ELECTROCHEMICAL PROCESSING, INORGANIC

1. Introduction

Electrochemical processes have been used to produce reactive inorganic chemicals and metals since the early 1800s. Many reactive elements were first isolated by electrolysis. Electrochemical processes involve cell components, reactor designs, and operating principles that can be very process-specific. The amount of electric energy required depends on the electrode material and the species reacting at the electrode. Electrode potentials range up to 3.5 V. This moderate level of energy is sufficient to produce the strongest oxidizing and reducing agents known, fluorine and solvated electrons, respectively. Efficient chemical and electrochemical processes exist for the production of some chemicals. Process choice then depends on a number of factors including capital costs, operating costs, and health and environmental considerations. Environmental factors generally favor electrochemical processing. It would be difficult, if not impossible, to develop chemical manufacturing processes for such highly reactive chemicals as sodium [*7440–23-5*], Na (see SODIUM AND SODIUM ALLOYS) and fluorine (qv) [*7782-41-4*], F_2.

The electrochemical production of inorganic chemicals and metals in the United States consumes about 5% of all the electricity generated annually, and about 16% of the electric power consumed by industry. This includes the production of such commodity chemicals as sodium hydroxide [*1310-73-2*], NaOH, and chlorine [*7782-50-2*], Cl_2, ranked eight and ninth in volume of production in 1991, respectively (1). Table 1 lists the most important inorganic products of electrochemical processes. Electroplating (qv), electropolishing (see METAL SURFACE TREATMENTS), anodizing, electrolytic machining, energy sources such as batteries (qv) and fuel cells (qv), and other industrial operations involving the use of electric power and electrode reactions are all discussed elsewhere.

2. Hardware for Electrochemical Processing

Power supplies and electrolytic cells are the distinguishing features of electrochemical processes. Nearly all electric power is generated and transported as high voltage multiple-phase alternating current. Industrial electrochemical processes require direct current; thus transformers are needed to decrease voltage, and rectifiers are required to convert the alternating current to direct current. Rectifiers may be rated for voltages up to 400 V or more and for any amperage up to hundreds of thousands of amperes. Rectifier efficiencies generally increase as voltages increase. Very high amperages are achieved by connecting rectifier units in parallel. State-of-the-art rectifiers use thyristers which are semiconductor devices that conduct only when a triggering potential is applied (see SEMICONDUCTORS). Thyristers can be made to conduct for half of an alternating current cycle and not conduct the other half-cycle, rectifying alternating current to direct current.

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Table 1. **1991 U.S. Production of Electrochemical Products**[a]

Product	Quantity, $t \times 10^3$	Reference	Price,[b] \$/t	Product value, $\$ \times 10^6$
aluminum	4100	3	1320	5.41
beryllium	0.17	3[c]		
cadmium	1.6	3	2200	0.0035
caustic potash	273	4	∼700	0.191
caustic soda	11,091	5	330	3.66
chlorine	10,727	6	137.50	1.475
chromium	420	3[c]	∼2860	1.2
copper	1,630	3	2618	4.267
lithium	2.8	3[c]	69,300	0.194
magnesium	130	3	3146	0.063
manganese metal	20	7	1188	0.024
manganese dioxide	39	7	1540	0.06
nickel	8.4	3	7480	0.063
perchlorates	20	7	∼1100	0.02
permanganates	21	8	2750	0.058
sodium	71.8	9[d]	2530	0.182
sodium chlorate	315	4	456	0.144
titanium	16	3		
zinc	520	3	1430	0.744
Total				*17.76*

[a] Fluorine and persulfates were also produced electrochemically.
[b] All product values are based on prices quoted in Ref. 2.
[c] Value represents consumption rather than production.
[d] Value is production for 1990.

Electrochemical processes require feedstock preparation for the electrolytic cells. Additionally, the electrolysis product usually requires further processing. This often involves additional equipment, as is demonstrated by the flow diagram shown in Figure 1 for a membrane chlor-alkali cell process (see ALKALI AND CHLORINE PRODUCTS). Only the electrolytic cells and components are discussed herein.

Design possibilities for electrolytic cells are numerous, and the design chosen for a particular electrochemical process depends on factors such as the need to separate anode and cathode reactants or products, the concentrations of feedstocks, desired subsequent chemical reactions of electrolysis products, transport of electroactive species to electrode surfaces, and electrode materials and shapes. Cells may be arranged in series and/or parallel circuits. Some cell design possibilities for electrolytic cells are

Cell type	Process
one-compartment cells	
open-top inert tank	
monopolar electrodes	MnO_2
bipolar electrodes	chlorate
open-top cathodic tank	chlorate and perchlorate
enclosed horizontal liquid metal cathode	chlorine–caustic and aluminum

two-compartment cells	
diaphragm cells	
monopolar electrodes	chlorine–caustic and Mn metal
bipolar electrodes	chlorine–caustic
membrane cells	
monopolar electrodes	chlorine–caustic
bipolar electrodes	chlorine–caustic
pressurized cells	
filter press	
bipolar electrodes	hydrogen–oxygen
rotating cylindrical cathode	continuous production of metal
particle-bed electrodes	removal of low concentration of metals from waste streams

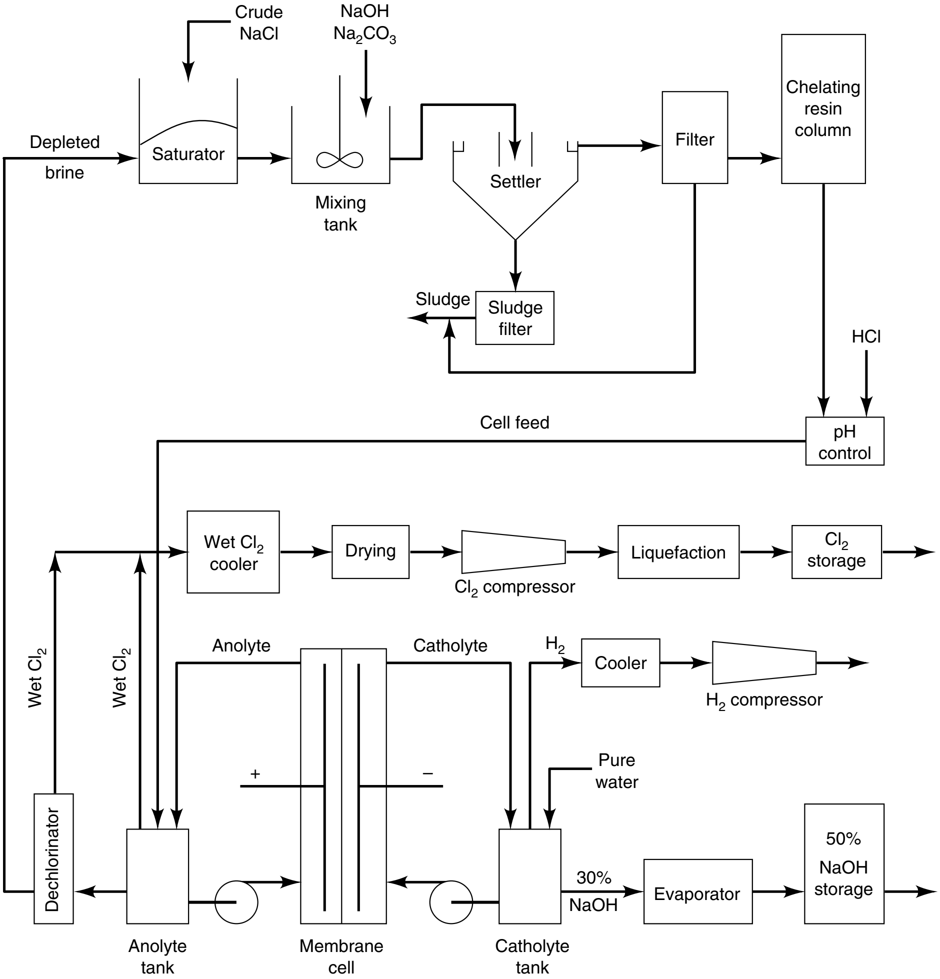

Fig. 1. Flow diagram for chlor-alkali production by a membrane cell process.

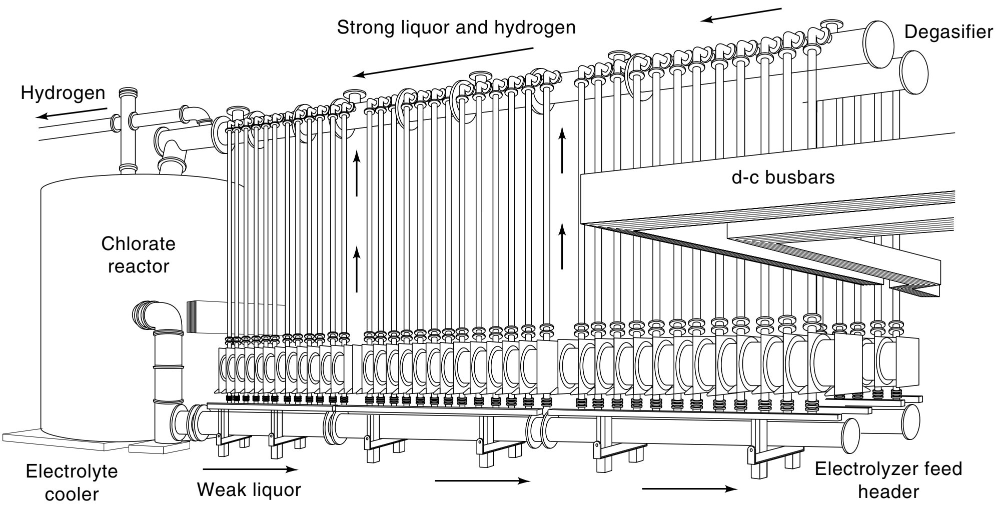

Fig. 2. Chemetics sodium chlorate cellroom. (Courtesy of Chemetics International Co., Ltd.)

