CHLORIC ACID AND CHLORATES

1. Chloric Acid

Chlorates are salts of chloric acid [7790-93-4], $HClO_3$.

1.1. Physical Properties. Aqueous chloric acid is a clear, colorless solution stable when cold up to ca 40 wt% (1). Upon heating, chlorine [7782-50-5], Cl_2, and chlorine dioxide [10049-04-4], ClO_2, may evolve. Concentration of chloric

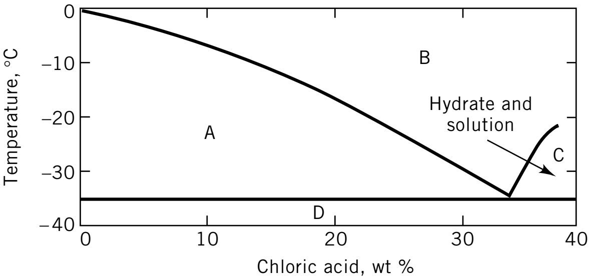

Fig. 1. Solubility of chloric acid in water where A represents ice and chloric acid solution; B, solution; C, chloric acid hydrate and solution; and D, a eutectic of ice and the hydrate (2).

acid by evaporation may be carried to $>40\%$ under reduced pressure. Decomposition at concentrations in excess of 40% is accompanied by evolution of chlorine and oxygen [7782-44-7] and the formation of perchloric acid [7601-90-3], $HOCl_4$, in proportions approximating those shown in equation 1.

$$8\ HClO_3 \longrightarrow 4\ HClO_4 + 2\ H_2O + 3\ O_2 + 2\ Cl_2 \tag{1}$$

Impurities such as chloride ion or other reducing agents generate chlorine dioxide when the chloric acid solution is heated. Transition-metal ions do not affect the stability of pure chloric acid at room temperature. Thirty-five percent solutions of $HClO_3$ have been shown to be stable for 20 days at room temperature containing up to 1000 ppm Ni^{2+}, 800 ppm Zn^{2+}, 700 ppm Fe^{3+}, or 600 ppm Cr^{3+} (2). The solubility of chloric acid in water is shown in Figure 1.

Chloric acid, a strong acid, has $pK_a = -2.7$ (3). It is a strong oxidizing agent, $E_0 = 1.175$ V with ClO_2 as the reduction product (4). The heat of formation is −99.2 kJ/mol (− 23.7 kcal/mol) and the Gibbs free energy of formation is −3.3 kJ/mol (− 0.79 kcal/mol) for both chloric acid and the chlorate ion (4).

1.2. Chemical Properties. Chloric acid is a strong acid and an oxidizing agent. It reacts with metal oxides or hydroxides to form chlorate salts, and it is readily reduced to form chlorine dioxide.

$$ClO_3^- + 2\ H^+ + e^- \longrightarrow ClO_2 + H_2O \tag{2}$$

Titanium, Hastelloy (grades C22 and C276), and 316 stainless steel all exhibit corrosion rates of less than 0.08 mm/yr at room temperature in 35 wt% chloric acid solutions (2).

1.3. Manufacture. Chloric acid is the precursor for generation of chlorine dioxide for pulp bleaching and other applications (see BLEACHING AGENTS), and is formed *in situ* by reaction of sodium chlorate [7775-09-9], $NaClO_3$, and a strong acid, eg,

$$H_2SO_4 + 2\ NaClO_3 \longrightarrow Na_2SO_4 + 2\ HClO_3 \tag{3}$$

Any chloride present in the solution is oxidized to chlorine by the chloric acid.

$$4\,H^+ + 2\,Cl^- + 2\,ClO_3^- \longrightarrow 2\,ClO_2 + Cl_2 + 2\,H_2O \qquad (4)$$

In order to eliminate or reduce the sodium sulfate by-product of reaction (3), activity has focused on the direct manufacture of chloric acid.

Emerging technologies for the commercial manufacture of chloric acid fall into three categories: (*1*) generation of high purity chloric acid by thermal decomposition of pure solutions of hypochlorous acid [7790-92-3], HClO (5).

