidation of chlorate occurs according to the following overall reaction:

$$ClO_3^- + H_2O - 2\,e \longrightarrow ClO_4^- + 2\,H^+$$

The standard potential of the anodic process (1.19 V) is very close to that of water oxidation (1.228 V), which gives rise to oxygen evolution. Both reactions compete strongly, independent of the acidity of the solution. To obtain a satisfactory current efficiency, the anode potential should be as large as possible, because a high polarization enhances the chlorate oxidation rate more than the oxygen evolution [255]. This is achieved by selecting a suitable anode material and a high current density. Several reaction mechanisms have been proposed for chlorate oxidation to perchlorate [39].

Cell design and operating conditions must be selected to optimize electricity consumption, which depends on cell voltage and current efficiency. Both are affected by a number of variables in conflicting ways. In particular, the current efficiency is improved by increasing the current density, but this also increases the cell voltage. A temperature rise operates in reverse in that not only the voltage, but also the current efficiency is diminished. A high sodium chlorate concentration in the effluent liquor improves current efficiency as well as voltage, but requires more expensive procedures and higher chlorate consumption to obtain a sufficiently pure perchlorate solution.

Industrial Cells. Contrary to electrochemical chlorate production, the residence time of the electrolyte in the perchlorate cell is not a critical parameter. The cell is undivided and hydrogen gas evolution provides sufficient agitation to decrease the sodium chlorate concentration gradient between the cell inlet and outlet. Because of the relatively high heat dissipation, the cell is normally provided with internal cooling.

Smooth platinum anodes yield the highest oxygen overpotential and, hence, the highest current efficiency (95 – 97 %). Platinum is either used in foils or cladded onto rods of some other metal, such as tantalum or copper. Lead dioxide anodes are also used [256]; they consist of a lead dioxide deposit plated on some conductive substrate, such as graphite rods or plates [257–260]. They are less expensive than platinum, which more than offsets their lower current efficiency (85 %). When a small amount of sodium fluoride (2 g/L) is added to the electrolyte, the current efficiency increases [257]. More recently, platinate-coated titanium has been claimed to substitute profitably for massive smooth platinum in perchlorate manufacture [261].

Cathodes are made from carbon steel, chromium – nickel steel, nickel, or bronze. As in chlorate electrosynthesis, sodium dichromate is added to the solution to minimize the current efficiency loss caused by cathodic reduction of perchlorate. At the same time, dichromate inhibits corrosion of the steel parts that are directly exposed to the electrolyte, in addition to their cathodic protection. However, dichromate cannot be used with lead dioxide anodes, because it catalyzes oxygen evolution [255]. In that case, the most suitable cathode material is nickel or chromium – nickel steel.

Figure 20 shows some typical cell models [262]. In the *Bitterfeld* cell, each anode, made from platinum foil, works between a pair of cathodes made from perforated steel plates. The cell is kept at 35 °C by cooling water running through a steel pipe bundle.

In the *Cardox* cell, the anodes consist of platinum cladded onto copper rods 1.3 cm in diameter. Each anode is surrounded by a cathodic tube 7.6 cm in diameter, which is made from steel and perforated at both ends. This allows hydrogen gas to escape into the interelectrode space and ensures convective circulation.

