Kirk-Othmer Encyclopedia of Chemical Technology.

OXYGEN-GENERATION SYSTEMS

Oxygen (qv) generation from oxygen-containing compounds is used for systems for respiratory support in submarines, aircraft, spacecraft, and bomb shelters, as well as in breathing apparatus (1). Convenience and reliability, rather than low cost, are stressed. Discussed herein are systems primarily based on chlorates, perchlorates, peroxides, and superoxides (see Chlorine oxygen acids and salts; Perchloric acid and perchlorates; Peroxides and peroxide compounds). It does not include oxygen-separation systems or photosynthesis.

1. Chlorates and Perchlorates

The chlorates and perchlorates of lithium, sodium, and potassium evolve oxygen when heated. These salts may be compounded with a fuel to form a chlorate-based candle that produces oxygen by a continuous reaction. Components include the oxygen-producing material, a fuel, a material which fixes traces of chlorine, and usually an inert binder. Once the reaction begins, oxygen is released from the hot salt by thermal decomposition. A portion of the oxygen reacts with the fuel to produce more heat resulting in production of more oxygen, and so on.

Relevant properties of the chlorates are given in Table 1. Sodium chlorate is generally used. The lithium and potassium salts are more expensive and present some problems in maintaining candle integrity during use. Lithium chlorate is also difficult to dry. However, a lithium perchlorate candle of very high oxygen storage density has been described (2).

Chlorate candles are quite stable. While normally hermetically sealed, these candles have been stored uncontained for as long as 20 years, and then operated successfully with no loss of oxygen output. Thus, they are well suited as emergency oxygen-generation systems (3). Chlorate candles also produce oxygen under pressure and, therefore, can be stored in or operated from pressurized cylinders.

1.1. Materials and Reactions

Candle systems vary in mechanical design and shape but contain the same generic components (Fig. 1). The candle mass contains a cone of material high in iron which initiates reaction of the solid chlorate composite. Reaction of the cone material is started by a flash powder train fired by a spring-actuated hammer against a primer. An electrically heated wire has also been used. The candle is wrapped in insulation and held in an outer housing that is equipped with a gas exit port and relief valve. Other elements of the assembly include gas-conditioning filters and chemicals and supports for vibration and shock resistance (4).

A fuel provides heat upon reaction with some of the generated oxygen. Whereas a variety of powdered elements, eg, Fe, B, Al, Co, etc, have been used with varying degrees of success, iron is the universal choice for commercial applications. Some of the oxygen from the chlorate decomposition combines with the iron to generate heat to effect decomposition of the chlorate, leaving a mixture of iron oxides (3). Generalized principle

Table 1. Chlorates and Perchlorates as Sources for Oxygen

Substance	Molecular formula	CAS Registry Number	Mp, °C	Decomp., °C[a]	Oxygen density g/g cmpd	Oxygen density g/cm³[b]
lithium chlorate	$LiClO_3$	[13453-71-9]	129	270	0.53	1.39
sodium chlorate	$NaClO_3$	[7775-09-9]	261	478	0.45	1.12
potassium chlorate	$KClO_3$	[3811-04-9]	357	400	0.39	0.93
lithium perchlorate	$LiClO_4$	[7791-03-9]	247	410	0.60	1.46
sodium perchlorate	$NaClO_4$	[7601-89-0]	471	482	0.52	1.31
potassium perchlorate	$KClO_4$	[7778-74-7]	585	400	0.46	1.17
oxygen liquid	O_2				1.0	1.14
at 52 MPa[c]					1.0	0.58
hydrogen peroxide	H_2O_2	[7722-84-1]	−89		0.94	1.37
water	H_2O		0		0.89	0.80

[a] Without catalyst.
[b] Based on crystal densities.
[c] To convert MPa to psi, multiply by 145.