$$5\,HOCl \longrightarrow HClO_3 + 2\,Cl_2 + 2\,H_2O \qquad (5)$$

The chlorine generated as a by-product is recovered. Stable solutions of up to 40% by weight chloric acid are generated by evaporative concentration. The chloric acid obtained is free of metal cations and chloride and sulfate anions; (*2*) generation of chloric acid by passing a solution of sodium chlorate through a cation ion-exchange resin (6,7). Electrochemical methods for producing chloric acid from sodium chlorate have also been developed (see ELECTROCHEMICAL PROCESSING). These include electrodialysis (qv) methods employing discrete anion and cation membrane separated compartments or bipolar membranes (8,9) (see MEMBRANE TECHNOLOGY). An alternative electrochemical process employs perfluorinated cation-exchange membrane bounded cell compartments to produce high concentration chloric acid–sodium chlorate mixtures. The mixture is evaporated under vacuum to crystallize out sodium chlorate and produce a low sodium content chloric acid (10). All of the electrochemical routes to chloric acid produce sodium hydroxide, oxygen, and hydrogen as coproducts. The resulting $HClO_3$ solution contains some dissolved sodium chlorate as well as the impurities that were present in the initial sodium chlorate solution; (*3*) and hypochlorous acid can be oxidatively electrolyzed to chloric acid (11,12). Chloric acid prepared by oxidizing HOCl is both metal- and chloride-ion free. It can be reduced to chlorine dioxide without the formation of solid by-products or chlorine. This reduction can be conducted electrochemically (7,13,14) or chemically.

1.4. Shipment. Solutions of greater than 10 wt% chloric acid may be shipped using the label, "oxidizing substance, liquid, corrosive, n.o.s.," and using identification number UN3098, packing group II.

1.5. Health and Safety Factors. Chloric acid is a strong oxidizing agent and concentrated solutions ignite organic matter on contact. The acid must be stored apart from reducing agents and organic materials. Concentrated solutions are corrosive to the skin (1). It is a strong irritant by ingestion and inhalation (21).

1.6. Uses. Chloric acid is formed *in situ* by reaction of sodium chlorate and a strong acid during chlorine dioxide production. Stoichiometric amounts of sodium salts are also formed as a by-product. The use of chlorine dioxide for pulp (qv) bleaching applications is growing and disposal of the by-product solids is a primary environmental concern. Use of chloric acid to generate chlorine dioxide can eliminate this problem. A process for bleaching pulp which employs chloric acid as the oxidizing agent, in the absence of a transition metal catalyst, has been reported (12).

Chloric acid also has found limited applications as a catalyst for the polymerization of acrylonitrile (qv) [107-13-1], C_3H_3N, and in the oxidation of cyclohexanone [108-94-1], $C_6H_{10}O$ (22) (see CYCLOHEXANOL AND CYCLOHEXANONE).

2. Sodium and Potassium Chlorate

2.1. Physical Properties. The physical properties of sodium chlorate [7775-09-9] and potassium chlorate [3811-04-9], $KClO_3$, are summarized in Table 1 (23). The solubilities of these chlorates in water are given in Figure 2 (24–26).

Table 1. **Physical Properties of Sodium and Potassium Chlorates**

Properties	$NaClO_3$	$KClO_3$
molecular weight	106.44	122.55
crystal system	cubic	monoclinic
mp, °C	248–260	356–368
dec pt, °C	265	400
density, g/mL	2.487[a]	2.338[b]
n_D^{20}	1.515	1.440
affinity towards water	hygroscopic	nonhygroscopic
enthalpy of fusion, ΔH_{fus}, kJ/mol[c]	21.3	
molar heat capacity, J/(mol · K)[c]	100[b,d]	99.8[b]
standard enthalpy of formation, kJ/mol[c]		
crystals	−365.8	−391
ideal soln of unit activity	−344.1	
standard entropy J/(mol · K)[c] crystals	123.4	143
ideal solution of unit activity	22.3	
enthalpy of dissolution,[e] kJ/mol[c]	21.6	40.9

[a] At 25°C.
[b] At 20°C.
[c] To convert J to cal, divide by 4.184.
[d] From 298 to 533 K.
[e] 1 mol of chlorate per 200 mol H_2O at 25°C.

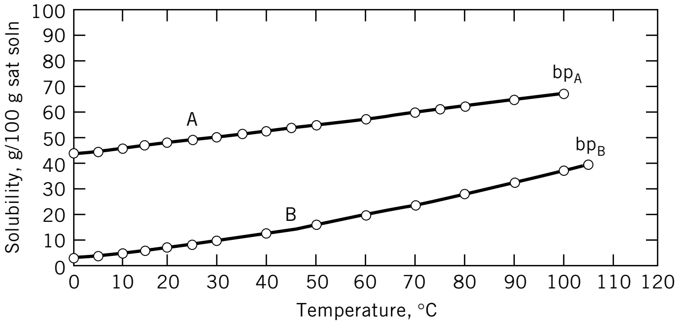

Fig. 2. Aqueous solubility of A, sodium chlorate and B, potassium chlorate where bp_A represents 122°C, the boiling point of a saturated solution of sodium chlorate is 122°C; bp_B represents the boiling point, 104°C, of potassium chlorate solution.

Table 2. **Electrical Conductivity of Aqueous Sodium Chlorate Solutions (ohm · m^{-1})**

	Temperature		
Concentration, 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

The electrical conductivity of a pure aqueous sodium chlorate solution is given in Table 2. Additional data are given (29). Table 3 summarizes the solubility data for two aqueous chlorate–chloride systems (30–32).