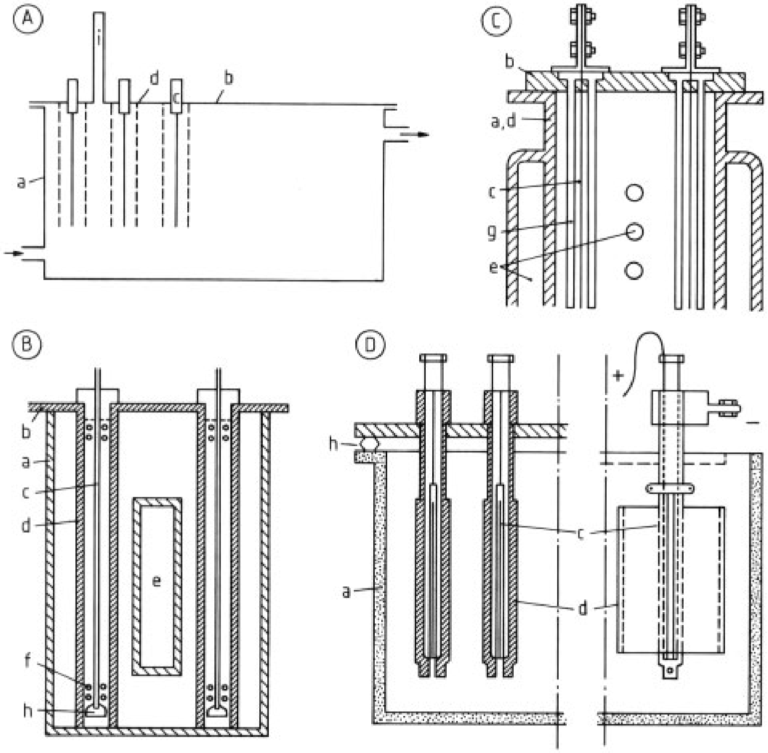

Figure 20. Some typical models of perchlorate cells
A) I. G. Farbenindustrie, Bitterfeld; B) Cardox Corp.; C) American Potash and Chemical Corp.; D) Pechiney, Chedde
a) Cell tank; b) Cover; c) Anode; d) Cathode; e) Cooling system; f) Circulation holes; g) Glass rods; h) Porcelain insulators; i) Gas outlet

Table 16. Typical operational data for perchlorate cells

Current	500 – 12 000 A
Current density	1500 – 5000 A/m^2
Cell potential	5 – 6.5 V
Current efficiency	
Platinum anodes	90 – 97 %
Lead dioxide anodes	85 %
Electric energy (d.c.)	
per ton of $NaClO_4$	2500 – 3000 kWh
Electrolyte temperature	35 – 50 °C
pH	6 – 10
Concentrations, g/L	
$Na_2Cr_2O_7$	0 – 5
Cell inlet	
$NaClO_3$	400 – 700
$NaClO_4$	0 – 100
Cell outlet	
$NaClO_3$	3 – 50
$NaClO_4$	800 – 1000
Platinum consumption per ton of $NaClO_4$	2 – 7 g

In the model of *American Potash and Chemicals* (formerly Western Electrochemical Co.), a set of anodic platinum foils is arranged around the inner wall of the cylindrical cell body performing as the cathode; the interelectrode gap is stabilized by a number of glass rod spacers. The temperature is kept at 40 – 45 °C by internal cooling and by a water jacket surrounding the cylindrical cell tank.

In the *Pechiney* model, the anodes are platinum foils and the cathodes are plates made from bronze.

Operation. Table 16 shows typical operational data [39], [239], [262]. Sodium perchlorate can be separated from the cell effluent either as hydrate or as anhydrous salt. Depending on concentration, separation is carried out by cooling alone or by evaporation, followed by cooling. The monohydrate precipitates from the solution below ca. 52 °C; above this temperature, the perchlorate crystallizes as the anhydrous salt. In either case, the mother liquor still contains a large amount of perchlorate. After enrichment with sodium chlorate, this solution is recycled to the electrolysis process.

When the sodium perchlorate is used for conversion to other perchlorates, it need not be separated from the cell effluent. Sodium chlorate is destroyed by chemical treatment and dichromate precipitated as insoluble chromic hydroxide. The purified and concentrated solution is then ready for conversion to other salts [263].

8.3. Environmental Protection

On account of the limited volume produced and their slight toxicity, perchlorates do not constitute an environmental pollution problem. Aquatic life (fish, leeches, and tadpoles) survives indefinitely even when the perchlorate concentration in water exceeds 500 mg/L [264]. However, because of the antithyroid effect of perchlorate, some chronic symptoms may appear at low levels.

Some bacteria, such as *Vibrio dechloraticans,* can metabolize perchlorates; this is exploited for perchlorate destruction in the sanitation of contaminated sewage waters.

8.4. Chemical Analysis

Perchlorate is analyzed by its decomposition to chloride. This occurs by melting the perchlorate salt in a platinum dish with sodium carbonate, which accelerates the thermal decomposition. Sodium carbonate can be replaced with ammonium chloride if alkali-metal perchlorates are analyzed that decompose rapidly at 450 – 550 °C. The cooled melt is then dissolved in water or dilute nitric acid, and the total chloride is determined by normal volumetric or gravimetric methods. The chlorate or chloride content initially present in the sample must be subtracted to obtain the amount of perchlorate in the sample.