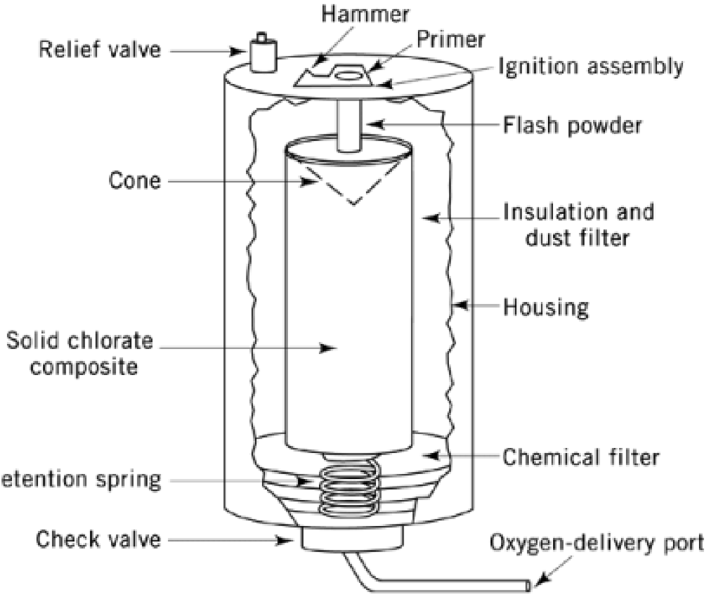

Fig. 1. Cutaway view of generator housing.

reactions are as follows:

$$2\ NaClO_3 \longrightarrow 2\ NaCl + 3\ O_2$$

$$2x\ Fe + y\ O_2 \longrightarrow 2\ Fe_xO_y$$

where Fe_xO_y represents an intermediate between FeO, Fe_3O_4, and Fe_2O_3. An additional endothermic minor reaction is

$$4\ NaClO_3 \longrightarrow 2\ Na_2O + 2\ Cl_2 + 5\ O_2$$

A bleach odor, usually produced during oxygen evolution, is attributed to chlorine-containing compounds, eg, chlorine dioxide or elemental chlorine. These materials are undesirable for breathing oxygen. Thus barium peroxide [1304-29-6] (2–5 wt %) is usually added to the candle mix to scavenge these materials. Some oxygen evolves from this reaction, producing barium chloride (5).

Glass fiber or steel wool are used as binders to improve structural integrity, and account for 4–5 wt % of the candle. The burning zone is reinforced so that the ash and the unused portions cohere. Binders may also enhance oxygen generation. Glass fiber is generally used. In the past, asbestos (qv) was employed, but asbestos catalyzes evolution of chlorine and is unsuitable for breathing apparatus. Steel wool acts as both binder and fuel, but results in a hotter burning candle.

Basic oxides of metals such as Co, Mn, Fe, and Cu catalyze the decomposition of chlorate by lowering the decomposition temperature. Consequently, less fuel is needed and the reaction continues at a lower temperature. Cobalt metal, which forms the basic oxide *in situ,* lowers the decomposition of pure sodium chlorate from 478 to 280°C while serving as fuel (6, 7). Composition of a cobalt-fueled system, compared with an iron-fueled system, is 90 wt % NaClO, 4 wt % Co, and 6 wt % glass fiber vs 86% NaClO, 4% Fe, 6% glass fiber, and 4% BaO. Initiation of the former is at 270°C, compared to 370°C for the iron-fueled candle. Cobalt hydroxide produces a more pronounced lowering of the decomposition temperature than the metal alone, although the water produced by decomposition of the hydroxide to form the oxide is thought to increase chlorine contaminate levels. Alkaline earths and transition-metal ferrates also have catalytic activity and improve chlorine retention (8).

1.2. Oxygen Purity

Impurities in oxygen-generating systems that have been identified are the chlorine-containing compounds, CO, CO_2, H_2O, and simple organics. All can be minimized by using high purity ingredients and control of moisture, or by gas conditioning. Aside from the chlorate and barium peroxide, materials are degreased by heating at 472°C before manufacture. Iron powders usually are reduced with hydrogen.

Carbon, present in iron or remaining after inadequate degreasing, can form CO or CO_2. Carbon particles may occur in the chlorate if graphite anodes were used in the production process. Additionally, barium peroxide contains carbonate as a contaminant.

Water in the candles influences the evolution of chlorine and chlorine dioxide (9, 10). Hydrogen chloride generated from trace impurities in the chlorate can react to produce the same compounds.

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

$$5\ NaClO_3 + 6\ HCl \longrightarrow 6\ ClO_2 + 3\ H_2O + 5\ NaCl$$

Hydrocarbon impurities can be introduced by contamination of the outer surface of the candle if mold release compounds are used. Candles are sometimes shaved to reduce such contamination.