2.2. Chemical Properties. On thermal decomposition, both sodium and potassium chlorate salts produce the corresponding perchlorate, salt, and oxygen (34). Mixtures of potassium chlorate and metal oxide catalysts, especially manganese dioxide [1313-13-9], MnO_2, are employed as a laboratory source of oxygen. The evolution of oxygen starts at ~70°C and becomes rapid at 100°C, below the fusion point (35). The molten chlorates are powerful oxidizing agents. Mixtures of chlorates and organic materials have been employed as explosives. However, because of extreme shock sensitivity and unpredictability, such mixtures are not classed as permissible explosives in the United States. Chlorates also form flammable and explosive mixtures with phosphorus, ammonium compounds, some metal compounds, and some metal salts (36). Chlorates in neutral and alkaline solutions at room temperature do not show oxidizing properties. Concentrated acidic solutions of chlorates are strong oxidants as a result of chloric acid formation and may also liberate chlorine dioxide gas.

2.3. Manufacture. Most chlorate is manufactured by the electrolysis of sodium chloride solution in electrochemical cells without diaphragms. Potassium chloride can be electrolyzed for the direct production of potassium chlorate

Table 3. **Mass Ratio of Crystalline Chloride and Chlorate Salts in Equilibrium with an Aqueous Solution**

	Solution system, kg/kg of water[a]			
Temperature, °C	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

[a] Densities of the $NaClO_3$–NaCl and $KClO_3$–KCl aqueous solutions are given in Ref. 33.

(37,38), but because sodium chlorate is so much more soluble (see Fig. 2), the production of the sodium salt is generally preferred. Potassium chlorate may be obtained from the sodium chlorate by a metathesis reaction with potassium chloride (39).

The sodium chlorate manufacturing process can be divided into six steps: (*1*) brine treatment; (*2*) electrolysis; (*3*) crystallization and salt recovery; (*4*) chromium removal; (*5*) hydrogen purification and collection; and (*6*) electrical distribution. These steps are outlined in Figure 3.

The production of sodium chlorate is very energy intensive requiring between 4950–6050 kW·h of electricity per metric ton of sodium chlorate produced (40). More than 95% of the energy is used in the electrolysis step. Increases in energy cost have resulted in use of highly efficient noble metal coated titanium anodes and elimination of the less efficient graphite anodes (41). The by-product hydrogen generated from the cell is also recovered for its fuel value. Advances in electrical bus connection design have also been incorporated to reduce the cell-to-cell voltage drop. The use of noble metal anodes requires that hardness, ie, Ca^{2+} and Mg^{2+} ions, and metals be removed from the sodium chloride brine, hence the brine treatment technology that was originally developed for chlor-alkali industry has now become an integral part of sodium chlorate manufacture (see ALKALI AND CHLORINE PRODUCTS). Sodium chlorate manufacturing technology now incorporates a low chloride–chlorate solution manufacture coupled with a chromium removal system, or the use of a crystallizer to produce crystal chlorate as the final project.

Electrolysis. The overall chemical reaction is

$$NaCl + 3\ H_2O \longrightarrow NaClO_3 + 3\ H_2 \qquad (6)$$

The reaction in equation 6 requires six Faradays to produce one mole of chlorate. The reaction is endothermic, $\Delta H = 224$ kcal/mol (53.5 kcal/mol) of chlorate or

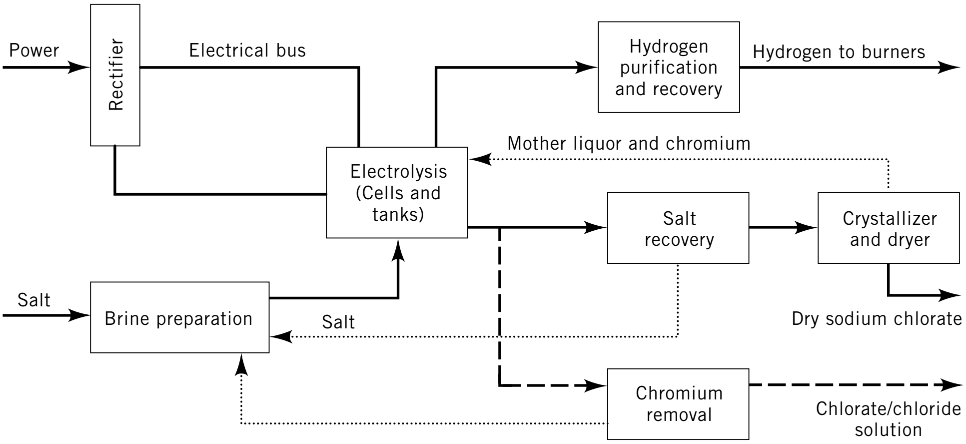

Fig. 3. Schematic of the key steps in a sodium chlorate plant where (···) represents recycle streams and (– – –), process for solution product. Most plants produce crystalline product.