Industrial electrolytic cells that produce gas at one or both electrodes are usually designed to take advantage of gas lift electrolyte circulation. Good electrolyte circulation provides transport of electroactive species to the electrode surfaces, and in some cases moves electrode products away from the electrode. Internal gas lift circulation in a well-designed cell is much more efficient than mechanically pumped circulation. The Chemetics sodium chlorate [775-09-9], $NaClO_3$, cell shown in Figure 2 is a good example of gas lift electrolyte circulation (see also CHLORINE OXYGEN ACIDS, CHLORIC ACID AND CHLORATES). Other examples are the Huron sodium chlorate cell shown in Figure 3, the Oxytech chlor-alkali membrane cell shown in Figure 4, the Lurgi membrane cell (Fig. 5), improved Hooker fluorine cell (Fig. 6), and a typical metal electrowinning cell (Fig. 7).

The electrolytic cells shown in Figures 2–7 represent both monopolar and bipolar types. The Chemetics chlorate cell (Fig. 2) contains bipolar anode/cathode assemblies. The cathodes are Stahrmet, a registered trademark of Chemetics International Co., and the anodes are titanium [7440-32-6], Ti, coated either with ruthenium dioxide [12036-10-1], RuO_2, or platinum [7440-06-4], Pt–iridium [7439-88-5], Ir (see METAL ANODES). Anodes and cathodes are joined to carrier plates of explosion-bonded titanium and Stahrmet, respectively. Several individual cells electrically connected in series are associated with one reaction vessel.

Monopolar electrodes have a direct electrical connection with an external power supply. This requires the distribution of current over the total area of one monopolar electrode, collecting the current from the other monopolar electrode for conduction to the next cell through intercell busbars. Monopolar cells operate at low voltages, and may require high amperages. Industrial circuits of cells may consist of one hundred or more monopolar cells in series. Monopolar electrodes are used in some membrane chlor-alkali cells (Figs. 4 and 5), fluorine cells (Fig. 6), and in metal electrowinning cells (Fig. 7).

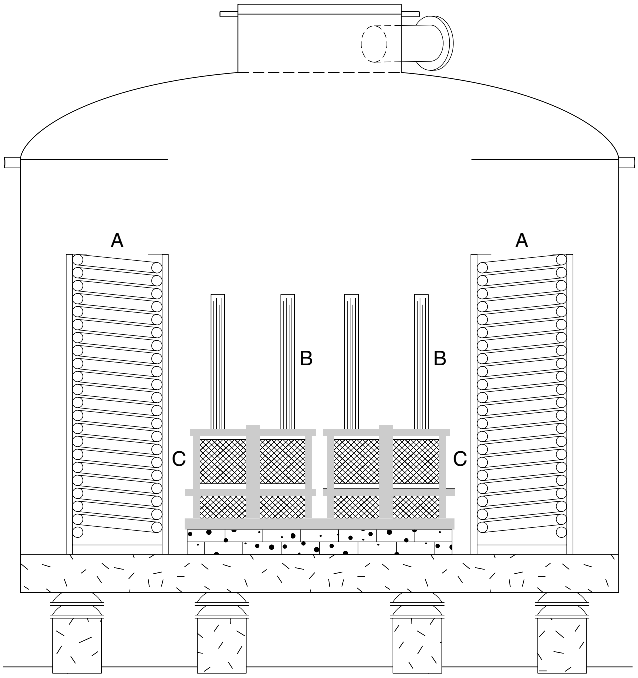

Fig. 3. Huron sodium chlorate cell system, where A corresponds to cooling coils; B to chimneys to promote gas lift circulation; and C to cell boxes. Electric bus connections are not shown. (Courtesy of Huron Technologies Inc.)

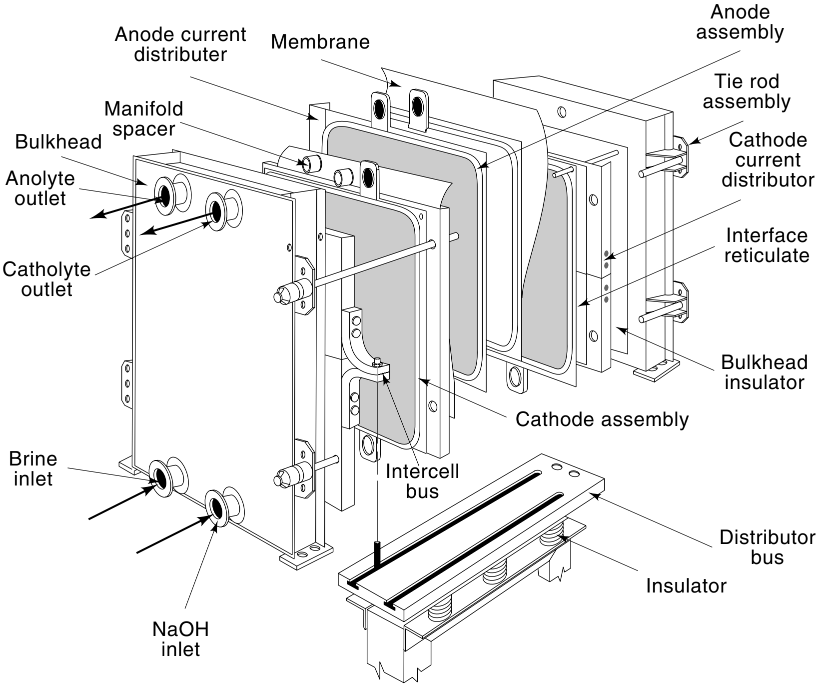

Fig. 4. OxyTech membrane gap cell electrolyzer assembly. (Courtesy of OxyTech Systems, Inc.)

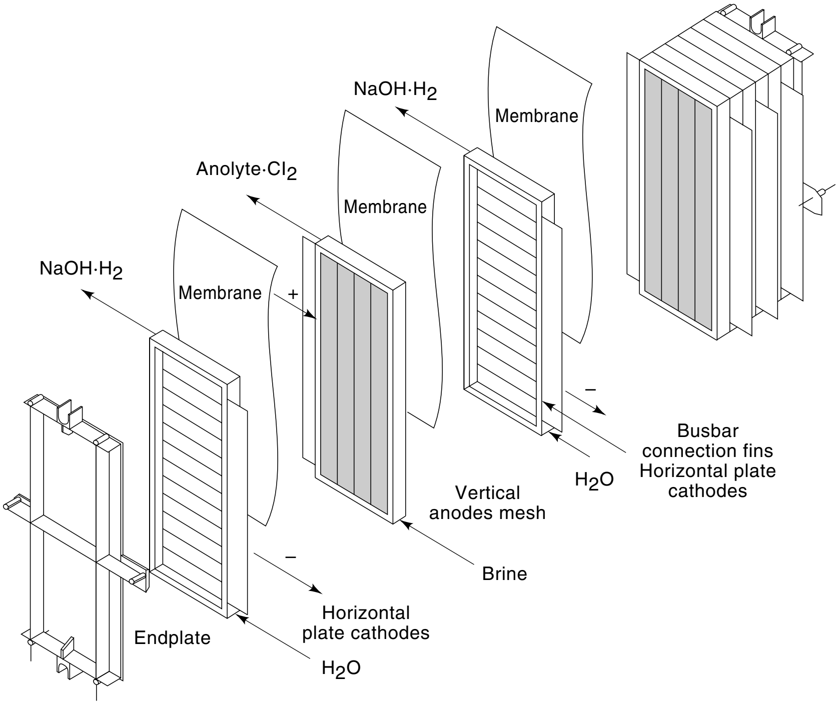

Fig. 5. Lurgi membrane electrolyzer. (Courtesy of Lurgi AG.)

Bipolar electrodes have no direct electrical busbar connection to a power supply. Only the terminal electrodes that lead current into and out of a bank of cells are connected to a power source. These terminal electrodes are monopolar. Bipolar cells are polarized by potential gradients that force current to flow through the bipolar units. If conducting pathways around bipolar units are available, some current bypasses or leaks past bipolar units. Care must be taken when designing bipolar cells to minimize current leakage through cell feed manifolds and other possible current leakage pathways. Bipolar electrodes are polarized anodically on the side facing the negative terminal electrode, and cathodically on its reverse side. Bipolar cells may be flat side to side units or elongated units that are bipolar end to end (Figs. 2 and 3). Banks of cells are called electrolyzers. Electrolyzers may contain up to one hundred or more unit cells. The voltage required by a bipolar electrolyzer is the individual cell voltage multiplied by the number of cells in the electrolyzer. Bipolar cells generally require relatively low amperages. Large numbers of cells in electrolyzers and several electrolyzers in a circuit may require a relatively high rectifier voltage and relatively low amperage. Discussions of monopolar and bipolar cells, advantages and disadvantages, are found in References 11 and 12. Bipolar cell designs minimize energy consumption by operating at lower unit cell voltage.