The purity of oxygen from chlorate candles before and after gas filtration is indicated in Table 2. A particulate filter is always used. Filter chemicals are Hopcalite, which oxidizes CO to CO_2; molecular sieves (qv), which remove chlorine compounds; and basic materials, eg, soda lime, which removes CO_2 and chlorine compounds. Other than H_2O and N_2, impurity levels of <1 ppm can be attained. Moisture can be reduced by

Table 2. Impurity Levels in O_2 from Chlorate Candles

	Quantity, ppm	
Impurity	Unfiltered	Filtered
H_2O	1000	1000
CO	5–25	1
CO_2	50–400	5
Cl_2	2–10	0.2
hydrocarbon	2	1

using a desiccant (see Desiccants). Gas purity is a function of candle packaging as well as composition. A hotter burning unit, eg, one in which steel wool is the binder, generates more impurities.

1.3. Candle Fabrication

All ingredients must be contaminant-free (especially grease) and the chemical materials must be dry. The oxygen-generating mass is made by mixing and then pressing or casting the ingredients. Care must be exercised to assure thorough mixing or reaction rates can vary throughout the candle. Shape can be varied as desired, especially if casting is used. With pressing, the shape is limited to some extent, although hydrostatic pressing provides freedom in candle form. All other factors being equal, the rate of oxygen evolution is directly proportional to the cross-sectional area of the unit. Some oxygen evolution rate control can be achieved using graded compositions along the length of the candle (7, 11).

Casting is done by heating the ingredients to just above the melting point of the chlorates, eg, 261°C for sodium chlorate. Materials that do not become molten must remain in suspension to maintain a constant composition throughout the cast candle. When the mixed slurry is poured into the mold some settling may occur, depending on the length-to-diameter ratio of the mold. Some items may be cast on their sides, rather than upright to reduce settling in deep molds. Cast items are characterized by high density and maximum resistance to breaking.

Pressing can be done at room temperature using a damp mix or at elevated temperature using finely divided materials. Hydrostatic pressing can be done. For a length-to-diameter ratio of ca 2:1, wet pressing is satisfactory. Units used by the U.S. Navy are ca 17.8 cm in diameter and ca 30.5 cm long, and are produced by pressing a composition containing ca 1.5 wt % water to ca 28 MPa (4060 psi). They are dried to ca 0.5 wt % moisture before packaging for shipment.

Hot pressing has been used, especially for smaller shapes. No moisture is added to the mix, and generally the materials are more finely divided than in cold pressing. The mixture and molds are heated to ca 200°C and pressed as required. Room temperature pressing can sometimes be done using very finely divided materials, eg, ca 0.04-mm (300-mesh) particle size, but the mechanical integrity of the candle is poor. This process is considered for low cost production for special applications. In any pressing technique, density gradations along the length of the candle produce differences in burning rates. Excessive pressure and densification can result in nonfunctioning of the candle.

Reaction can be initiated by several means, all of which depend on delivery of heat at a relatively high temperature to a starting cone. Cartridge-actuated and electric match units are usually used. The former is in the majority. A water-activated unit has been described (12). The heat generated by the starting device initiates reaction in a cone, which is a small amount of candle that is higher in fuel content, eg, 30 wt % iron. Compared to the candle composition, more heat is generated per unit mass and smaller amounts of oxygen are evolved.

Cones usually are pressed. These are easier to ignite than cast cones. Pressure used for cone formation is considerably lower than that used for candle formation to prevent excessive densification. The preformed cone can be added to the mold before pressing or casting the body of the candle, being held in place by the resulting bond. Alternatively, a cavity is pressed into the formed candle, and cone material is added and pressed into place. The bond formed by this method is weak but generally sufficient for most purposes.

1.4. Operational Characteristics

Oxygen generation from chlorate candles is exothermic and management of the heat released is a function of design of the total unit into which the candle is incorporated. Because of the low heat content of the evolved gas, the gas exit temperature usually is less than ca 93°C. Some of the heat is taken up within the candle mass by specific heat or heat of fusion of the sodium chloride. The reacted candle mass continues to evolve heat after reaction ends. The heat release during reaction is primarily a function of the fuel type and content, but averages 3.7 MJ/m^3 (100 Btu/ft^3) of evolved oxygen at STP for 4–8 wt % iron compositions.