2.43 kW · h/kg. In practice, it takes about 5 kW · h of energy to produce a kilogram of sodium chlorate. The remaining energy is lost to electrolyte solution resistance and heat.

In the sodium chlorate cell, free chlorine is formed at the anode:

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \tag{7}$$

The E_0 at 25°C is 1.36 V vs a normal hydrogen electrode (NHE). The chlorine reacts in the boundary layer and hydrolyzes to form HOCl and HCl

$$Cl_2 + H_2O \leftrightarrows HOCl + HCl \tag{8}$$

which reacts in the bulk electrolyte to form chlorate (42). Hypochlorous acid, HClO, or hypochlorite ions can be converted to chlorate by two separate simultaneous reactions: by the decomposition of hypochlorite ion and free hypochlorous acid (eq. 9) (43) and by the electrochemical formation of chlorate by the anodic oxidation of hypochlorite (eq. 10).

$$2\,HClO + ClO^- \longrightarrow ClO_3^- + 2\,Cl^- + 2\,H^+ \tag{9}$$

$$6\,ClO^- + 3\,H_2O \longrightarrow ClO_3^- + 4\,Cl^- + 1.5\,O_2 + 6\,H^+ + 6\,e^- \tag{10}$$

The reaction described in equation 9 occurs at 100% current efficiency; current efficiency of that in equation 10 is only 66.7% (44,45).

The most favorable conditions for equation 9 are temperature from 60–75°C and pH 5.8–7.0. The optimum pH depends on temperature. This reaction is quite slow and takes place in the bulk electrolyte rather than at or near the anode surface (46–48). Usually 2–5 g/L of sodium dichromate is added to the electrolysis solution. The dichromate forms a protective Cr_2O_3 film or diaphragm on the cathode surface, creating an adverse potential gradient that prevents the reduction of OCl^-; to Cl^-; ion (46). Dichromate also serves as a buffering agent, which tends to stabilize the pH of the solution (47,48). Chromate also suppresses corrosion of steel cathodes and inhibits O_2 evolution at the anode (49–53).

There are other parallel electrochemical reactions that can occur at the electrodes within the cell, lowering the overall efficiency for $ClO^-;_3$ formation. Oxygen evolution accounts for about 1–3% loss in the current efficiency on noble metal-based electrodes in the pH range 5.5–6.5.

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^- \tag{11}$$

Where E_0 at 25°C is 1.23 V vs NHE at $pH = 0$, and 0.876 V vs NHE at $pH = 6$. Oxidation of chlorates to perchlorate can also occur if the cell voltage increases above 6.5 V, or if the chloride concentration is depleted below about 80 g/L.

$$ClO_3^- + H_2O \longrightarrow ClO_4^- + 2\,H^+ + 2\,e^- \tag{12}$$

In addition to the electrochemical reactions, there are some undesirable nonelectrolytic reactions that produce chlorine and oxygen gases, thus lowering the current efficiency (18). Oxygen generated from decomposition of hypochlorite species in bulk accounts for about half of the oxygen involved. The decomposition of the hypochlorite species is catalyzed by low levels of ionic metal impurities, specifically Ni^{2+}, Co^{2+}, Ir^{3+}, and Ir^{4+}. The current efficiency in the chlorate cell can be monitored by analyzing the exit gas stream and can be calculated by using the following formula:

$$\text{chlorate efficiency} = (100 - 3\,W_{\mathrm{O}} - 2\,W_{\mathrm{Cl}})/(100 - W_{\mathrm{O}} - W_{\mathrm{Cl}}) \qquad (13)$$

where W_{O} = vol % of oxygen in exit gas and W_{Cl} = vol % of chlorine in the exit gas. The approximate energy consumption P in (kW · h)/t of a chlorate cell is a function of current efficiency CE expressed as a fraction and cell voltage V in volts

$$\frac{1509V}{CE} \qquad (14)$$

Current efficiency depends on operating characteristics, eg, pH, temperature, and cell design, and is generally in the 90–98% range. The cell voltage is a function of electrode characteristics and electrolyte conductivity and can be expressed as

$$\begin{aligned} V = {} & (\text{thermodynamic decomposition voltage of the anode and the cathode}) \\ & + (\text{anode overvoltage}) + (\text{cathode overvoltage}) \\ & + (\text{ohmic drop between the anode and cathode resulting from} \\ & \quad \text{the electrolyte/gas mixture}) \\ & + (\text{ohmic drop in the electrical connections and hardware}) \end{aligned}$$

Typical energy requirement and operating condition are summarized in Table 4.