The separation of anode and cathode products is often necessary. Electrolysis products are often very reactive and mixing can be hazardous. Examples are the electrolysis of water to produce oxygen [7782-44-7], O_2, at the anode

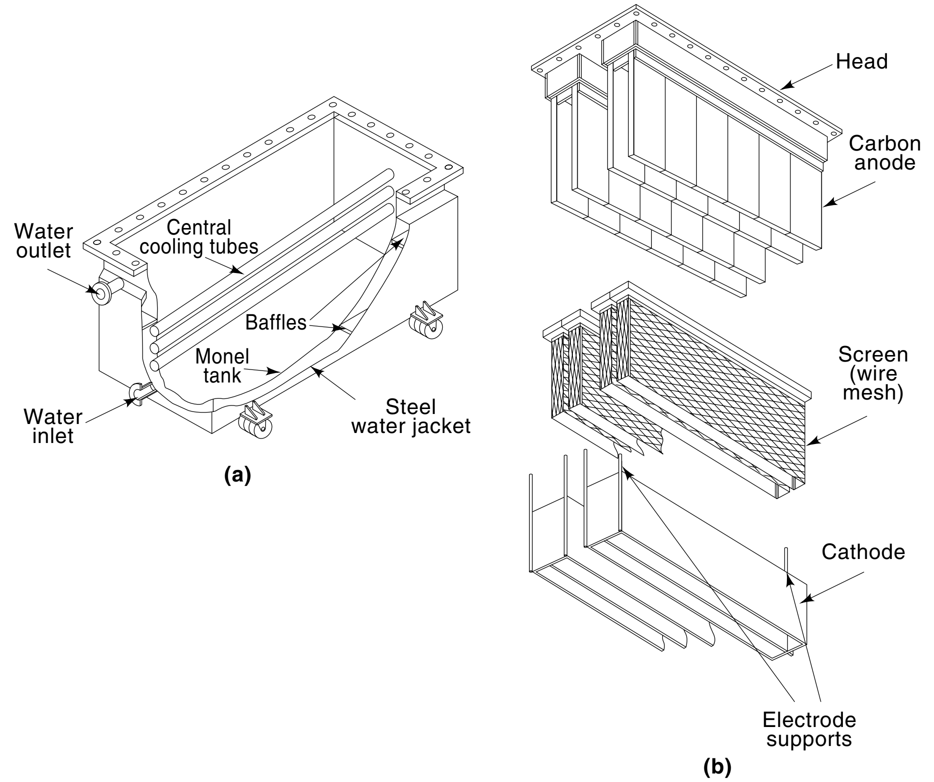

Fig. 6. Improved fluorine cell assembly: (**a**), cell tank; (**b**), electrode and diaphragm components. (Courtesy of American Chemical Society (10).)

and hydrogen [1333-74-0], H_2, at the cathode, and the electrolysis of sodium chloride [7647-14-5], NaCl, brine to produce chlorine [7782-50-5], Cl_2, and hydrogen. Cells for these electrochemical processes include a membrane or diaphragm to separate the anode and cathode compartments. Porous diaphragms made of

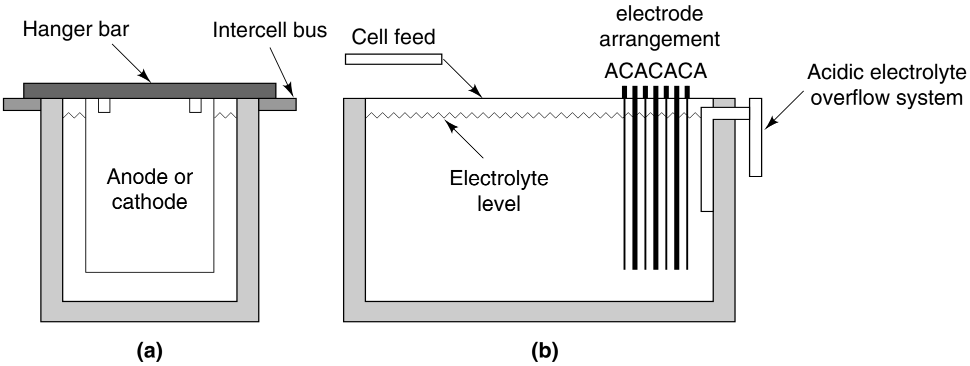

Fig. 7. Sections of metal electrowinning cell without diaphragm: (**a**), end view; (**b**), side view where A is anode and C is cathode.

deposited fibers, woven fabrics, or metallic wire mesh may be used in many cases. Porous diaphragms or ion-exchange (qv) membranes are used in water electrolysis cells and diaphragm-chlor-alkali cells (see MEMBRANE TECHNOLOGY). Woven nickel [7440-02-0], Ni, wire mesh diaphragms are used in fluorine cells (Fig. 6), and woven plastic fabrics are used in some metal electrowinning cells. The latter are sometimes referred to as bags, and may be around the cathodes or anodes. A neutral cell feed (pH ~7) may enter the cathode compartment, percolate through the diaphragm, and become acidic anolyte.

Ion-exchange membranes are used when selective ion transport between compartments is desired and liquid flow through pores is undesirable. The chlor-alkali cells (Figs. 4 and 5) are examples of membrane cells. Very good ion-exchange membranes for electrolytic cells have been developed and are used commercially. Most newer chlorine and caustic plants are based on membrane cells, and several chlor-alkali plants have been converted to membrane cells (4). In chlor-alkali cells, cation-exchange membranes allow the transport of sodium ions from the anolyte compartment to the catholyte compartment, and nearly eliminate other ionic transport through the membrane. Membrane cells produce caustic that contains very little (ppm) sodium chloride. Commercial, ie, 50%, caustic soda from diaphragm cells contains about 1% sodium chloride.

Electrode materials and shapes may have a profound effect on cell designs. Anode materials encountered in electrochemical processes are

Anode material	Process
carbon	fluorine aluminum
graphite	chlorine–caustic chlorate
DSA	chlorine–caustic chlorate
Pt	perchlorates persulfates
lead dioxide, PbO_2, on graphite or titanium	chlorate perchlorate
lead alloy (Pb, 1% Ag)	zinc electrowinning manganese electrowinning

Ideal anode materials should allow high anodic polarizations without being oxidized or deteriorated in any way. Depending on the process, some anode materials such as carbon [7440-44-0], C, graphite [7782-42-5], and lead dioxide [1309-60-0], PbO_2, corrode significantly and have relatively short useful lives. Hydrogen diffusion anodes similar to those used in fuel cells (qv) are being developed for use in Zn and Mn electrowinning cells (13).

Dimensionally stable anodes (DSA) are titanium anodes coated with ruthenium dioxide, RuO_2, and titanium dioxide, TiO_2 (14). DSA is a registered trademark of Eltech Systems Corp. DSA have replaced graphite anodes in nearly all commercial chlor-alkali and chlorate cells. The service life of DSA in diaphragm chlor-alkali cells has exceeded 12 years in many cases. DSA are produced by baking a catalyst layer, RuO_2–TiO_2, on a valve metal support (Ti,Ta). Other noble metal or noble metal oxide coatings on titanium are used in some applications. These may be platinum, platinum–iridium, platinum oxide, or ruthenium oxide in proprietary mixtures of catalyst, binder, and stabilizer. Activated electrodes offer superior corrosion resistance, lower reaction voltages, and lower electric power consumption per unit of production.

Cathode materials and electrochemical applications are

Cathode material	Process
mild steel	chlorine–caustic, chlorate, perchlorate
mercury	chlorine–caustic
nickel	fluorine
stainless steel	chlorine–caustic
active cathode coating	chlorine–caustic
O_2 or air reduction	chlorine–caustic

Attempts to decrease the hydrogen overvoltage by applying active coatings of Ni–Zn, Ni–Al, and proprietary combinations of metals on steel, stainless steel, and nickel have met with some success (15). Cell voltages have been decreased by up to 0.2 V for more than 800 days (16,17). Oxygen or air cathodes similar to those used in fuel cells have been investigated for potential application in chlor-alkali cells, chlorate cells, and other cells producing hydrogen at the cathode (18). As of this writing, there are none used in inorganic electrochemical processing.

Mild steel cathodes are used extensively in chlor-alkali and chlorate cells. Newer activated cathode materials have been developed that decrease cell voltages about 0.2 V below that for cells having mild steel cathodes. Some activated cathodes have operated in production membrane cells for three years with only minor increases in voltage (17). Activated cathodes can decrease the energy consumption for chlorine–caustic production by 5 to 6.5%.

3. Industrial Process Conditions

3.1. Electrolysis of Chloride Solutions. Chloride may be oxidized electrochemically to chlorine or hypochlorite, chlorate, and perchlorate. The distribution of products of the first oxidation step

$$2\,Cl^- - 2e^- \longrightarrow Cl_2 \tag{1}$$

is very pH-dependent and is determined by the equilibria (19,20):

$$Cl_2 + H_2O \rightleftharpoons ClO^- + Cl^- + 2\,H^+ \qquad K_{eq} = 3.88 \times 10^{-4} \tag{2}$$

$$ClO^- + H^+ \rightleftharpoons HOCl \qquad K_{eq} = 3.13 \times 10^{7} \tag{3}$$

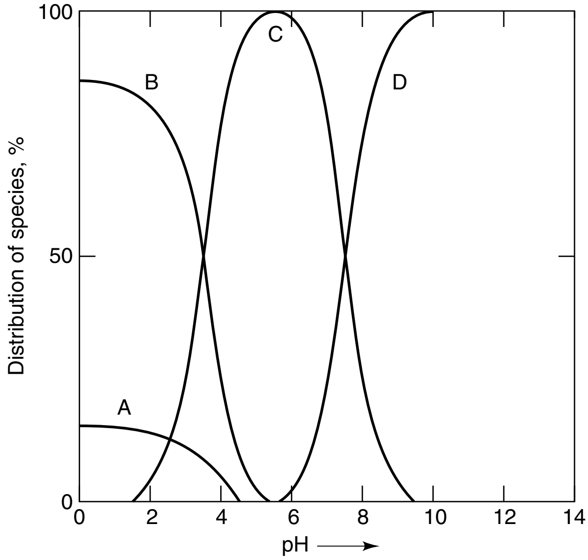

Fig. 8. Distribution of chlorine-containing species in a 1 *M* chloride solution. A, ClO_3^-; B, Cl_2; C, HOCl; and D, ClO^-.

The distribution of species as a function of anolyte pH is shown in Figure 8 (21). Chlorine is the primary product at pH <4. Hypochlorous acid [7790-92-3], HOCl, is the dominant species from pH 4 to pH 6. Above pH 6 combinations of HOCl and hypochlorite ion, ClO^-, exist but react to produce ClO_3^- (22):

$$2\,HOCl + ClO^- \rightleftharpoons ClO_3^- + 2\,Cl^- + 2\,H^+ \tag{4}$$

Hypochlorite ions also react at the anode to produce chlorate electrochemically. This reaction

$$6\,ClO^- + 3\,H_2O \longrightarrow 2\,ClO_3^- + 4\,Cl^- + 6\,H^+ + 1.5\,O_2 + 6\,e^- \tag{5}$$

is undesirable in commercial cells because it requires more electric power. The theoretical electric current required to produce chlorate by equations 1–4 is 6 Faraday per mole. Equations 1, 2, 3, and 5 require 9 Faradays per mole of chlorate produced. In commercial cells, reaction volume is provided to promote equation 4 and minimize equation 5.