The oxygen release rate is directly proportional to the cross-sectional area of the candle for a specific composition and also depends on the linear burn rate. Lower fuel contents decrease the burn rate slightly, eg, ca 2 wt % iron is the lower limit for reliable room temperature operation. Low temperature starts require at least 3.5 wt % iron. Another factor is direction of flow of the evolved gas. If the hot oxygen flows over the unburned portion of the candle, as much as 15% rate increases can be produced. The burn time is halved for each 3.4 MPa (500 psi) pressure rise. The highest pressure that can be produced is ca 138 MPa (20,000 psi).

1.5. Uses

A primary early use was the incorporation of a small cast candle in a quick-start canister, which was filled with potassium superoxide [12030-88-5] and used in a portable breathing apparatus. The candle rapidly produced an initial supply of oxygen until the superoxide became fully activated, particularly at lower temperatures. Large candles, delivering 3–4 m^3 (120 ft^3) oxygen in 45 minutes, are used in long-duration submergence submarine operation. A furnace holds a stack of two candles; the upper one is ignited, which subsequently ignites the lower one. Together these furnish enough oxygen for 120 people for 1.5 hours.

Special uses include oxygen for fuels intended for long-term unattended service (13). Candles are fired on demand by a pressure sensor in the oxygen accumulator. Chlorate candles were incorporated into backpacks designed for use in the Apollo moon missions (14).

A large-scale use of chlorate candles is oxygen supply in the event of decompression in passenger aircraft (15). Candles meet the requirements of no maintenance (qv), no oxygen leakage, high reliability, and long (15-yr min) storage life. Both percussion cap and electrical ignition are used. Candle sizes vary, supplying up to five passengers from one unit. A system for the U.S. Army is a 12-candle array that maintains pressure in an oxygen accumulator bottle for a helicopter crew. Operation is completely automatic.

In projecting uses for candles, the characteristics to be considered are volumetric oxygen density that is nearly equal to that of liquid oxygen, development of extremely high pressure, high oxygen purity, long storage life with no leakage, preprogrammed oxygen delivery, and heat release. General parameters are given in Table 3.

2. Peroxides and Superoxides

Whereas chlorate candles produce oxygen, devices made with peroxides and superoxides produce oxygen and absorb carbon dioxide. For every volume of oxygen that a person inhales, 0.82 volumes of carbon dioxide are exhaled giving a respiratory coefficient (RQ) of 0.82. An oxygen-generation device used in a closed system

Table 3. Chlorate Oxygen-Generator Parameters

Parameter	Value
average composition[a], wt %	
$NaClO_3$	80–85
Fe	3–10
BaO_2	4
O_2 available[b], wt %	40
sp gr of mixture	2.3–2.5
average reaction rate through shape, cm/min	0.64
heat evolution, J/g[c]	837
reaction zone temperature, °C	538
shape of chlorate unit	unlimited
starting method	hot wire, Bouchon cup
cone material[d], wt %	
Fe	30
$NaClO_3$	60
time before O_2 evolved[b], s	1
gas purity, %	>99.8

[a] Remainder is binder.
[b] Value is maximum.
[c] To convert J to cal, divide by 4.184.
[d] Remainder is binder and BaO_2.

Table 4. Peroxides and Superoxides as Oxygen Sources[a]

			Quantity of gas, kg/kg cmpd				
Substance	Molecular formula	CAS Registry Number	O_2	CO_2[b]	RQ[c]	Unstable above, °C	Mp, °C
lithium peroxide	Li_2O_2	[12031-80-0]	0.35	0.96	1.94	315	315
sodium peroxide	Na_2O_2	[1313-60-6]	0.21	0.56	1.94	311–400	596
sodium superoxide	NaO_2	[12034-12-7]	0.43	0.40	0.67	100	[d]
potassium superoxide	KO_2	[12030-88-5]	0.34	0.31	0.67	145–425	440
calcium superoxide	$Ca(O_2)_2$	[12133-35-6]	0.46	0.42	0.67	200[e]	

[a] Ref. 16
[b] To form carbonate.
[c] Respiratory quotient.
[d] Forms series of solid solutions; forms Na_2O_2 at 250°C.
[e] Value is estimated.

should mirror this RQ, ie, absorb 0.82 volumes of carbon dioxide for each 1.0 volume of oxygen liberated. However, even complete recovery of oxygen from the carbon dioxide which is exhaled is not sufficient to sustain human life. Thus, long-term space flight requires additional oxygen, usually supplied by electrolysis of water.