Table 4. **Electrical Energy Requirement for a Chlorate Cell Using Steel Cathodes and Pt–Ir Anodes**[a]

current density, kA/m^2	2–3
current efficiency, %	94
cell voltage components, V	
thermodynamic decomposition	1.71
anode overvoltage	0.05
cathode overvoltage	0.94
ohmic drops[b]	0.80
average cell voltage, V	3–3.50
electrical energy requirement, kW · h/t[c]	5700
operating conditions	
temperature, °C	80
solution composition, g/L	
NaCl	150
NaOCl	3–5
$NaClO_3$	450
$Na_2Cr_2O_7$	2–5

[a] Ref. 54.

[b] The gap is from 3 to 5 mm.

[c] Per metric ton of chlorate formed.

Electrolyzer System. The basic criteria for electrolyzer system design is to minimize capital and operating costs. There are about a dozen electrolyzer system configurations being used for sodium chlorate manufacture. These combinations range from high capital/low operating cost to low capital/high operating cost (55–92). Electrolyzer systems have four basic components: an electrolysis zone, a reaction zone, a cooling zone, and a circulation zone.

In the electrolysis zone, the electrochemical reactions take place. Two basic electrode configurations are used: (*1*) monopolar cells where the same cell voltage is applied to all anode/cathode combinations; and (*2*) bipolar cells where the same current passes through all electrodes (Fig. 4). To minimize the anodic oxidation of OCl^-;, the solution must be quickly moved out of this zone to a reaction zone. Because the reaction to convert OCl^- to ClO^{3-} (eq. 9) is slow, a relatively large volume reaction zone is required to carry out the reaction. Moreover, because the energy supplied to the cell is about twice the energy required to carry out the reaction, a cooling zone is required. Then, a circulation zone and circulation mechanism are provided.

Many combinations of these component zones have been designed. Some are shown in Figure 4. The combination range from all zones in one vessel to vessels for each zone.

Brine Preparation. Rock salt and solar salt (see CHEMICALS FROM BRINE) can be used for preparing sodium chloride solution for electrolysis. These salts contain Ca, Mg, and other impurities that must be removed prior to electrolysis. Otherwise these impurities are deposited on electrodes and increase the energy requirements. The raw brine can be treated by addition of sodium carbonate and hydroxide to reduce calcium and magnesium levels to below 10 ppm. If further reduction in hardness is required, an ion-exchange resin can be used. A typical brine specification for the Huron chlorate cell design is given in Table 5.

Hydrogen Purification and Recovery. Because the operation of the modern chlorate cell is quite efficient, ie,$CE = 90 - 98\%$, the hydrogen generated from the cell is quite pure and can be recovered for its fuel value. The hydrogen typically contains 2–3% chlorine and less than 2% oxygen by volume. If the cells are operated at lower than a normal pH of from 5.8–6.4, Cl_2 concentration in the hydrogen can be higher. The chlor-alkali industry has developed an extensive hydrogen recovery technology, which has been transferred to chlorate technology. Typically the hydrogen recovery system includes a caustic scrubber to remove chlorine and a compressor or blower to send hydrogen gas to a fuel burner or boiler (93).

Chlorate Recovery and Salt Removal. Prior to chlorate recovery, the residual hypochlorite in the electrolyzer liquor is destroyed by adding a reducing agent such as formate or urea (93,94). The liquor that contains sodium chlorate, chloride, sulfate, and dichromate is filtered to remove any insoluble particles. The liquor is concentrated by evaporation and sodium chloride is precipitated, filtered, and recycled back to the cell. The liquor is then cooled to yield sodium chlorate crystals, which are separated by centrifugation. The chromium containing centrate is returned to the evaporator or cell feed. Since the feed brine contains sodium sulfate, the sodium sulfate can be removed from the system by purging a small amount of filtrate from the crystallizer (95–98). Alternatively, the sodium sulfate from the filtrate can be crystallized out by the method