Quantitative precipitation of perchlorate from an aqueous solution by one of the following reagents is also possible: methylene blue [265]; potassium, rubidium, or cesium salts in cold ethanol – water solution [266]; or tetraphenylphosphonium chloride [267], [268]. The most sensitive quantitative determination of perchlorate ($10^{-6} - 10^{-7}$) is possible by means of ion-specific electrodes [269], [270].

8.5. Storage, Transportation, and Safety

The same storage and shipping regulations that apply to chlorates (Section 7.8) are also applicable to perchlorates.

According to the U.S. Department of Transportation (DOT) regulations for hazardous materials, perchloric acid and perchlorates are shipped in glass containers or metal drums as specified in [271]. They are classified as oxidizing substances and require oxidizer shipping labels. Transportation is forbidden on passenger-carrying aircraft or railcars. Shipment of perchloric acid in concentrations greater than 72 % is forbidden. Ammonium perchlorate may be shipped in steel drums with plastic liners; large quantities are transported in portable aluminum containers holding up to 2.27 t. Lower-side or hopper-type product discharge openings are not permitted.

Sodium or magnesium perchlorate may be shipped wet in tank cars with a minimum of 10 % water, which must be equally distributed. All perchlorates not specifically covered by DOT regulations should carry special precautionary labels indicating the specific fire or explosion hazards expected from the individual perchlorate.

Despite their limited toxicity, perchloric acid and perchlorates must be considered, like chlorates, as hazardous chemicals during fabrication, transportation, and handling. Because of its tendency toward spontaneous explosion, anhydrous perchloric acid should be prepared only in very small batches and in the absolute absence of impurities. It can be stored for a limited time at low temperature and must be protected from any kind of contamination. Distillation must be carried out under vacuum (2.4 kPa at 16 °C) and with protective shielding. One must never try to obtain the acid in anhydrous form by treatment with a drying agent. It should be stored in glass containers with glass stoppers, possibly embedded in kieselguhr or glass wool for protection.

Ammonium perchlorate and alkali-metal and alkaline-earth metal perchlorates are relatively insensitive to rubbing, heating, and shock. They also require special precautions in manufacturing and further handling [225], [226]. Clean work clothing must be worn each day and laundered afterward; it must not be taken home.

Clothing wet with perchlorate solution should be changed before drying. No smoking can be permitted in perchlorate working areas or while wearing work clothes. Deluge type safety showers or jump tanks should be provided. Only rubber shoes and rubber or rubberized gloves are permitted.

Perchlorates should not be stored close to flammable materials, reducing agents, or other hazardous substances. Buildings in working areas should be fireproof. Dust control or dust prevention in perchlorate solutions is particularly important. Since mixtures of such solutions with oil or grease are violently explosive, motor and pump bearings must be provided with special lubricating and washing devices [225]. Fires must be extinguished with water, but carbon dioxide may provide sufficient cooling to extinguish small fires. Dry powder is ineffective because it cannot smother a self-sustaining fire. For burns, cold water treatment should be used as quickly as possible. For other first aid measures, consult [226].

A second class of more hazardous compounds is formed by inorganic perchlorates containing nitrogen or heavy metals, organic perchlorates, or mixtures of inorganic perchlorates with organic substances, finely divided metals, or sulfur. They are all very sensitive to rubbing, shock, percussion, sparks, and heating and must, therefore, be handled with the same precautions as high explosives (→ Explosives).

8.6. Uses

Perchloric Acid. The commercial product is the azeotropic, aqueous solution of 72.5 % $HClO_4$ (*bp* 203 °C). In analytical chemistry, it serves to determine the metallic elements present in oxidizable substances, such as organic compounds [272–277]. Perchloric acid is an acetylation catalyst for cellulose and glucose and is used in the preparation of cellulose fibers.

Perchlorates. The most outstanding property of ammonium perchlorate is its high oxygen concentration (54.5 % O_2) and the fact that it decomposes without leaving a solid residue. Therefore, it is used as an oxidizing component in solid rocket propellants.

Lithium perchlorate is used in lithium–nickel sulfide dry batteries [278], and sodium perchlorate in electrochemical machining [279]; potassium perchlorate is a component of pyrotechnics and an ignition ingredient in flash bulbs [280]. Magnesium perchlorate is known as a very effective drying agent.

