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CHEMICAL OXYGEN
GENERAL INFORMATION

1. HISTORICAL BACKGROUND

Oxygen production by thermal decomposition of alkali metal chlorates has been known for many decades. Practical application of this principle dates to before World War II, when attempts were made to utilize such chlorates as a source of aviators' breathing oxygen. The oxygen so produced did not fully meet purity standards; however, this early work did highlight the basic advantage of chemically generating oxygen using solidified chlorates, the specific advantage being compactness, ease of handling, and long-term stability.

After subsequent developmental effort, the chlorates gained U. S. Navy acceptance and were successfully used, initially for emergency oxygen supply, and then as the main supply aboard Navy submarines, where they were designated "candles." As the production of Navy "candles" grew to many thousands, the oxygen produced was found to be physiologically acceptable. A number of excellent articles were written describing both the history and the fundamentals of oxygen generation from chlorates (see Appendix A).

In 1967, development emphasis was placed on prototype systems for aircraft passenger emergency use following cabin decompression of both military and commercial air transports. This report's objective is to discuss certain of the more important considerations in developing such equipment. Also presented are the preliminary results of environmental testing along with general parameters for sizing of Chemical Oxygen Generators (COGS) for other applications.

Potassium superoxide (KO_2) is routinely used by fire departments, disaster and mine rescue and operations personnel. It is also used as a standby oxygen source for missile system command centers. Sodium chlorate ($NaClO_3$) "candles" are used in submarines as operational or emergency oxygen sources.

2. CHEMICAL DESIGN PARAMETERS

In its simplest form, the chemical core consists of a mixture of alkali metal chlorate, metallic fuel, a "getter" to remove contaminants, and an inorganic binder. This mixture is either wet pressed, hot pressed, or cast into the proper shape for a particular application. Wet pressed "candles" are oven dried to remove the moisture. The basic reaction is exothermic; however, heat must be applied to initiate the reaction. The pertinent chemical reactions are believed to be as follows:

$$\begin{tikzcd} 6\ NaClO_3 \arrow[rr] \arrow[d, "370\ C"] & & NaCl + 3\ NaClO_4 + 80\ k\ cal \arrow[d, "500\ C"] \\ 2\ NaCl + 3O_2 & & 3\ NaCl + 6O_2 \\ +28\ k\ cal & & -24\ k\ cal \end{tikzcd}$$

The composite reaction heat for actual candles is reported to be about 1,000 Btu per lb of oxygen liberated.

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Reaction may be instituted by heating an iron rich region of a chlorate mixture known as the ignition cone, which is situated in the "top" layer of the chemical core. Heat may be supplied in various ways, by a phosphorous strike match, or more reliably, by an electrically actuated Pyrofuse or by a percussion bouchon (grenade ignitor).

Oxygen is generated practically at the instant of actuation as the ignition cone itself contains sodium chlorate. Upon actuation, a hot reaction zone is formed which is about 3/32 in. thick. The zone propagates, traversing the longitudinal axis of the core at a "burn" rate of about 1/4 in. per minute.

Burning can proceed down, up, or in any other direction, even turning corners or doubling back in a "U" as long as reaction zone "contact" can be maintained. A sufficiently low length-to-diameter ratio must also be maintained to prevent excessive reaction-zone heat loss, a loss which may cause premature extinguishment. The minimum practical diameter is reported to be approximately 1/2 inch. Correspondingly, there is a maximum candle diameter, the magnitude of which is dictated by heat dissipation efficiency.

2.1 Physical Properties:

The density of chemical core material is approximately 150 lb per cu ft exclusive of container or insulation. The theoretical oxygen content of the chlorate material is 45%. Actual oxygen yields are about 5% lower than the theoretical figures due to the loss of the oxygen that reacts with the iron-fuel during burning.

During the 1960's considerable progress was made in the development of chlorate chemical oxygen generators (COGS) that would follow specific flow profiles and operate well under various conditions of ambient temperatures and pressures. At the same time, contaminants were minimized, the overall design configurations were miniaturized, and surface temperatures were maintained at a comfortable level. Specifications as above required a design with much more sophistication than that used to make Navy "candles" where only the quantity of oxygen (not the flow rate) was essential and the chemical cores were burned inside a furnace at normal temperature and pressure. Some impurities were acceptable. The weight and size of the submarine hardware was not critical.

Prototype chemical oxygen generating systems were developed through the application of data resulting from a series of parametric studies involving variations of chemical formulation, geometry, density, chemical and physical filters, ignition staging, preheat and insulation requirements, as well as operation at high and low temperature and pressures. Performance variations, as a function of some of these variables, are presented in Appendix B.