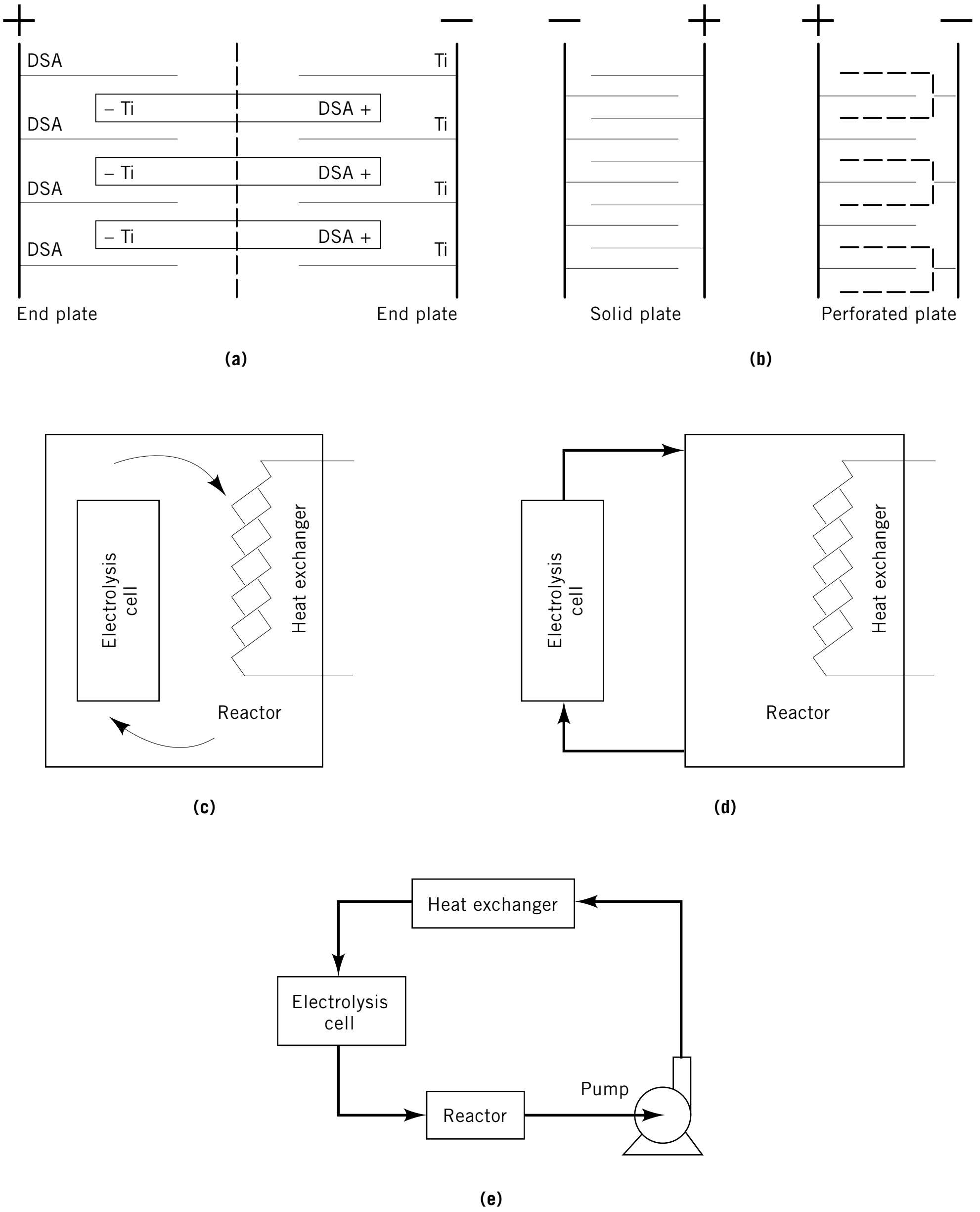

Fig. 4. Sodium chlorate cell designs (**a**) the horizontal bipolar cells used by Huron having narrow gap vertical plates or horizontal mesh where (– – –) represents an insulating partition, DSA is dimensionally stabilized anode, and (**b**) the parallel plate monopolar cells and electrolyzer configurations used by Chemetics, Krebs, etc where (– – –) represents a perforated plate; (**c**) the single vessel system used by DeNora, Huron, and OCC; (**d**) the double vessel system used by Krebs; and (**e**) the three vessel system used by Pennwalt, Ugine-Kuhlmann, and Kemanord. Materials of construction given in Table 5.

Table 5. **Brine Specification for Huron Sodium Chlorate Cell**[a]

Component	Maximum concentration, ppm
Mn	0.01
Ni	0.01
Fe	1.0
Al	1.0
Ba	0.1
Zn	0.01
F	1.0
cyanide	0.1
total organics	3.0
hardness as Ca	4.0[b]
Na_2SO_4	25.0[c]
NaCl	200 to 315[c,d]

[a] Temperature is a maximum of 75°C.

[b] For mild steel cathodes maximum hardness is 2 ppm. Somebrines contain up to 20 ppm.

[c] Units are g/L.

[d] Value varies depending on application.

described in reference 99. Recent advances in chlorine dioxide generation technology require that the sodium chloride content be less than 5% of the solution of sodium chlorate concentration. Sodium chlorate recovered by crystallization meets this requirement.

Chromium Removal System. Chlorate manufacturers must remove chromium from the chlorate solution as a result of environmental regulations. During crystallization of sodium chlorate, essentially all of the sodium dichromate is recycled back to the electrolyzer. Alternatively, hexavalent chromium, Cr^{6+}, can be reduced and coprecipitated in an agitated reactor using a choice of reducing agents, eg, sodium sulfide, sulfite, thiosulfate, hydrosulfite, hydrazine, etc. The product is chromium(III) oxide [1333-82-0], Cr_2O_3 (100–108). Ion exchange and solvent extraction techniques have also been utilized for recycling chromium (109–111). The resulting precipitate is easily filtered using ceramic or Teflon filters without the use of precoats so that the filtered chromium oxide can be returned directly to the chlorate process without further treatment. Once in the chlorate cell, the chromium reoxidizes immediately to hexavalent sodium dichromate. Essentially no chromium ever leaves the system (112). Chromium levels of less than 1 ppm are achieved in the final chlorate product.