The oxidation of chlorate to perchlorate, $ClO_4{}^-$, is an electrochemical anode reaction independent of pH.

$$ClO_3^- + H_2O \longrightarrow ClO_4^- + 2\,H^+ + 2\,e^- \tag{6}$$

Perchlorate is usually produced by first producing chlorate, separating chlorate from chloride by crystallizing $NaClO_3$, and redissolving $NaClO_3$ to produce a nearly chloride-free chlorate solution for perchlorate production. Optimum electrolysis conditions and cell designs for chlorate and perchlorate production are different. Chlorate cells may use graphite, DSA, or PbO_2 anodes, are pH sensitive, and require a reaction volume to promote equation 4. Perchlorate cells may use platinum or PbO_2 anodes, are not pH sensitive, and require no reaction volume (see PERCHLORIC ACID AND PERCHLORATES).

The electrolysis of NaCl brine for the production of chlorine and caustic soda is one of the oldest and certainly one of the most important industrial electrochemical processes (22–26). The overall reaction is

$$2\,NaCl + 2\,H_2O \xrightarrow[\text{energy}]{\text{electrical}} 2\,NaOH + Cl_2 + H_2 \qquad (7)$$

There are three main technologies available for carrying out this process: diaphragm cells, mercury cells, and membrane cells. Membrane cells are the most recent development, and are generally chosen for new production capacity.

Diaphragm Cell Technology. Diaphragm cells feature a porous diaphragm that separates anode and cathode compartments of the cell. Diaphragms should provide resistance to liquid flow, require minimum space between anode and cathode, produce minimum electrical resistance, and be durable. At the anode, which is generally a DSA, chloride ions are oxidized to chlorine (see eq. 1) and at the cathode, which is usually a woven steel wire mesh, water is reduced to hydrogen.

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^- \qquad (8)$$

The diaphragm, generally vacuum deposited on the cathode, separates the hydrogen and chlorine gases produced and the anolyte from the caustic soda containing catholyte. Purified brine containing about 26% NaCl is fed into the anode compartment. The electrolyte flows through the diaphragm into the cathode compartment and out of the cell as a 10–12% NaOH solution containing unreacted NaCl. This NaOH solution is evaporated to produce 50% NaOH. The solubility of NaCl decreases as NaOH concentrations increase in the evaporators, causing NaCl to precipitate. Solid NaCl is removed from the concentrated NaOH solution. Diaphragm cell caustic soda generally contains about 1% NaCl.

Diaphragm cells have been improved by using DSA instead of graphite anodes and by using modified asbestos (qv) diaphragms (27,28) and nonasbestos diaphragms (29). The operating characteristics of some diaphragm cells are given in Table 2.

Mercury Cells. The cathode material in mercury cells, mercury [7439-97-6], Hg, has a high hydrogen overvoltage. Hydrogen evolution is suppressed and sodium ion reduction produces sodium amalgam [11110-52-4], HgNa.

$$Na^+ + e^- + Hg \longrightarrow HgNa \qquad (9)$$

Because little hydrogen is generated at the cathode of mercury cells it is possible to construct cells without a diaphragm. Mercury (cathode) flows continuously down a long, gently sloping trough. The anodes, generally DSA, are held a minimum distance above the mercury. Chlorine is produced at the anode as in equation 1. Sodium amalgam leaving the mercury cell passes through a decomposer

Table 2. **Operating Characteristics of Diaphragm Cells**[a]

Cell parameter	Oxytech				Glanor		Uhde	
model	H2A	H4	MDC29	MDC55	V-1144	V-1161	HU30[b]	HU60[b]
current rating, kA	80	150	80	150	72	72	60	120
current density, kA/m^2	2.21	2.33	2.76	2.74	2.05	1.47		
cell voltage, V	3.35	3.40	3.60	3.59	3.50	3.08		
energy (d-c) consumed, kW·h/t	2655	2694	2847	2839	2800	2400		
cells/electrolyzer	1	1	1	1	11	11	1	1
chlorine capacity, t/d	2.42	4.54	2.43	4.55	24.2[c]	24.2[c]	1.82	3.64
caustic capacity, t/d	2.73	5.13	2.74	5.14	27.0[c]	27.0[c]	2.05	4.10
diaphragm life, d	300	275	200	200				
cell to cell distance, m	2.32	3.05	1.6	2.13			1.5	1.5
types of electrodes	monopolar	monopolar	monopolar	monopolar	bipolar	bipolar	monopolar	monopolar

[a] All cells employ DSA anodes.

[b] Designed to accommodate rectifier amperages from 30 to 150 kA. Cells of various kA ratings vary in the length of cell and number of anodes and cathodes. Operating characteristics vary with current density (30).

[c] Capacity per electrolyzer.

or denuder containing graphite where water is reduced to hydrogen and sodium is oxidized to caustic soda.

$$2\,\mathrm{HgNa} + 2\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{NaOH} + \mathrm{H_2} + 2\,\mathrm{Hg} \qquad (10)$$

Mercury denuded of sodium is pumped back into the cell for continuous recirculation.

Caustic soda concentrations of 50% are produced directly from equation 11. This advantage is offset by higher operating cell voltages and some mercury contamination of the environment. This latter problem has been diminished or solved to an acceptable extent (31); however, it continues to influence the choice of cells for new plants. No new mercury cells have been installed in the United States since 1970 (32).

Membrane Cells. Membrane cells are separated into anode and cathode compartments by selective ion-exchange membranes. Sodium chloride brine is fed into the anode compartment. Chlorine is produced at the anode (eq. 1). Sodium ions and some water of hydration are transported through the membrane into the cathode compartment. Depleted brine is removed from the anode compartment saturated, treated, and returned to the cell. Hydrogen and 30–35% caustic soda are produced at the cathode. To achieve good caustic soda concentration control, some caustic soda is usually recirculated to the cathode compartment along with the required additions of water. The advent of selective ion-exchange membranes in 1971 made membrane cells practical (33). Membrane cells have many advantages over diaphragm cells and mercury cells, including higher caustic concentrations and nearly chloride-free caustic without mercury pollution. Mercury cells produce high quality caustic soda, but create a pollution problem.

Membrane cells are the state of the art chlor-alkali technology as of this writing. There are about 14 different membrane cell designs in use worldwide (34). The operating characteristics of some membrane cells are given in Table 3. The membranes are perfluorosulfonate polymers, perfluorocarboxylate polymers, and combinations of these polymers. Membranes are usually reinforced with a Teflon fabric. Many improvements have been made in membrane cell designs to accommodate membranes in recent years (35,36).

Chlorates. Sodium chlorate is produced by the electrolysis of sodium chloride at pH 6.5–7.5 in a one-compartment cell. DSA anodes and steel cathodes are generally used in chlorate cells. The electrolysis products, hypochlorous acid, and hypochlorite ions, react chemically to produce chlorate (eq. 4). Chlorate cells are designed with reaction volumes to provide time for equation 4 to proceed. Figures 2 and 3 show chlorate cells with their associated reaction volumes. The Chemetics cells in Figure 2 are separate from the reaction tank. Gas lift circulation causes the liquors to circulate through the cells into the reaction volume and back to the cells. The Huron cells in Figure 3 are submerged into the reaction tank. Liquors circulate through the cells by gas lift and by more dense cooled liquors descending from cooling coils.

Sodium dichromate [31924-34-2], $\mathrm{Na_2Cr_2O_7}$, is added to chlorate cell electrolytes. The chromate minimizes the reduction of hypochlorite and chlorate at the cathode. Chromate also minimizes the corrosion of cathodes when or where

Table 3. **Operating Characteristics of Membrane Cells**

	Bipolar cells		Monopolar cells				
Parameter	Hoechst Uhde	Asahi chemical acilyzer	Chlorine engineers DCM 406 × 2	ICI FM21 SP	Asahi glass azec	Oxytech MGC	Lurgi
current rating, kA	2–18	5.8–21.6	36–73	1–100	18–340	6–225	
current density, kA/m^2	2–6	2–4	1.98–4	1.5–4.1	3–4	1.5–4.5	1–4
cell voltage, V	2.95–3.4	3.2–3.3	3.0–3.1		3.0–3.05		
energy (d-c) consumed, kW·h/t, NaOH	2080–2405	2150–2230	2000–2050	2150–2200		2050–2300	1850–2300
cells/electrolyzer	2–120	50–100	12	1–120	30–540	2–30	$2 - 10^+$
electrode area, m^2	0.9–2.7	2.7–5.4	3.03				~0.8
current efficiency, %	93–96	94–97			92–97		
height, mm			1300		1200	1960	1200
width, mm			2560		2400	1140	660
length, mm			1195			460–1900	

cathodic current densities are inadequate to cathodically protect the steel cathodes from the very corrosive electrolyte. The reaction tanks are generally constructed of corrosion-resistant plastics. Huron cells (Fig. 3) are contained in a fiber-reinforced plastic tank with a proprietary lining. Chemetics cells (Fig. 2) are contained in titanium housings, and the reaction tank is titanium. The use of plastic materials in chlorate cells usually limits the operating temperature to about 65°C. Chlorate cell systems constructed predominately of metals allow higher operating temperatures, up to 80°C. Some chlorate plants operate several of the cell-reactor tank units in cascade fashion. Sodium chloride brine may enter one end of a series of Huron cell units, flow from one cell unit to the next until the cell liquor contains up to 600 g/L of $NaClO_3$ and about 100 g/L NaCl. Other plants operate each cell system at essentially final conditions. The entire electrolysis from NaCl to $NaClO_3$ cell liquor is done in a single-cell-reaction tank unit. Chlorate cell liquor is treated to convert as much hypochlorite to chlorate as is practical. Residual hypochlorite is destroyed to protect downstream equipment from corrosive attack. Chlorate liquors are cooled and evaporated in crystallizers to produce solid $NaClO_3$. Crystallizer liquors containing NaCl, $NaClO_3$, and chromate are resaturated with NaCl and recycled to the chlorate cells. Operating characteristics for some chlorate cells are given in Table 4.