The relevant properties of peroxide and superoxide salts are given in Table 4 (see Peroxides and peroxide compounds, inorganic). Potassium peroxide is difficult to prepare and lithium superoxide is very unstable. The ozonides, MO_3, of the alkali metals contain a very high percentage of oxygen, but are only stable below room temperature (see Ozone).

2.1. Peroxides

In the presence of lithium peroxide, both water and carbon dioxide react, resulting in evolution of oxygen. The following steps have been postulated (17):

$$Li_2O_2 + 2\ H_2O \longrightarrow 2\ LiOH + H_2O_2$$

$$2\ LiOH + CO_2 \longrightarrow Li_2CO_3 + H_2O$$

$$H_2O_2 \longrightarrow H_2O + 0.5\ O_2$$

$$Li_2O_2 + CO_2 \longrightarrow Li_2CO_3 + 0.5\ O_2$$

Because of the delay in decomposition of the peroxide, oxygen evolution follows carbon dioxide sorption. A catalyst is required to obtain total decomposition of the peroxides; 2 wt % nickel sulfate often is used. The temperature of the bed is the controlling variable; 204°C is required to produce the best decomposition rates (18). The reaction mechanism for sodium peroxide is the same as for lithium peroxide, ie, both carbon dioxide and moisture are required to generate oxygen. Sodium peroxide has been used extensively in breathing apparatus.

All the peroxides are colorless and diamagnetic when pure. Traces of the superoxide in technical-grade sodium peroxide impart a yellow color. Storage containers must be sealed to prevent reaction with atmospheric carbon dioxide and water vapor.

2.2. Superoxides

The superoxides are colored and paramagnetic: KO_2 is yellow, NaO_2 is orange-yellow, and $Ca(O_2)_2$ is red. In uses as oxygen suppliers and carbon dioxide scrubbers, these materials are demand chemicals, ie, react to the load imposed by generating more oxygen as more water is introduced. Reactions during use, where M is monovalent, are reaction with water to liberate oxygen and then reactions involving carbon dioxide:

$$2\ MO_2 + H_2O \longrightarrow 2\ MOH + 1.5\ O_2$$

$$2\ MOH + CO_2 \longrightarrow M_2CO_3 + H_2O$$

$$2\ MOH + 2\ CO_2 \longrightarrow 2\ MHCO_3$$

Some moisture must be present to promote these reactions. Dry carbon dioxide does not react with the superoxides. One mole of MO_2 yields 1.5 mol oxygen and then absorbs one mole of carbon dioxide to form carbonate, or two moles to form bicarbonate. Thus, if only carbonate is formed, an RQ of 0.67 is reached; if only bicarbonate is formed, an RQ of 1.33 results. The required stoichiometry for an RQ of 0.82 is.

$$2\ MO_2 + 1.23\ CO_2 + 0.23\ H_2O \longrightarrow 0.77\ M_2CO_3 + 0.46\ MHCO_3 + 1.5\ O_2$$

By control of the bed temperature and of the moisture content of the inlet gas, some control over the ratio of carbonate to bicarbonate can be obtained.

Potassium superoxide, the most commonly used superoxide of the alkali metals, is produced by spraying the molten metal into dry air. The superoxide is formed as a fine yellow powder which is processed to the desired size. Copper oxychloride is added to activate the superoxide at low temperatures. Sodium superoxide is produced from an open-pore sodium peroxide which is produced by spraying liquid sodium into dry air. Oxygen at 13.8 MPa (2000 psi) and 400°C is used to oxidize the peroxide to the superoxide. The material then can be pressed and regranulated as required. Calcium superoxide has been produced to 65% purity by careful dehydration of $CaO_2{\cdot}2H_2O_2$ (19). Calcium superoxide is of interest for breathing apparatus because calcium hydroxide has a higher melting point than the hydroxides of potassium or sodium, and calcium superoxide is less sensitive to water (20).

2.3. Analytical Methods

Analysis of fresh and spent peroxides and superoxides is done by adding the material to water. Approximately 0.1 wt % permanganate is used in the water to decompose the peroxide ion which otherwise forms. The evolved oxygen is measured volumetrically. If the material is spent, the base strength is titrated to a phenolphthalein end point, acidified further, and the carbon dioxide is determined volumetrically.