3. EQUIPMENT DEVELOPMENT

A number of prototype units were built in 1967 for aircraft and general emergency use in oxygen deficient atmospheres. Special developmental effort produced designs and prototypes for large military transport airplanes. These units provided oxygen for 30 minutes, with flows that followed a prescribed profile, tailored to altitude requirements. They also featured quick start at high altitudes at both high and low temperatures. Chemical oxygen generators developed for this application included filters, igniters, and oxygen producing chemical, all packaged in a disposable tinned steel container.

The Chemical Oxygen Generator was housed (for portable types) in a fiber-glass filament wound epoxy heat shield that also contained mask, reservoir bags, seals, and mountings. Immediate oxygen was obtained when the unit was activated by removing the housing cover. The fixed types were housed in expanded aluminum heat shields. Full flow, 4.5 lpm, was developed at the mask within 2 seconds. The 4.5 lpm flow was sustained for 3 minutes. This flow is followed by a transition time of 7 minutes, as the flow drops to 2.7 lpm. The 2.7 lpm flow is then maintained for the remainder of the 30 minute period.

Prototype units, equipped with full face masks to facilitate egress through smoke-filled environments, have been designed, built, and tested. This same unit would provide adequate oxygen for unpressurized descent of aircraft.

Prototype units with quick donning full head protection were also developed and tested. A 12-minute 2.7 lpm supply was provided for this unit. This same basic design can be adapted for other uses, including passenger protection during cabin decompression on commercial air transports.

4. RELIABILITY

Since reliability was and is of major importance, a concerted scientific effort to establish reliability of various chemical oxygen system designs and configurations was instituted in 1967. Tests have been performed to establish safety margins for applications currently under consideration. Basic parametric data also continues to be collected relative to the effect of temperature, pressure, chemical composition, geometry, and packaging.

5. ENVIRONMENTAL TESTING

In order to establish qualification criteria, environmental tests have mostly been performed in accordance with MIL-STD-810. Chemical oxygen generators have successfully performed after soaking at temperatures ranging from -65 F to +160 F. Ignition has been tested at simulated altitudes. Generator performance was checked throughout the prescribed vibration spectrum in every position.

As a result of these tests, design data has been developed for chemical core formulation. This provides a basis for chemical oxygen generator design.

Oxygen purity from solid state generators is now over 99.99%. Typical values of the contaminants are:

Chlorine - .2 ppm
Carbon Monoxide - 8 ppm
Carbon Dioxide - Trace
Water Vapor - 10 mg/liter

With the use of external filters, it is possible to limit the total of these impurities to a maximum of 1 ppm.

6. SAFETY

Thousands of special chlorate chemical cores, tested in many different prototype generator systems, have demonstrated the inherent stability of the sodium chlorate oxygen generating systems. The residue from the expended core, being mainly salt (NaCl), can be safely discarded in any area. This is in contrast to residue from superoxide oxygen production. Spent superoxide canisters require special disposal procedures.

Chlorate oxygen generators operate at low pressure, thus eliminating the hazards of high pressure oxygen and the added expense of high pressure control regulators.

Because of the apparently unlimited shelf life of the chemical cores and the generating systems, logistic problems are minimized. Storage of chemical oxygen can be unattended in any climate. This unattended storage alone is a tremendous advantage considering the complexity and maintenance required for either liquid or gaseous oxygen supply depots.

6.1 Fire Behavior:

With uninsulated chemical cores, considerable heat may be absorbed before autoignition takes place. The temperature level at which autoignition occurs is about 400 to 700 F in the candleblock ignition cone. Once ignited, burning continues in a regulated, orderly fashion at the intended design rate. In a crash fire, with the type of chemical core packaging that would be used (nickel alloy containers with internal thermal insulation), many minutes would elapse before the autoignition temperature was reached. After heat soak, the core ignition cones would burn followed in time by burning of the candle sides. In the case of portable units, oxygen would slowly be released locally. In the case of a central core system source, the oxygen produced would be vented overboard via a rupture disc. In the latter case, the burn rate would be slower than the design rate because of the lower pressure. Chemical oxygen generators would reduce the potential hazard from that present with the existing high pressure gaseous sources in a crash fire emergency.

7. POTASSIUM SUPEROXIDE - KO_2

Potassium superoxide (KO_2) is the most inexpensive and widely used of the alkali superoxide chemical oxygen sources. It is obtained technically by atomizing molten potassium metal in an excess of air. It is a canary yellow powder that may be processed into regular or sintered granules, pressed geometrical shapes or a low density fluff.

Oxygen is liberated from KO_2 by reaction with water vapor and carbon dioxide, components of human breath. The overall reaction is the result of a series of reactions of which the primary ones are shown.