Nearly 95% of the sodium chlorate produced in North America is used to produce chlorine dioxide [10049-04-4], ClO_2, for pulp (qv) bleaching (see Bleaching agents, pulp and paper) (37). Minor amounts are used to produce other chemicals such as $KClO_3$, $NaClO_2$, $NaClO_4$, etc, to recover uranium [7440-61-1], U (see Uranium and uranium compounds) and for agricultural uses as a defoliant or herbicide (see Herbicides).

Perchlorates. Concentrated solutions of sodium chlorate are electrolyzed to produce sodium perchlorate [7601-89-0], $NaClO_4$ (see Perchloric acid and perchlorates). The electrolytic cells for perchlorate production are usually simple tank electrolyzers. Anode materials are limited to platinum, platinum-clad titanium, or lead dioxide on graphite or titanium. The cathodes are generally mild

Table 4. **Operating Characteristics of Chlorate Cells**

Parameter	Chemetics	Eka Nobel	Huron	Krebs Paris
cell type[a]	B	B	B	M (NC-24)
current, kA	22.5–87.5	25–36	20	77.4
current density, kA/m$_2$	1.5–3.5	1.0–1.2	3.2	2.4
current efficiency, %	95+	95–96	95+	94–96
energy (d-c), kW·h/t	4250+	4650–4800	5200	4910–5210
temperature, °C	80		65	80
pH	6.5	6.5–6.7	6.5–7.0	6.5–6.5
anode materials	DSA	DSA	DSA	DSA
cathode material	Stahrmet	steel	Ti	steel
product, g/L				
$NaClO_3$	650	550–600	600–650	540–580
NaCl	110	135	60–80	100–120
$Na_2Cr_2O_7$, g/L	3	1.0	1.5	3.5–5
cells/electrolyzer	up to 17	8	48	3

[a] B = bipolar; M = monopolar electrodes.

steel. Cell feed solutions may contain 600 g/L of $NaClO_3$. Production of very high (1000 g/L or more) concentrations of $NaClO_4$ is achieved by resaturating partially converted electrolyte with $NaClO_3$ and continuing the electrolysis to minimum final $NaClO_3$ concentrations. A mechanism of perchlorate formation has been proposed involving the reaction of chlorate ion and an absorbed active oxygen species at the anode (38,39).

Most of the $NaClO_4$ produced is converted to ammonium perchlorate [7790-98-9], NH_4ClO_4.

$$NaClO_4 + HCl + NH_3 \longrightarrow NH_4ClO_4 + NaCl \tag{11}$$

The products of equation 11 are separated by controlled crystallizations to produce high purity crystalline anhydrous ammonium perchlorate and sodium chloride. The main use for ammonium perchlorate is as an oxidizer in the propellant of rockets and missiles (see EXPLOSIVES AND PROPELLANTS).

3.2. Manganese Dioxide. High performance alkaline batteries (qv) and some lithium batteries require pure electrolytic manganese dioxide [1313-13-9] (EMD), MnO_2. Other forms of MnO_2, natural ore (NMD) and chemical manganese dioxide (CMD), are used in large batteries where performance requirements are less demanding. The production of EMD involves the following unit operations: first, high quality manganese ores are reduced. Reduced ore is then leached using acidic electrolyte from the cells and makeup sulfuric acid [7664-93-9], H_2SO_4. Crude manganese sulfate [10124-55-7], $MnSO_4$, solution is treated to remove impurities. Purified manganese sulfate solution is fed into an electrolytic cell where MnO_2 is deposited on the anode. Deposited MnO_2 is periodically harvested, milled, neutralized, and packaged for market (see MANGANESE COMPOUNDS).

Electrolytic cells for EMD production consist of open-top tanks having titanium anodes and graphite or metallic cathodes. No separators are required. High quality EMD is produced at very low (60–80 A/m^2) anode current densities on titanium anodes. Suspensions of small particles of EMD in the electrolyte of EMD cells allow good quality EMD to be produced on titanium anodes at higher current densities, 100–200 A/m^2. The use of suspensions in EMD cell electrolytes was first patented by Japan Metals and Chemicals Co., Ltd. in 1976 (40). Numerous other publications and patents have appeared (41–44). A novel fiber glass reinforced plastic (FRP) isotensoid cell tank design is being used in Australia. The tank consists of a suspended FRP bag supported in a rectangular steel frame (45). Table 5 details some operating conditions for EMD production.

The electrolytic deposition of MnO_2 at an anode may be described by

$$Mn^{2+} \longrightarrow Mn^{3+} + e^- \tag{12}$$

$$2\,Mn^{3+} \longrightarrow Mn^{4+} + Mn^{2+} \tag{13}$$

$$Mn^{4+} + H_2O \longrightarrow MnO^{2+} + 2\,H^+ \tag{14}$$

The cathode reaction is the reduction of water to produce hydrogen (eq. 8). The mechanism of the anodic deposition of MnO_2 has been investigated (44,47).

World production capacity for electrolytic manganese dioxide was estimated to be about 198,000 t/yr in 1988 (48). An EMD production facility having 18,000 t/yr

Table 5. **Production Conditions for Electrolytic Manganese Dioxide**

Parameter	Typical[a]	Suspensions[b]
$MnSO_4$ feed solution, g/L	130–160	105[c]
electrolyte		
H_2SO_4, g/kg	30 ± 5	30–50[d]
$MnSO_4$, g/kg	40 ± 10	[e]
anode	Ti	Ti
cathode	graphite	graphite
temperature, °C	95–98	90–95
cell voltage, V	2.7–3.0	2.4–3.2
current density, A/m^2	60–80	85–150

[a] Ref. 46.

[b] Ref. 42.

[c] NaOH is added to a pH of 7.8^+. Air agitation is employed.

[d] Value is g/L.

[e] $MnSO_4$ plus 10–200 mg/L of hydrated manganese oxide.

capacity was built in Australia by Australian Manganese Co., Ltd., in 1987–1989 (46). U.S. production in 1991 was about 39,000 t (7).

3.3. Water Electrolysis.

The electrolysis of water for hydrogen and oxygen production is economically attractive only in those areas where electric power is available at very low cost. Hydrogen (qv) is usually the primary product (see HYDROGEN ENERGY); oxygen (qv) is a co-product. Hydrogen in large quantities is produced by steam (qv) reforming methane, ie, natural gas (see GAS, NATURAL). Hydrogen produced in chlor-alkali and chlorate cells is available in some areas, and in some cases is compressed and sold in cylinders and as liquid hydrogen. Oxygen is commonly produced by the separation of air (see CRYOGENICS).

Total production of hydrogen in the United States in 1988 was 61.5×10^9 m^3 (49). Total hydrogen production by electrolysis of water in 1988 was about 5.7×10^6 m^3 (<0.01%). U.S. capacity for liquid hydrogen production as of June 1989 was about 42,500 t/yr, equivalent to about 481×10^6 m^3/yr.

Cells for the electrolysis of water are available from several sources. These cells have been described (50,51). Water electrolysis cells must operate at low voltages to achieve good energy efficiency. The theoretical decomposition voltage for hydrogen and oxygen production is 1.23 V. Actual cell voltages are 1.8–2.6 V. Current efficiencies closely approach 100%. Cells are usually of a filter-press design incorporating bipolar electrodes, porous diaphragms or ion-exchange membranes, alkaline electrolyte, KOH, and catalyzed electrodes. Most cells operate at high pressures, about 3 MPa (30 atm) (52,53).

Recent developments in water electrolysis cells include the use of ion-exchange membranes (54), optimization of pressure and temperature (55), and suggestions for better electrolysis cell designs (56). Interest in water electrolysis is associated with load leveling and space exploration (57). Electric power available during periods of low usage, ie, off-peak periods, can be used to electrolyze water. The hydrogen and oxygen produced can be stored and used in fuel cells (qv) to produce electric power when peak power demands occur.

Heavy water [11105-15-0], D_2O, was produced by a combination of electrolysis and catalytic exchange reactions. Some nuclear reactors (qv) require heavy water as a moderator of neutrons. Plants for the production of heavy water were built by the U.S. government during World War II. These plants, located at Trail, British Columbia, Morgantown, West Virginia, and Savannah River, South Carolina, have been shut down except for a portion of the Savannah River plant, which produces heavy water by a three-stage process (see DEUTERIUM AND TRITIUM): an H_2S/H_2O exchange process produces 15% D_2O; a vacuum distillation increases the concentration to 90% D_2O; an electrolysis system produces 99.75% D_2O (58).

Cold fusion has been reported to result from electrolyzing heavy water using palladium [7440-05-3], Pd, cathodes (59,60). Experimental verification of the significant excess heat output and various nuclear products are still under active investigation (61,62) (see FUSION ENERGY).

3.4. Fluorine. Fluorine is the most reactive product of all electrochemical processes (63). It was first prepared in 1886, but important quantities of fluorine were not produced until the early 1940s. Fluorine was required for the production of uranium hexafluoride [7783-81-5], UF_6, necessary for the enrichment of ^{235}U (see DIFFUSION SEPARATION METHODS). The Manhattan Project in the United States and the Tube Alloy project in England contained parallel developments of electrolytic cells for fluorine production (63). The principal use of fluorine continues to be the production of UF_6 from UF_4.

$$UF_4 + F_2 \longrightarrow UF_6 \tag{15}$$

The electrolyte used in fluorine cells is KF–HF in a ratio that minimizes melting point, HF vapor pressure, and corrosion of materials. Various ratios have been used. The manufacture of fluorine in the early 1990s was based on the electrolysis of KF:2HF, which allows cell operating temperatures of 100–105°C.

Fluorine has been compressed, liquified, and shipped. However, most fluorine is produced and used on site. Fluorine production in the United States is based on electrolytic cells developed in the 1940s. Modern type "E" cells are rated for 6 kA (64).

Fluorine cells use carbon anodes, steel cathodes, and nickel or monel wire mesh diaphragms contained in a monel tank with a water jacket for cooling. Cells operate at about 6 kA, 10 –12 V, and 95–105°C. Energy consumption for fluorine production is about 22 kWh/kg. Figure 6 is a diagram of a fluorine cell. Fluorine cell voltages are increased by the formation of fluorinated carbon. Conditions for the formation of $(CF)_n$ and $(C_2F)_n$ on anode surfaces have been studied (65). Cell voltages have been decreased somewhat by impregnating carbon anodes with molten fluoride at high temperatures and pressures (66).