Ammonium perchlorate mixed with an epoxy resin forms a temporary adhesive between two metallic surfaces, such as two steel plates. These can be separated whenever desired by heating at ca. 300 °C because of the self-sustained combustion of the adhesive layer [281]. Ammonium perchlorate has been tried as a feed supplement to increase the weight of livestock, with an optimum dose of 2 – 5 mg/kg [282–286]. Perchlorates have also proven to be helpful in oxygen-regenerating systems to be used in enclosed environments, such as submarines and spacecraft, and in breathing equipment [287]. Potassium values from enriched bittern, obtained from the Dead Sea or the Great Salt Lake, can be recovered by precipitating potassium perchlorate with sodium perchlorate [288], [289].

8.7. Economic Aspects

Statistical data about the production and use of perchlorates are not easily accessible because of their strategic importance. The United States' production in 1974 was reported to be ca. 25 000 t, or ca. 12 % of the chlorate production [290]. On account of the increasing developments of artificial satellites and space shuttle programs, perchlorate production will increase, due to their major use in solid propellants.

9. Toxicology and Occupational Health

Hypochlorous acid and hypochlorites are toxic because they liberate chlorine on contact with acid. Sodium hypochlorite solution produced by on-site electrolyzers (available chlorine concentration 0.5 – 10 g/L) is regarded as corrosive and as an irritant when ingested or inhaled. It is also a mild skin irritant, and prolonged exposure may result in a burn or rash [56]. However, concentrated hypochlorous acid burns human skin in seconds.

Chlorine Dioxide. Chlorine dioxide gas is the most toxic and hazardous of all chlorine oxides. Even when small amounts of chlorine dioxide are inhaled, the respiratory system is severely damaged [291]. The symptoms of chlorine dioxide intoxication depend on its concentration and on the exposure time; they include lacrimation, headache, vomiting, severe cough, asthmatic bronchitis, dyspnea, and even death. Such defects as dyspnea or asthmatic bronchitis only heal slowly after the exposure to chlorine dioxide has ceased.

Exposure to 5 ppm of chlorine dioxide in air during several hours severely irritates the mucous membranes [292]; short-term exposure to 20 ppm may cause death. According to animal experiments and observations of employees in chlorine dioxide production plants, the human and animal organisms are extremely sensitive to chlorine dioxide, in particular when the concentrations are higher than 1 ppm [291–294].

Chlorine dioxide levels below 0.1 ppm are relatively harmless [295], [296]. Exposure of rats to 0.1 ppm of chlorine dioxide (5 h/d; 10 weeks) showed no toxic effects whereas repeated inhalation of 10 ppm of chlorine dioxide caused death.

The odor threshold of chlorine dioxide is less than 0.1 ppm [297], [298]. The MAK and the TLV of chlorine dioxide have been established at 0.1 ppm (0.3 mg/m^3).

Chlorine dioxide production plants must be operated at slightly subatmospheric pressure. The plant design must also account for the high explosiveness of chlorine dioxide; therefore, chlorine dioxide is diluted with air to below 15 % before it leaves the generator. No attempt should ever be made to transport chlorine dioxide over long distances in any form.

Chlorates. The major health hazard of the chlorates arises from their extreme danger of flammability on contact with oxidizable substances. Irritation of the skin, mucous membranes, and eyes may occur from prolonged exposure to dusty atmospheres. Contrary to chlorides, the chlorates are strong blood toxins. Chlorates are readily absorbed by the mucous membranes; doses of a few grams of chlorate are lethal for humans. Abdominal pain, nausea and vomiting, diarrhea, pallor, blueness, shortness of breath, and unconsciousness are the immediate symptoms when toxic amounts of chlorates are ingested. In workplaces with dust formation, dust masks must be worn. Cases of chronic toxicity have not been reported. The instructions for industrial safety must carefully be observed [226], [227], [229]. For detailed information on precautionary and first aid procedures, see [228], [233–237].

Perchlorates. Sodium perchlorate appears in the urine of humans within 10 min after ingestion and is largely eliminated within 5 h. During many years of large-scale production of alkali-metal perchlorates, no case of perchlorate intoxication has been reported [239]. Industrial experience also indicates that these salts are not particularly irritating to the skin or mucous membranes, although inhalation should be avoided. A sodium perchlorate dose of 2 – 4 g/kg is lethal to rabbits.

10. References

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