2.4. Economic Aspects. North America, Western Europe, and Japan represented 94% of the total sodium chlorate consumption in 2002. The remaining 6% was distributed among South America, other Asia, and the rest of the world.

World operating capacity was 2.8×10^6 t in 2002. North America and Canada represent 69% of this total. Western Europe follows at 25%, South America at 5%, Japan and other Asia at 1% (113).

Table 6 lists U.S. and Canadian producers of sodium chlorate and their capacities (114).

Table 6. **Sodium Chlorate Producers and 1998 Capacities, × 10^3 t**[a]

Producer	Location	Capacity[b]
United States		
CXY	Taft, La.	122
Eka Nobel	Columbus, Miss.	199
Eka Nobel	Moses Lake, Wash.	57
Elf Atochem	Portland, Ore.	53
Georgia Gulf	Plaquemine, La.	24
Huron Tech	Clairborne, Ala.	36
Huron Tech	Augusta, Ga	131
Kerr McGee	Hamilton, Miss.	130
Sterling Pulp Chemicals	Valdosta, Ga.	100
Western Electrochemical	Cedar City, Utah	6
Total		*858*
Canada		
Albchem	Bruderheim, Alberta	75
B.C. Chemicals	Prince George, B.C.	71
CXY	Amherstburg, Ont.	48
CXY	Beauhamois, Que.	44
CXY	Brandon, Man.	103
CXY	Bruderheim, Alberta.	68
CXY	Nanaimo, B.C.	18
Eka Nobel Canada	Magog Que.	150
Eka Nobel Canada	Valleyfield, Que.	113
PCI Chemicals	Delhousie, N.B.	22
St. Anne Chemical	Nackawic, N.B.	10
Sterling Pulp Chemicals	Buckingham, Que.	120
Sterling Pulp Chemicals	Grand Prairie, Alberta	50
Sterling Pulp Chemicals	North Vancouver, B.C.	92
Sterling Pulp Chemicals	Saskatoon, Sask.	50
Sterling Pulp Chemicals	Thunder Bay, Ont.	50
Total		*1084*
Total, North America		*1942*

[a] Ref. 114.

[b] Both solution and crystal material. Commercial production is by electrolysis of a sodium chloride solution.

An estimated 1.87 × 10^6 t was used in North America in 2002 to generate chlorine dioxide for bleaching of chemical pulp. Of this total, 68% was used in the U.S. and 32% was used in Canada. This represented 99% of demand for sodium chlorate.

EPA cluster rules are in favor of elemental-free-chlorine bleaching agents for pulp rather than total chlorine-free bleaching agents. Chlorine dioxide is generated from sodium chlorate and is a substitute for chlorine gas in bleaching applications. Full implementation of the cluster rules was to be finalized in 2001. The chlorate market is expected to level off and track a modest increase in demand after the full implementation. North American consumption is expected to grow at a rate of 0.9% in 2001–2006. Canada's growth rate is expected at 0.8% (113).

Western Europe uses less sodium chlorate for pulp bleaching and consumption in Japan is small. Japanese paper producers are expected to use elemental-chlorine-free bleaching agents by 2005 despite Japan's weak economy.

2.5. Product Specification. Sodium chlorate can be shipped either as solid crystals or preblended chlorate–chloride solution. A typical specification for technical-grade sodium chlorate is $NaClO_3$, 99.5 wt% min; NaCl, 0.12 wt% max; moisture, 0.20 wt% max; and 5 ppm chromium.

The crystalline sodium chlorate is usually dried in rotary driers to less than 0.2 wt% moisture content and is loaded into shipping containers or stored in moisture-free bins or silos prior to packaging. For conventional chlorine dioxide generators, sodium chlorate is shipped as a solution containing: ca 200 g/L (15 wt%, 3.4 *M*) sodium chloride; ca 350 g/L (26 wt%, 3.3 *M*) sodium chlorate; and 130 ppm chromium. Alternatively, for newer chlorine dioxide generators, 600 g/L sodium chlorate; 30 g/L sodium chloride; and less than 30 ppm chromium is used.

2.6. Analytical Methods. Chlorate ion concentration is determined by reaction with a reducing agent. Ferrous sulfate is preferred for quality control (115), but other reagents, such as arsenious acid, stannous chloride, andpotassium iodide, have also been used (116). When ferrous sulfate is used, a measured excess of the reagent is added to a strong hydrochloric acid solution of the chlorate for reduction, after which the excess ferrous sulfate is titrated with an oxidant, usually potassium permanganate or potassium dichromate.