3.5. Permanganate. Potassium permanganate [7722-64-7], $KMnO_4$, is produced in commercial quantities. It may be prepared from manganese dioxide or directly from manganese metal, ferromanganese, or other manganese alloys (67). The Carus Chemical Co. produces potassium permanganate from manganese dioxide in the United States. First potassium manganate [10294-64-1], K_2MnO_4, is prepared by a liquid-phase oxidation of manganese dioxide with potassium hydroxide in air

$$MnO_2 + 2\,KOH + 0.5\,O_2 \longrightarrow K_2MnO_4 + H_2O \qquad (16)$$

The reaction mixture is filtered. The solids containing K_2MnO_4 are leached, filtered, and the filtrate composition adjusted for electrolysis. The solids are gangue. The Carus Chemical Co. electrolyzes a solution containing 120–150 g/L KOH and 50–60 g/L K_2MnO_4. The cells are bipolar (68). The anode side is monel and the cathode mild steel. The cathode consists of small protrusions from the bipolar unit. The base of the cathode is coated with a corrosion-resistant plastic such that the ratio of active cathode area to anode area is about 1 to 140. Cells operate at 1.2–1.4 kA. Anode and cathode current densities are about 85–100 A/m^2 and 13–15 kA/m^2, respectively. The small cathode areas and large anode areas are used to minimize the reduction of permanganate at the cathode (69). Potassium permanganate is continuously crystallized from cell liquors. The caustic mother liquors are evaporated and returned to the cell feed preparation system.

The direct electrochemical oxidation of manganese alloys was developed and commercialized at the Rustavi Chemical Combine in the Georgian Republic (formerly the USSR). The electrode reactions are

Anode $$Mn + KOH + 3\,H_2O \longrightarrow KMnO_4 + 7\,H^+ + 7\,e^- \qquad (17)$$

Cathode $$7\,H^+ + 7\,e^- \longrightarrow 3.5\,H_2 \qquad (18)$$

The anodes used were cast ferromanganese; the electrolyte, KOH/K_2CO_3, and current efficiencies for this process were about 40%. Energy requirements for this process, about 15 kWh/kg of $KMnO_4$, plus the cooling requirement to maintain cells at 20°C, made this process uneconomical (70,71).

Production of potassium permanganate in the CIS is believed to be from potassium manganate. Electrolysis of potassium manganate in a continuous-flow electrolytic cell with turbulent electrolyte flow and continuous crystallization has been reported (72).

Direct electrochemical oxidation of manganese dioxide suspended in KOH to produce potassium permanganate has been patented (73). It is not known whether this is a commercial process. Metal cathodes having adherent surface deposits of manganese dioxide improve permanganate production efficiencies by decreasing the manganate and permanganate reduction reactions at the cathode (74). Production capacity for potassium permanganate in the United States was about 21,000 t/yr in 1991 (8).

3.6. Hydrogen Peroxide.

Peroxydisulfuric acid [13445-49-3], $H_2S_2O_8$, is one of the strongest oxidizing agents known. It and other peroxydisulfates are produced electrochemically (75). The production of peroxydisulfates was once important for the manufacture of hydrogen peroxide [7722-84-1] (qv), H_2O_2 (76). In 1956 more than 80% of the production of H_2O_2 was from peroxydisulfates. Peroxydisulfates are produced by electrolyzing bisulfates or sulfates in acidic solution at smooth platinum anodes:

$$2\,NH_4HSO_4 \longrightarrow (NH_4)_2S_2O_8 + 2\,H^+ + 2\,e^- \qquad (19)$$

Hydrogen peroxide was produced by hydrolysis:

$$2(NH_4)_2S_2O_8 + 2\,H_2O \longrightarrow 2\,NH_4HSO_4 + H_2O_2 \qquad (20)$$

The development of the autoxidation of alkyl anthraquinones led to a rapid increase in the production of H_2O_2 but a sharp decline in the importance of the electrolytic process. In 1991 the total North American, Western European, and Japanese capacity for H_2O_2 production was more than 870,000 t (77). No H_2O_2 was produced by the electrolytic peroxydisulfate process. The last plant using this process closed in 1983.

Rapid growth in demand for H_2O_2 in the late 1980s created widespread interest in new processes for H_2O_2 production (78). New process development efforts were generally focused either on direct combination of hydrogen and oxygen to produce H_2O_2 (79) or the electrolytic reduction of oxygen to produce H_2O_2. HD Tech Inc., a joint venture of Dow Chemical Canada Inc. and Huron Technologies Inc., has developed and commercialized an electrolytic reduction of oxygen process (77,78). The electrolytic cell is divided into two compartments by a porous separator. A solution of caustic soda and sodium silicate is fed into the anode compartment. Oxygen is produced at the anode. Oxygen enters the top of a catalytic trickle bed cathode and is reduced to form H_2O_2 and caustic soda. The alkaline peroxide product has a H_2O_2 to NaOH ratio of about 1 to 1.7, and can be used immediately for bleaching pulp (80). This process is best suited for plants that use five or more tons per day of H_2O_2, and are 500 km or more from a commercial H_2O_2 production source.

4. Electrowinning of Metals

The metals that are produced by electrolysis (81) are included in Table 6. Fused salt processes are used when the reactivity of the metal does not allow electrowinning from aqueous solutions. Manganese is the most reactive metal that is produced by electrolysis of an aqueous solution.

4.1. Electrowinning from Aqueous Solutions.

The aqueous processes for electrowinning of metals from ores have the following common unit operations or steps: (*1*) the metal in the ore is converted to an acid-soluble form and this may be an oxidizing roast or a reduction; (*2*) ores from step 1 are leached, usually in sulfuric acid; (*3*) metal solutions from step 2 are purified and in some cases concentrated; (*4*) purified metal solutions are electrolyzed in cells where the metal is deposited on the cathode; and (*5*) acid is produced at the anode and recycled to the leaching step 2. Some acid values are lost, usually in the purification step, 3. Makeup acid is added in the leaching step, 2. In most cases the metal solution from leaching step 2 contains impurities, other metals. Many of these metals have the characteristic of low hydrogen overvoltage. Codeposition of the impurity metals causes contamination of the desired product and decreases current efficiencies. The removal of impurities before electrolysis is very important. This is especially true in the case of the more reactive metals such as zinc [7440-66-6], Zn, and manganese [7439-96-5], Mn. These metals have deposition potentials close to the hydrogen evolution potential. The current

Table 6. **Production of Metals by Electrolysis of Aqueous Solutions**[a]

Metal	Anode	Diaphragm	Cathode	Cell feed[b], g/L	Electrolyte[b], g/L	Temperature, °C	Cell voltage, V	Cathode current density, A/m^2	Energy requirement, kW·h/kg	Current efficiency, %
Cd	Pb–Ag	no	Al	90–200 Cd, 20–40 Zn	10–20 Cd, 20–40 Zn, 60–140 H^+	30–35	2.5–2.7	80	1.5	90
Cr	Pb–Ag	yes	316 stainless steel		[c]	53	4.2	700	18	45
Cu	Pb–Sb–Ag	no	Cu	20–70 Cu, 20–70 H^+		30–35	2.0–2.2	130	2.2	80–90
Mn	Pb–Ag	yes	stainless steel or Ti	30–40 Mn, 125–150 NH_4^+, 0.1 SO_2 + glue[d]	[d]	35	5.1	400–600	8–9	60–68
Ni	Pb	yes	Ni 99.9%		[e]	52	3.4	180		91–96
Zn	Pb–Ag	no	Al	100–200 Zn	100–200 H^+, 20–40 Zn	35	3.2–3.6	350–1000	3.3	90

[a] Refs. (82,83).

[b] As sulfates unless otherwise noted.

[c] Anolyte in g/L: 13 Cr(VI), 2 Cr(III), 24 NH_3, 280 H_2SO_4. Catholyte in g/L: 11.5 Cr(III), 12.5 Cr(II), 84 NH_3; pH = 2.1 – 2.4.

[d] Anolyte in g/L: 10–20 Mn, 25–40 H_2SO_4, 125–150 NH_4^+. Catholyte in g/L: pH 6–7.2.

[e] Catholyte in g/L: 70 Ni(II) + H_3BO_3, Na_2SO_4; pH = 3.0 – 3.5. Anolyte in g/L: 40 H_2SO_4.

efficiency of manganese electrowinning is about 60 to 68%. The principal inefficiency is hydrogen evolution.

The electrowinning of metals from aqueous solutions is generally carried out in tank cells. Figure 7 shows a typical metal electrowinning cell. Process conditions for electrowinning metals from aqueous solutions are given in Table 6 (82,83). Developments in the electrowinning of metals from aqueous solutions have been directed toward improved anodes, improved additives, higher current densities, the use of ion-exchange membranes, better electrolyte quality control, and computer modeling of the processes.

Corrosion rates of lead–silver anodes containing various amounts of silver were studied under various operating conditions. Data are available for optimizing anode composition for minimum overall cost (84). Titanium anodes coated with various catalytic materials have been developed for metal electrowinning cells (85–87). Hydrogen diffusion anodes are being developed (88). These anodes would consume hydrogen in fuel cell fashion and decrease cell voltages by about 1.8–2.0 V.

Additives are used in metal electrowinning to improve the quality of deposited metal, increase current efficiencies, and decrease the work required to remove metals from cathodes. Improvements in these additives have been developed (89,90).

Production rates and profits can generally be increased when higher current densities can be applied to electrowinning cells. Capital investments required to achieve higher current densities are a critical factor. Zinc electrowinning on rotary drum cathodes produces continuous ribbons of zinc at very high current densities, up to 5000 A/m^2 (91,92). Small-scale cells have been operated, but no commercial applications are known as of this writing (93). Ion-exchange membranes may be used in some metal electrowinning cells (94,95).

Systems for evaluating electrolytes for metal electrowinning have been developed and are being used commercially in zinc production (96). Computerized mathematical models of zinc electrowinning cells have been developed and validated by comparison with experimental data taken from pilot-plant cells (97).