2.4. Uses

The peroxides and the superoxides must be hermetically sealed for storage. The superoxides especially are strong oxidizing agents and should be kept away from grease, oil, and organic materials. In general, sodium peroxide is used more widely than lithium peroxide. A breathing apparatus based on peroxides often is supplied with bottled oxygen, because the peroxides are not very oxygen-weight efficient.

Superoxides are used in breathing applications requiring no auxiliary source of oxygen. Sodium superoxide is ca 10 times as expensive as potassium superoxide because high temperature, high pressure autoclaves are required for its production. Use of calcium superoxide is experimental. Potassium superoxide is the most commonly used superoxide oxygen generator.

Portable breathing apparatus are used by fire departments, damage-control teams, and workers in unbreathable atmospheres (21). The wearer uses a canister containing the chemical, a breathing bag, and a mask. The chemical is packaged as 4.8–9.5-mm (2–4-mesh) granules with glass fiber filters which trap any dust. Approximately three breaths are required to start the chemical reaction and deliver oxygen. Alternatively, a small chlorate candle can be used to deliver oxygen immediately.

In portable breathing apparatus, efficiency is ca 70% in terms of oxygen used by the wearer vs total available; 30% is associated with excessive water vapor which is generated at high work rates and vented to ambient. At low work rates, efficiency is as high as 95%. The same canister of KO_2 sustains the oxygen needs of a person at hard work for an hour or for seven hours if the person is resting. Superoxides are valuable because these evolve only as much oxygen as is required. When a chlorate candle is used, the candle must be sized for the maximum work rate, resulting in waste of oxygen at lower work rates.

Numerous physical forms of the oxygen-generating chemical can be used, eg, granules of various sizes, densities, and porosities or plates pressed from powder. Granules are produced by pressing, grinding, and screening KO_2. Plates are made by pressing the powdery KO_2 to a coherent mass but not so as to impede penetration of the gases (22).

In air conditioning (qv) of closed spaces, a wider latitude in design features can be exercised (23, 24). Blowers are used to pass room or cabin air through arrays of granules or plates. Efficiencies usually are 95% or better. The primary limiting factor is the decreased rate of absorption of carbon dioxide. However, an auxiliary small CO_2 sorption canister can be used. Control of moisture entering the KO_2 canister extends the life of the chemical and helps maintain the RQ at 0.82.

Generally the systems operate in the gas phase, but a system in which the superoxides react with liquid-phase water and absorb CO_2 in the resultant KOH solution has been built (25). The RQ is fixed at 0.67.

An unusual application is the use of KO_2 in a closed-cycle diesel system. Oxygen is supplied and CO_2 is removed in a KO_2 bed, through which the exhaust is recycled to the engine. Such a system would supply power in undersea and nonatmospheric operations.

The superoxides compare well with a combination of liquid oxygen or gaseous oxygen systems and a CO_2 scrubber, eg, LiOH. Heat release is somewhat less than the combination system, and the volume of superoxides which is required is roughly equivalent to that of lithium hydroxide.

On-board oxygen-generation (OBOG) systems are used in military aviation. The OBOG systems obviate the use of stored liquid oxygen or high pressure gaseous oxygen. In OBOG systems, oxygen is separated from air using chelating agents (qv), (26, 27), ion exchange (qv) (27), barium oxide–dioxide shift (27), or molecular sieves (qv). Commercial units supplying therapeutic oxygen are also available (28, 29).

3. Other Chemical Systems

Regenerative systems that dissociate carbon dioxide to recover the oxygen are of interest to the U.S. space program and in long-duration habitat support. The Bosch process utilizes an iron catalyst for the single-step reaction of hydrogen, carbon dioxide, water, and carbon at 700°C. Oxygen is produced by water electrolysis, and the hydrogen is recycled to the Bosch reactor. Carbon is removed as a solid.