2.7. Health and Safety Facters. Sodium chlorate is harmful if swallowed, inhaled, or absorbed through the skin. Symptoms of inhalation include burning sensation, coughing, wheezing, and laryngitis. Symptoms of ingestion include nausea, vomiting, abdominal pain, cyanasis, and diarrhea (117–119). Acute oral toxicity in laboratory animals for different species are in 1200–1800 mg/kg range. Lethal doses for children are 2 g and for adults are from 15 to 30 g (200–400 mg/kg). Permissible exposure limit for total dust is 15 mg/m^3 and for respirator protection, 5 mg/m^3.

Sodium chlorate and potassium chlorate are human poisons by unspecified routes. They are moderately toxic by ingestion and intraperitoneal routes. They both damage red blood cells when ingested (21).

Chlorates are strong oxidizing agents. Dry materials, such as cloth, leather, or paper, contaminated with chlorate may be ignited easily by heat or friction. Extreme care must be taken to ensure that chlorates do not come in contact with heat, organic materials, phosphorus, ammonium compounds, sulfur compounds, oils, greases or waxes, powdered metals, paint, metal salts (especially copper), and solvents. Chlorates should be stored separately from all flammable materials in a cool, dry, fireproof building.

Flammable resistant clothing such as Nomex should be worn when working with chlorates. Clothing splashed with chlorate solution should be removed before it dries. Shoes and gloves should be rubberized. Leather (qv) should not be worn. Goggles, face shields, and dust respirators should be worn when necessary to protect against dust, splashing, or spillage. Workers should bathe before leaving the working area.

Sodium chlorate does not burn if exposed to fire, but it decomposes to give off oxygen. Consequently only water is effective in the event of a spill or fire.

Table 7. **Hazard Ratings for Sodium Chlorate**

Situation	Nonfire[a]	Fire[a]
health (blue)	1	0
flammability	0	0
reactivity	2	2
other	oxy	oxy

[a] 4 = extreme, 3 = high, 2 = moderate, 1 = slight, and 0 = insignificant.

Water cools and dilutes the sodium chlorate. Carbon dioxide, Halon, dry chemical or dry powder types of fire extinguishers are ineffective. EPA classifies sodium chlorate waste as D001 (ignitable waste). The Clean Water Act lists sodium chlorate as a hazardous substance, which if discharged into or upon water, may require immediate response to mitigate danger to public health and welfare. Hazard ratings for sodium chlorate according to the National Fire Protection Association (NFPA) are shown in Table 7.

2.8. Uses. The primary (99%) use of sodium chlorate is in the production of chlorine dioxide for bleaching in the pulp (qv) and paper industry (qv).

Chemical wood (qv) pulp bleached with chlorine dioxide has superior brightness over pulps bleached using other reagents (see BLEACHING AGENTS). The strength of the cellulose (qv) fiber is not degraded; thus a whiter and stronger paper is obtained using chlorine dioxide. When chlorine dioxide is used in place of chlorine for bleaching pulp, the adsorbable organic halides (AOX), which include dioxins, are reduced by as much as 90%. However, chlorine dioxide cannot be shipped and is therefore generated by the pulp producers at the bleaching plant.

The second most important use of sodium chlorate was as an intermediate in the production of other chlorates and of perchlorates.

The agricultural use of sodium chlorate is as a herbicide, as a defoliant for cotton (qv). Magnesium chlorate is used as a desiccant for soybeans to remove the leaves prior to mechanical picking (see DESICCANTS).

Sodium chlorate is used in uranium mixing. This usage was expected to decline sharply. Minor uses of sodium chlorate include the preparation of certain dyes and the processing of textiles (qv) and furs.

Potassium chlorate is used mainly in the manufacture of matches (qv) and pharmaceutical preparation. In pyrotechnics, chlorate salts may be mixed with certain organic compounds such as lactose to give a relatively cool flame, so that certain dyes may be incorporated in the mixture to give colored flares.

3. Other Chlorates

Barium chlorate monohydrate [10294-38-9], $Ba(ClO_3)_2{:}H_2O$, has colorless monoclinic crystals; mp or loss of water at 120°C; sp gr, 3.18; n_D^{20}, 1.562; is prepared by the reaction of barium chloride [10361-37-2], $BaCl_2$, and sodium chlorate in solution. Barium chlorate precipitates on cooling and is purified by recrystallizing. It is used in pyrotechnics.

Lithium chlorate [13453-71-9], $LiClO_3$, has rhombic needles; mp 124–129°C; decomposes on heating to 270°C. It is one of the most soluble salts known and it is very hygroscopic. $LiClO_3$ is prepared by adding lithium chloride [7447-41-8] to sodium chlorate solution. Sodium chloride precipitates, the liquor is concentrated, and the lithium chlorate is filtered and dried. It has limited use in pyrotechnics.

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