4.2. Electrowinning from Fused Salts.

Aluminum. Aluminum [7429-90-5], Al, is produced worldwide by the Bayer-Hall-Heroult process. This process involves the electrolysis of alumina [1344-28-1], Al_2O_3, dissolved in molten cryolite [15096-52-3], Na_3AlF_6 (see ALUMINUM AND ALUMINUM ALLOYS). The electrolytic cells or pots operate at about 975°C. The overall reaction is

$$2\,Al_2O_3 + 3\,C \longrightarrow 3\,CO_2 + 4\,Al \qquad (21)$$

Graphite anodes are oxidized to CO_2 and CO. Cell gas contains about 70–90% CO_2. Reactions occurring in aluminum cell cathodes have been studied extensively (98). The cells are constructed from large steel tanks lined with refractory insulating bricks, then lined with an inner covering of graphite which conducts current to the molten aluminum cathode pool. The graphite anodes are of two types, prebaked anodes and Soderberg anodes. The prebaked anodes are large graphite blocks that must be replaced as they are consumed in equation 21. The Soderberg anode is continuously formed by addition of a carbon/pitch paste to a mold held above the molten electrolyte in the cell. The paste is added at the rate of graphite consumption in the cell. The whole mass moves slowly down toward the melt and is baked *in situ* (see CARBON).

Developments have taken place in the areas of improved insulation, pot linings, and cathode and anode materials. A compressible insulation was developed to minimize potlining heaving (99). Potlining heaving is caused by sodium in the graphite linings. Substantial increases in pot lives are to be expected when new graphite cathodes are preheated using gas burners. Cathode surfaces are heated slowly up to about 700°C (100). Molten pools of cathodic aluminum have rippling surfaces. This is the result of magnetohydrodynamic effects. Large anode to cathode gaps are required to prevent contact of molten aluminum to the anodes. This results in high voltages. Aluminum cells with drained cathodes, that are molten aluminum wettable, allow smaller electrode gaps and lower cell voltages. Coatings of titanium diboride [12045-63-5], TiB_2, and titanium carbide [12070-08-5], TiC, on graphite have been used in these cells (101). The development of anode materials for aluminum cells has met with limited success (102,103). The electrical energy required to produce aluminum has been decreased from about 55 d-c kW·h/kg in 1900 to about 16 d-c kWh/kg in 1980 (104). An excellent discussion of energy consumption and efficiency of aluminum production and other electrochemical processes is found in Reference 104.

Sodium. Sodium is produced by the electrolysis of a fused salt mixture of calcium chloride [10043-52-4], $CaCl_2$, and NaCl in a Downs cell (105). $CaCl_2$ is used to lower the melting point of the electrolyte. Operating temperatures in the 570 to 590°C range are practical using $NaCl-CaCl_2$ mixtures. The Downs cell consist of several graphite anodes surrounded by steel cathodes. A metal diaphragm is placed between each anode and cathode to prevent contact of chlorine and sodium. The respective streams rise to the top of the cell. Chlorine is collected in a hood, and the liquid sodium and calcium are channeled to a riser pipe. The collected metal is allowed to cool to 110°C to precipitate the calcium [7440-70-2], Ca, metal codeposited with sodium. The calcium is filtered out and the liquid sodium contains less than 0.04 wt% calcium (see SODIUM AND SODIUM ALLOYS). Eutectic melts of $BaCl_2$, $CaCl_2$, and NaCl have been studied by electrochemical means (106). An improved cell for the production of sodium was patented (107). This cell utilizes an electrode separator, solid electrolyte tubes that are permeable to the flow of sodium ions but impermeable to fluids and the flow of other ions. Production of sodium from mixtures of NaCl and aluminum chloride [7446-70-0], $AlCl_3$, has been described (107).

Lithium. Several processes for lithium [7439-93-2], Li, metal production have been developed. The Downs cell with LiCl−KCl electrolyte produces lithium in much the same manner as sodium is produced. Lithium metal or lithium−aluminum alloy can be produced from a mixture of fused chloride salts (108). Granular Li metal has been produced electrochemically from lithium salts in organic solvents (109) (see LITHIUM AND LITHIUM COMPOUNDS).

Magnesium. There are three electrolytic processes for magnesium [7439-95-4], Mg, production: the Dow process, a process developed by I.G. Farbenindustrie in Germany, and an Alcan process. All processes involve the electrolysis of magnesium chloride [7786-30-3], $MgCl_2$. The Dow process uses partially dehydrated cell feed, and the German process requires completely anhydrous $MgCl_2$ as cell feed (110). The Dow cell is a large steel pot about 1.5 m wide,

Table 7. **Production of Metals by Electrolysis of Fused Salts**

Metal process	Anode	Cathode	Electrolyte melt, %	Temperature, °C	Cell voltage, V	Cathode current density, kA/m^2	energy (d-c) consumption, kW·h/kg	Current efficiency, %
Al Hall-Heroult	prebaked graphite or Soderberg graphite	Al	80–85 cryolite, 5–7 CaF_2, 5–7 AlF_3, 2–8 Al_2O_3	940–980	4.1	3–3.5	13–15	92–95
Na Downs	graphite	steel	58 $CaCl_2$ 42 NaCl	580 ± 10	5.7–7.0	9.7	10–11	80–85
Li Downs	graphite	steel	LiCl–KCl eutectic	450	6.8	5	36	
Mg DOW	graphite	steel	20 $MgCl_2$ 20 $CaCl_2$ 60 NaCl	700–720	6.3		18.5	75–80

1.8 m deep, and 4.0 m long. Graphite anodes are suspended through an arched refractory cell cover. The steel pot and steel baffles around each anode are the cathode. Chlorine is collected from the arched cell cover of the Dow cell. Magnesium rises to the top of the electrolyte and is directed through inverted troughs to a storage well from which it is removed.

The Alcan process has been used commercially by Osaka Titanium Co. in Amagasaki, Japan. Multipolar cells of 1000 t/yr capacity are in operation. Energy consumption is about 9.5–10 kWh/kg of magnesium metal (111).

Research and development efforts have been directed toward improved cell designs, theoretical electrochemical studies of magnesium cells, and improved cathode conditions. A stacked-type bipolar electrode cell has been operated on a lab scale (112). Electrochemical studies of the mechanism of magnesium ion reduction have determined that it is a two-electron reversible process that is mass-transfer controlled (113). A review of magnesium production is found in Reference 114.

Beryllium. Beryllium [7440-41-7], Be, metal is produced by electrolysis of KCl–NaCl–$BeCl_2$ melts. Temperatures up to 900°C are required. Cell voltages are 6 to 9 V (115). Electrolysis of mixtures of beryllium oxide [1304-56-9], BeO, in lithium fluoride [7789-24-4], LiF, and beryllium fluoride [7787-49-7], BeF_2, has produced beryllium metal at about 700°C and 2.6 V (116). Details of fused salt metal winning processes are given in Table 7.

5. Electrochemical Waste Treatment

In many instances the metal processing industry produces aqueous effluents containing dissolved metals. Many of these metals are toxic and controlled by Environmental Protection Agency (EPA) regulations. Most water treatment plants do not remove toxic metals, or they concentrate the toxic metals in sludges that are classified as hazardous waste. Compliance with EPA regulations adds to overall production costs, and adversely affects the competitive viability of some plants. Therefore, the capital and operating costs for waste treatment systems should be as low as possible. Concentrations of the metals in wastewater are generally very low. The flow rates may be relatively high. Electrodes with large areas operating at low current densities are desirable for this application. Various porous electrodes, particulate-bed electrodes, fluidized-bed electrodes, and roll cells (117) have been developed for metals recovery from dilute wastewater streams. Electrochemical processing has advantages over other chemical processes (117) because the electrochemical process usually requires no addition of materials. Chemical processes require the addition of chemicals that usually expand the volume and complexity of the overall waste disposal process. Electrochemical processes for wastewater treatment often provide recovery of metal resources that partially offset processing costs (118,119). Silver has been recovered electrolytically from spent photographic liquors for many years (120) (see PHOTOGRAPHY). Silver recovery was motivated by economics. More recently, heavy-metal recovery has been motivated by environmental regulations (see HAZARDOUS WASTE TREATMENT; RECYCLING; SILVER AND SILVER ALLOYS).

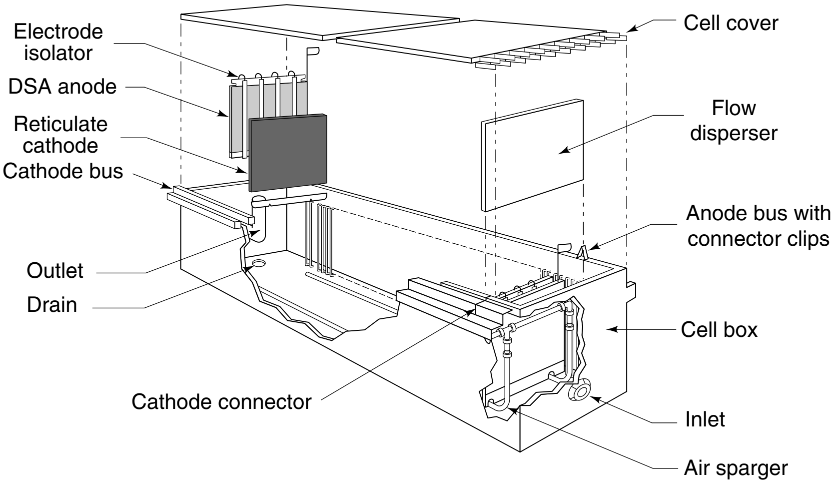

Fig. 9. Retec cell for heavy-metal recovery from wastewaters. (Courtesy of Eltech International Corp.)