$$CO_2 + 2\,H_2 \longrightarrow 2\,H_2O + C$$

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

In the Sabatier reaction, methane and water are formed over a nickel– nickel oxide catalyst at 250°C. The methane is recovered and cracked to carbon and hydrogen, which is then recycled:

$$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O$$

$$CH_4 \longrightarrow C + 2\,H_2$$

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

A fused-salt electrolysis process has been demonstrated (30). Carbon dioxide is introduced to the cathode area of a melt of 60 wt % LiCl–40 wt % Li_2CO_3 at 550°C. The carbon dioxide reacts with lithium oxide which is produced by electrolysis. Oxygen is released at the anode and carbon plates onto the cathode. The reaction requires a potential of 4.5 V. The reactions are as follows:

$$\textit{Cathode} \qquad 4\,Li^+ + 4\,e^- \longrightarrow 4\,Li$$

$$4\,Li + Li_2CO_3 \longrightarrow C + 3\,Li_2O$$

$$\textit{Anode} \qquad 2\,CO_3^{2-} \longrightarrow 2\,CO_2 + O_2 + 4\,e^-$$

$$CO_2 + Li_2O \longrightarrow Li_2CO_3$$

$$\textit{Total reaction} \qquad 4\,Li^+ + 2\,CO_3^{2-} \longrightarrow 2\,Li_2O + C + CO_2 + O_2$$

Although these other chemical systems are feasible chemically, there has been little impetus to solve associated equipment problems. The Bosch reaction appears to be the most promising.

Hydrogen peroxide can be dissociated over a catalyst to produce oxygen, water, and heat. It is an energetic reaction, and contaminants can spontaneously decompose the hydrogen peroxide. Oxygen from water electrolysis is used for life support on submarines.

4. Health and Safety

Peroxides, superoxides, and chlorates are oxidizing compounds and should not contact organic materials, eg, oil, greases, etc. This is especially true while oxygen is being produced. Caustic residues that may remain after use of peroxides and superoxides require disposal appropriate to alkali metal hydroxides. Spent candles containing barium may require special disposal considerations.

Dusts associated with these oxidizing compounds produce caustic irritation of skin, eyes, and nasal membranes. Appropriate protection should be worn when handling. Skin contact should be treated as for any caustic material, ie, flush with water and neutralize. Toxicity is low to moderate and is the same as for the hydroxides. Toxicity of the chlorate is greater than for the peroxides and superoxides, and the chlorate material also causes local irritation.

Properly designed respiratory support equipment is configured to safely contain the oxygen-generating chemicals. These systems, when hermetically sealed, are stable to storage and safe to use.

5. Economic Aspects

Potassium superoxide is utilized primarily in respiratory support equipment. The material is produced in the United States (Callery Chemical Company), France (Air Liquide), and China.

The large candles used by the U.S. Navy have been produced in the United States by three companies, Mine Safety Appliances Company, Puritan-Bennett Corporation, and Scott Aviation. These sell for \$50–\$60. Production is less than 10,000/yr. Smaller candles incorporated in breathing apparatus are produced by equipment suppliers. Production quantities are tied to the number of complete units and the candles are a small percentage of the total price. Production for aircraft oxygen supply during a decompression incident is about 50,000 units per year. In the United States, Puritan-Bennett and Scott Aviation are the primary suppliers as is Draeger in Germany.

BIBLIOGRAPHY

"Oxygen Generation Systems" in *ECT* 2nd ed., Suppl. Vol., pp. 658–667, by J. W. Mausteller, MSA Research Corp.; "Oxygen-Generation Systems" in *ECT* 3rd ed., Vol. 16, pp. 673–683, by J. W. Mausteller, MSA Research Corp.