(a) $4KO_2 + 3H_2O \longrightarrow 3O_2 + 4KOH$

from
breath

(b) $2\ KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$

from breath — Potassium carbonate

$\downarrow$ + KO_2
(hydration
reactions)

$O_2 + KOH$

(c) $4KO_2 + 2CO_2 \longrightarrow 3O_2 + 2K_2CO_3$

Reaction heat produced is on the order of 300 Btu per lb of oxygen liberated.

7.1 Physical Properties:

The density of KO_2 is 40 lb per cu ft for 2-4 mesh granules and 70 lb per cu ft for pressed shapes. The oxygen content is 34% by weight with an approximate yield of 50% of this figure for very short term usage. 80 to 90+% utilization is possible for long duration usage where water can diffuse into the chemical granules for more thorough hydration.

7.2 Fire Behavior:

Although KO_2 is a vigorous oxidizer when mixed in loose form with organic materials such as solvents or oils, the following test showed a different behavior in open flame. A granular sample of KO_2 was wrapped in a layer of metal fly screen and then thrown into a fire of burning fabric, lubricating oil and kerosene. About 7 seconds elapsed before the KO_2 sample decomposed sufficiently to cause a noticeable change. After decomposition, the fire around the sample burned vigorously with a white flame, but there was no explosion. In an operational emergency, if an insulated production KO_2 canister were exposed to an aircraft cabin fire, oxygen would be freely liberated only after the KO_2 reached disassociation temperature (1112 F). This process would increase the surrounding oxygen concentration which in turn would support local combustion.

7.3 Typical Applications:

The principal application of KO_2 is for individual rebreather units which operate at nominally ambient pressure. The chlorate chemicals alone have been well described. A quick start oxygen breathing apparatus canister is a combination of potassium superoxide and chlorate generator. The chlorate generator supplies oxygen for filling the breathing bags in an irrespirable atmosphere and for warming the potassium superoxide in a cold environment. It can also be used as an extender as the oxygen yield of the superoxide slowly stops before its carbon dioxide absorbing capacity is complete.

The alkali and alkaline earth metal peroxides and superoxides can be used for demand chemicals. The respiratory quotient (ratio of carbon dioxide produced to oxygen absorbed) of man is approximately 0.8. The ratio of carbon dioxide absorbed to oxygen produced in a peroxide is 2.0, so it is oxygen lean. The ratio of carbon dioxide absorbed to oxygen produced in a superoxide is 0.67, so it is oxygen rich.

Early apparatus used a peroxide for part of the oxygen supply and all of the carbon dioxide absorption. The supplemental oxygen was supplied from a high pressure oxygen cylinder.

Before a commercial method of producing potassium metal and potassium superoxide was developed, a mixed peroxide of sodium and superoxide of potassium was used. This material (MOX) was used in breathing apparatus and filled a need until the more efficient superoxide was developed.

Sodium superoxide has been produced in limited production quantities. It has a higher yield of oxygen (43.64%) per unit weight than potassium superoxide (33.76%), but is more expensive. It is also less thermally stable and has not been used as extensively as the potassium compound.

Several of the oxides and hydroxides are good carbon dioxide absorbents and can be used in combination with chlorate chemical oxygen generators for rebreather (closed circuit) apparatus. Basic elements of such a rebreather unit are: 1) a superoxide bed, through or over which the breath passes, and 2) a rebreather reservoir to contain the oxygen produced, excess oxygen and other gaseous constituents not utilized by the lungs or removed by the KO_2. The rebreather flow through the KO_2 bed may be one-way or two-way, pendulum or cyclical loop respectively, depending on the intended use of the unit. Units used for over 30 minutes of operation usually incorporate a carbon dioxide-absorbing chemical-bed upstream in series with the KO_2 bed to increase utilization efficiency.

PREPARED BY
COMMITTEE A-10, AIRCRAFT OXYGEN EQUIPMENT

APPENDIX A

1. Bovard, Potential Technical Variations of Solid State Generators. 38th Annual Meeting, Aerospace Medical Association, Washington, D.C. April 11, 1967.

2. Bovard, Solid Chemical Oxygen Sources. 30th Annual Meeting, Aero-Medical Association, Los Angeles, California. April 28, 1959.

3. Miller, Oxygen: Solid vs. Gaseous vs. Liquid. 38th Annual Meeting, Aerospace Medical Association, Washington, D.C. April 11, 1967.

4. Schechter, et al. "Chlorate Candles as a Source of Oxygen," Industrial and Engineering Chemistry. Vol. 42, November 1950. p. 2348.