In addition to metal recovery, which generally involves cathodic reduction, some waste may be treated by anodic oxidation processes. Many organic contaminants in wastewater can be oxidized by electrochemical treatments. High overvoltage anodes have been developed to improve the efficiency of these oxidations (121). Electrochemical oxidation of halogenated hydrocarbons has been achieved using barium peroxide [1304-29-6], BaO_2, in aqueous NaCl solutions. Cationic surfactants are used to suspend insoluble organic compounds and the BaO_2 (122). Carbon tetrachloride [56-23-5], CCl_4, has been oxidized by this system (123). Several cell systems are commercially available for wastewater treatment. One such cell system is that offered by Eltech International Corp. shown in Figure 9.

Electrolytically generated hypochlorite may be used for the oxidative destruction of cyanides (qv) or the sterilization of domestic wastes. Several on-site systems for swimming pool sterilization and municipal waste treatment works have been developed. One of these systems is described in Reference 124. On-site production and immediate use of chlorine is considered safer than the transportation of chlorine.

Some examples of electrochemical waste treatment are given in Table 8 (122,123,125–132). Other electrochemical processes such as electrodialysis (qv), electroflotation, and electrodecantation are also used in waste treatment.

6. Safety and Environmental Considerations

The electrochemical process industries are confronted with a wide range of hazards. These include electrical hazards, various explosion hazards, and the hazards associated with exposure to reactive chemicals.

Table 8. **Electrochemical Treatment of Wastewater**

Contaminant	Reaction	Source	Electrochemical system for treatment	References
Ag	$Ag^+ + e^- \longrightarrow Ag$	photographic fixers, etc	Eltech Retec cell	(126,127)
			Du Pont ESE cell	128
			Swiss roll cell	129
			rotating cylinder cell	125
Cu	$Cu^+ + 2\,e^- \longrightarrow Cu$	Cu plating rinse waters, etc	Swiss roll	129
			Du Pont ESE	128
			rotating cylinder	125
Fe	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	acidic coal mine waters	fixed-bed flow-through anode	130
Cr	recovery of CrO_3	Cr plating rinse water	Eltech Retec chrome recovery cell	131
Cr	$Cr(VI) + 3\,e^- \longrightarrow Cr(III)$	Cr plating wastewater	Swiss roll	129
organic compounds	oxidation	chemical process water	plate and frame filter press cell, SnO_2 anodes	121
phenol in water	oxidation	process wastewater	Pt anodes	132
halogenated	destructive oxidation	chemical process water	BaO_2 suspensions in aqueous	123
hydrocarbons			NaCl plus cationic surfactants at graphite anodes	122

6.1. Electrical Hazards. Electrical hazards include all those associated with both alternating and direct currents. Cell components carrying direct current are commonly exposed in cell rooms and tank houses. Most cell circuits are insulated from ground and designed to minimize potential difference from ground potential. A direct short to ground in an otherwise ungrounded circuit causes little if any damage. Strong magnetic fields exist in cell rooms. Safety rules generally prohibit magnetic and conductive materials beyond a specified length in the cell rooms. This is to avoid accidental contact with exposed electrical conductors.

6.2. Explosion Hazards. The electrolysis of aqueous solutions often lead to the formation of gaseous products at both the anode and cathode. Examples are hydrogen and chlorine from electrolysis of NaCl solutions and hydrogen and oxygen from electrolysis of water. The electrode reactions,

Anode $$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \quad (22)$$

or $$4\,OH^- \longrightarrow O_2 + 2\,H_2O + 4\,e^- \quad (23)$$

Cathode $$2\,H^+ + 2\,e^- \longrightarrow H_2 \quad (24)$$

are separated by a diaphragm or membrane to obtain pure products. Mixing of these gases is potentially dangerous because the range of explosive mixtures is very wide. This is clearly seen in Figure 10, which shows the explosion limits for chlorine–hydrogen–oxygen mixtures (133).

In chlor-alkali production the events that lead to a dangerous mixture of gases are dependent on the cell type. The following problems can lead to H_2–Cl_2 mixtures in diaphragm cells. Hydrogen may diffuse through thin spots in diaphragms. Hydrogen may escape through the diaphragms when anolyte levels fall

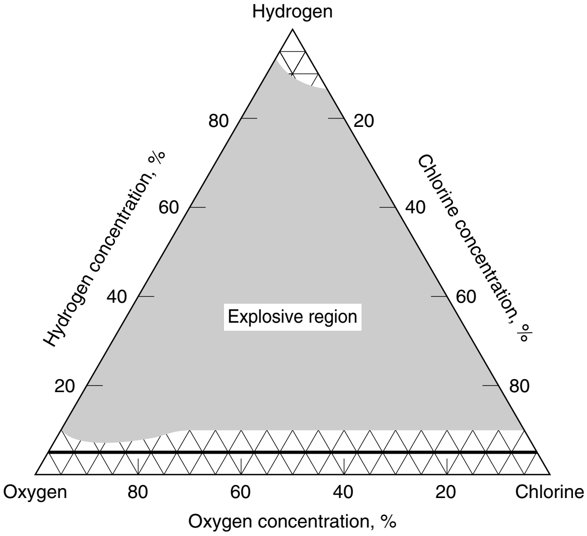

Fig. 10. Hydrogen–chlorine–oxygen explosive limits.

below the top of diaphragms. Excess back pressure from the hydrogen headers may force H_2 through the diaphragm. Metallic impurities in feed brine may precipitate in the alkaline diaphragm, become reduced to metals, and produce H_2 on the surface of the diaphragm. The normal operation of diaphragm cells produces chlorine containing 0.3 to 0.5% H_2. The drying, compression, and liquefaction of this chlorine produces an explosive mixture of Cl_2 and H_2 if dilution gases are not introduced into the system.

Chlorine–hydrogen hazards associated with mercury cells result from mercury pump failures; heavy-metal impurities, particularly those with very low hydrogen overvoltage, ie, Mo, Cr, W, Ni; excessively low pH of feed brine; low NaCl concentrations in feed brine; and poor decomposer operation, which leads to high sodium amalgam concentrations in the cell.

Membrane cells generally produce high quality chlorine. Higher than normal H_2 concentrations in Cl_2 indicate that holes exist in the membrane.

Modern cells for sodium chlorate production are diaphragmless. Hydrogen produced at the cathode is recovered and used as fuel or for higher value uses. The composition of gases from the cells is normally about 97.5% H_2, 2% O_2, and 0.5% Cl_2. These cells must operate at high current efficiencies to avoid dangerous H_2–Cl_2–O_2 mixtures. Conditions that cause explosive mixtures in these cells include low chloride concentrations, inadequate chromate concentrations, impurities that catalyze the decomposition of hypochlorite to chloride and oxygen, and loss of electric power. Gases released from chlorate cell liquors are particularly dangerous. Tanks for these liquors are either open-top tanks or tanks that are purged with air or nitrogen. Liquors exiting chlorate cells contain dissolved H_2, very small H_2 bubbles, and hypochlorite. The escape of H_2 and the decomposition of hypochlorite to produce O_2 can produce explosive mixtures above chlorate liquors. Most modern cell plants have automatic air or nitrogen purges on cells and other critical equipment. Instrumentation usually includes continuous on-stream gas analyzers, alarms, and automatic purge systems.

When hydrogen recovery is unsafe or otherwise impractical it is vented into the cell room or tank house. The light weight and high diffusion rate of hydrogen and good cell room ventilation have made this an accepted practice.

Explosions have occurred in aluminum and magnesium plants as a result of molten metals coming into contact with water (134).

6.3. Reactive Chemicals Exposure. The hazards associated with exposure to reactive chemicals vary with the chemicals produced. The multitude of chemicals produced electrochemically precludes a detailed discussion of these hazards. Material Safety Data Sheets (MSDS) are available from suppliers. Anyone contemplating the production of a chemical must become thoroughly familiar with all safety, health, and environmental aspects of such production.

Technical and trade organizations are concerned with safety and the environment. The Chlorine Institute in North America and Euro Chlor in Western Europe are examples of organizations dedicated to the safe production, transport, and use of chlorine. Hazard and operability studies (HAZOP) reviews for new designs, plants, and expansions (135) have become required by policy in many operating companies. Papers on safety and environmental subjects are given at most technical meetings (136–138).

Access to cell rooms is usually restricted to authorized personnel. Required personal safety equipment includes rubber shoes or overshoes, goggles, hard hat, and some sort of emergency respirator. Safety training courses are generally required before one is allowed to enter a cell house without a guide.

The Chemical Manufacturers Association (CMA) and its members are also concerned about health, safety, and environmental problems. Responsible Care(139), a program initiated by the CMA in 1988, is designed to make day-by-day improvements in all aspects of health, safety, and the environment.

Although the electrolytic process industries are confronted with a wide range of hazards, their safety record has been excellent. The U.S. Bureau of Labor has reported lost work days (injuries and illnesses) per 100 full-time workers for the year 1990 (140).

7. Economic Aspects

Some electrochemicals are produced in very large quantity. Chlorine and sodium hydroxide production in 1991 were 10,727,000 t and 11,091,000 t, respectively (1). Aluminum was produced at the rate of 4,100,000 t/yr and had an annual market value of about $5.4 billion. Other electrochemically produced products are required in smaller volume. The production of the metals cadmium, lithium, and nickel were at the rates of 1600 t, 2800 t, and 8400 t, respectively for 1991 (see Table 1). Electrochemical processing plants produce a variety of products in a wide range of capacities.

Most large electrochemical processing facilities are located where raw materials, including electric power, are readily available at reasonable costs. Other factors influencing the location of electrochemical plants are proximity to markets, established transportation facilities, availability of water, and a source of labor. Large electrochemical plants are capital intensive, requiring large capital investment cost per employee.

The total annual value of products produced by electrochemical processing (see Table 1) is roughly $18 billion. Electric power production in 1990 was 2908×10^9 kW·h (9). Production of electric power increased about 2% in 1991 (4) although the economy was in a recession; thus, electric power production in 1991 was about 2966×10^9 kW·h. About 5% of the total electric power produced is used by the electrochemical process industries. Published industrial rates for electric power ranged from a low of 4.15 ¢/kW·h from Public Service of Oklahoma to a high of 11.1 ¢/kW·h from Long Island Lighting (4). Many of the largest plants have long-term electric power contracts at considerably lower power cost. Electric power cost is the largest single cost item in producing most large-volume electrochemicals.

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