Cited Publications

1. E. B. Thompson, Jr., *An Investigation of the Chemical Formulation of Solid Chemical Oxygen Generators for Aircraft Emergency Oxygen Supply*, AFFDL-TM-70-4-FEFE, Flight Dynamics Laboratory, Wright-Patterson Air Force Base, Ohio, Sept. 1970.
2. U.S. Pat. 3,174,936 (Mar. 23, 1965), P. R. Gustafson and R. R. Miller (to U.S. Government).
3. W. H. Schecter, R. R. Miller, R. M. Bovard, C. B. Jackson, and J. R. Pappenheimer, *Ind. Eng. Chem.* **42**, 2348 (1950).
4. V. Hwoschinsky, *Safe Eng.* **4**(2), 21 (1970).
5. Y. Zhang, G. Kshirsagur, and J. Cannon, *Ind. Eng. Chem. Res.* **32**, 966 (1993).
6. W. J. O'Reilly and co-workers, *Development of Sodium Chlorate Candles for the Storage and Supply of Oxygen for Space Exploration Applications*, Rept. No. 69-4695, Air Research Corp., Los Angeles, Calif., July 1969.
7. U.S. Pat. 5,338,316 (Aug. 16, 1994), Y. Zhang and J. Cannon (to Puritan-Bennett Corp.).
8. U.S. Pat. 5,049,306 (Sept. 17, 1991), J. Greer (to Mine Safety Appliances Co.).
9. H. Nagate, K. Kusomoto, and N. K. Makai, *J. Ind. Explos. Soc. Jpn.* **27**, 99 (1966).
10. P. R. Gustafson, S. H. Smith, Jr., and R. R. Miller, *Chlorate Candle Fabrication by Hot Pressing*, NRL Rept. 5732, AP No. 272580, Naval Research Laboratory, Washington, D.C., Jan. 1962.
11. U.S. Pat. 5,198,147 (May 30, 1993), Y. Zhang and J. Cannon (to Puritan-Bennett Corp.).
12. U.S. Pat. 3,861,880 (Jan. 21, 1975), T. Thompson (to Dow Chemical Investment and Finance Corp.).
13. J. W. Mausteller and M. J. McGoff, MSA Research Corp., unpublished data, 1968.
14. R. N. Prince, T. L. Illes, and W. J. O'Reilly, "Development of the Portable Environment Control System," *Conference on Portable Life Support Systems*, NASA-Ames Research Center, Moffett Field, Calif., Apr. 1969.
15. *Exploratory Study of Potassium and Sodium Superoxides for Oxygen Control in Manned Space Vehicles*, Contract No. NASW-90, MSA Research Corp., Evans City, Pa., Mar. 1962.
16. *New Sci.* **27**, 628 (1970).
17. M. M. Markowitz and E. W. Dezmelyk, *A Study of the Application of Lithium Chemicals to Air Regeneration Techniques in Manned Sealed Environments*, AMRL-TDR-64-1, Wright-Patterson Air Force Base, Ohio, Feb. 1964.
18. K. J. Dressler and R. N. Prince, "Lithium Peroxide for Portable Life Support System Atmospheric Regeneration," *Conference on Portable Life Support Systems*, NASA-Ames Research Center, Moffett Field, Calif., Apr. 1969.
19. E. V. Ballan, P. C. Wood, L. A. Spitze, and T. Wydeven, paper presented at *The Intersociety Conference on Environmental Systems*, ASME, San Diego, Calif., July 12–15, 1976.
20. P. Wood, L. Spitze, and T. Wydeven, *The Use of Superoxides for Hyperbaric Air Revitalization*, NASA Technical Briefs ARC-11695, 1986.

21. K. Kyriazi and J. Shubilla, Rl 8876, *Performance of Oxygen Self-Rescurers* U.S. Department of the Interior, U.S. Bureau of Mines, Washington, D.C., 1984.
22. J. W. Mausteller, M. J. McGoff, D. A. Keating, and K. Weiswurn, paper presented at *36th Aerospace Medical Association Meeting*, New York, Apr. 1965.
23. J. Presti, H. Waalman, and A. Petrocelli, *Undersea Technol.* **8**(6), 20 (1967).
24. H. M. David, *Missiles Rockets* **9**(15), 30 (1961).
25. T. V. Bolles and H. Wallman, *Aerosp. Med.* **37**, 675 (1966).
26. A. J. Adduci, *Chemtech*, 575 (Sept. 1976).
27. R. Tallman, B. Seberg, and S. Budzynaki, *On-Board Oxygen Generating Systems*, Final Report on Contract N62269-72-C-0144 by Grumman Aerospace Corp. for Naval Air Development Center, Oct. 1972.
28. U.S. Pat. 4,545,790 (Oct. 8, 1985), G. Miller and S. Clark (to Bio-Care, Inc.).
29. U.S. Pat. 4,561,287 (Dec. 31, 1985), R. Rowland (to Hudson Oxygen Therapy Sales Co.).
30. R. E. Shearer, J. C. King, and J. M. Mausteller, *Aerosp. Med.* **33**, 213 (1962).

J. WILSON MAUSTELLER
Consultant

Related Articles

Oxygen; Chlorine oxygen acids and salts; Perchloric acid and perchlorates; Peroxides and peroxides compounds