Oxygen Sources for Space Flights

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OXYGEN IS combined in many solid chemical forms, but only a few of these have the capacity to readily release pure oxygen. One such group is composed of the alkali and alkaline earth peroxides, superoxides and ozonides. A second group is composed of the chlorates and perchlorates of the same metals. The former group releases oxygen upon reaction with water or carbon dioxide and can be classified as demand chemicals. That is, the supply of oxygen released can be made self-regulating by reaction of water and carbon dioxide in the expired breath.

In the second class of compounds, oxygen is released either by direct heating or by mixing with the oxygen-containing chemicals, a substance which will be oxidized by part of the evolved oxygen and thus generate sufficient heat to sustain the reaction. This type of reaction is generally known as a controlled type since the rate of oxygen evolution depends on the composition, size, and shape of the preformed chemical mixture.

The combination of oxygen supply and carbon dioxide absorbent is unique to the demand chemicals; the long shelf life and high oxygen density of the controlled oxygen supplied is also deserving of consideration. Both classes of compounds have been used extensively in high altitude flights and are currently attracting attention for a number of other applications.

Demand Chemicals.—Potassium superoxide (KO_2) and sodium peroxide (Na_2O_2) have been the most frequently used demand chemicals. Sodium superoxide has also been prepared in pilot plant quantities and tested for personal breathing apparatus applications with results similar to KO_2. Other heavier metal superoxides such as CaO_4 have been prepared only in low purities; this compound would offer a slight advantage in amount of oxygen released per unit weight. As the atomic weight of the metal in the superoxide increases, the difficulty of formation usually increases. Efforts are being made at several locations to synthesize the heavier superoxides. For purposes of this discussion, potassium superoxide will be taken as typical and available.

Potassium superoxide is a canary yellow solid at room temperature, but changes to white when cooled to liquid nitrogen temperature. It is manufactured by atomizing molten potassium into dry air, forming a yellow fluffy material which is later compacted and crushed to the desired particle size. During manufacture there is some contamination with K_2CO_3 and KOH by reaction with CO_2 and water vapor in the air: the product as packed in com-

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From the MSA Research Corporation, Callery, Pennsylvania.

mercial canisters contains less than 2 per cent total of the two contaminates. The oxygen producing characteristics are not significantly affected by these impurities and the guaranteed available oxygen is 32+ per cent by weight, giving an oxygen evolution of 224 cc. per gm. of KO_2. Density of the granules controls the reaction rates and abrasion resistance. Bulk density of 2-4 mesh material is 41 lb./cu. ft.

TABLE I.

Potassium Superoxide (KO_2) Reactions	
1. $2KO_2+H_2O$	$2KOH+3/2\ O_2+9.4$ Kcal
2. $2KO_2+CO_2$	$K_2CO_3+3/2\ O_2+43.1$ Kcal
3. $2KOH+CO_2$	$K_2CO_3+H_2O+33.7$ Kcal
4. $KOH+CO_2$	$KHCO_3+33.1$ Kcal
5. $KOH+3/4\ H_2O$	$KOH\ 3/4 \bullet H_2O+16.57$ Kcal
6. $KOH+H_2O$	$KOH \bullet H_2O+20.0$ Kcal
7. $KOH+2H_2O$	$KOH \bullet 2H_2O+33.8$ Kcal
8. $K_2CO_3+1/2\ H_2O$	$K_2CO_3 \bullet 1/2\ H_2O+7.6$ Kcal
9. $K_2CO_3+3/2\ H_2O$	$K_2CO_3 \bullet 3/2\,H_2O+22.77$ Kcal
10. $K_2CO_3+H_2O+CO_2$	$2KHCO_3+33.8$ Kcal
Sodium Chlorate ($NaClO_3$) Reactions	
11. $2NaClO_3$	$2NaCl+3O_2+25.02$ Kcal
12. $2Fe+O_2$	$2Fe\ O+127.4$ Kcal
13. $2NaClO_3$	$Na_2O+Cl_2+5/2\,O_2-72.06$Kcal
14. BaO_2+Cl_2	$BaCl_2+O_2+53$ Kcal

Reactions of KO_2 with water and carbon dioxide, which are readily understood, are shown in Table I. What actually occurs in a KO_2 bed is somewhat more complicated, with two points being immediately evident: 1. Water is absorbed without oxygen evolution. 2. Measured heat releases are not as high as may be suggested by some of the reactions. The first of these is explained on the basis of hydrate formation as per equations 5, 6, 7, 8 and 9, a happy circumstance which aids in preventing over-production of oxygen. Since the balance between carbonate, bicarbonate and hydrate formation is unknown the heat balance cannot be calculated.

Significant differences have been noted in using KO_2 in a personal canister (Chemox) where a single temperature front traverses the KO_2 bed, while a series of fronts was noted in a closed cycle forced circulating system. Primary differences in canister inputs was the higher, pulsing CO_2 concentration and high temperature in one case as opposed to a low continuous CO_2 concentration in the other. The personal KO_2 canister also retained a smaller amount of water than in the circulating system. Utilization of available oxygen was greater in the circulating system, up to 99.8 per cent being used in a 12 per man-hour test in a 210 cu. ft. compartment with controlled humidity.

Recent experiments at Mine Safety Appliances Research Corporation have shown that CO_2 does not react readily with completely dry KO_2; however, a trace of moisture initially present in the canister or on the KO_2 can suffice to sustain reaction for a much longer time than would be suspected if the moisture were to produce KOH, which in turn would react with CO_2. This also attests to the complexity of equilibria within a KO_2 bed. Examination by x-ray has shown that some bicarbonates are formed. If conditions could be controlled so that bicarbonates were preferentially formed the CO_2 absorption would be considerably enhanced with no penalty on oxygen evolution. Approximately equal volumes of KO_2 and LiOH would remove the same quantity of CO_2, while the KO_2 would also supply excess oxygen to meet the metabolic requirements.

Odoriferous compounds are removed by a KO_2 bed, as can be attested by anyone who has used a Chemox breathing apparatus or participated in manned chamber tests.

Controlled Oxygen Supply. — The sodium chlorate oxygen candle will be considered representative of the controlled supply chemicals.[5,6] It is composed of sodium chlorate, an inorganic binder, a source of heat, usually iron powder; and barium peroxide, which combines with any free chlorine that may be formed. The principal equations are shown in Table I. The barium peroxide acts as a heat source as well as the iron; therefore, the two must be balanced to produce the desired burning rate. Hydrogen reduced iron is generally used because a very active form is required. These materials may either be mixed with water, pressed into a mold and dried, or the sodium chlorate can be melted, the other materials thoroughly dispersed and the resultant suspension cast into a mold. The cast candle has a density of 2.4 and contains approximately 40 per cent oxygen by weight. The pressed candle is less expensive, but until recently it did not have the same oxygen producing capacity as the cast candles. However, improvements in manufacture have raised the oxygen content to within several per cent of that of the cast candle. The rate of oxygen evolution is directly proportional to the burning area, and the duration of evolution is proportional to the length of the candle. The candles may be formed in various shapes to give any desired oxygen evolution pattern. As an illustration of the oxygen storage capacity of chlorate candles, it can be noted that a candle the size of a cigar would furnish oxygen for the metabolic requirements of a man for approximately fifteen minutes. Ignition can be performed at a spot enriched with iron, using a modified percussion cap, phosphorous match or electric squib. There is no disintegration during burning. Shelf life appears to be unlimited since candles have been stored indoors for fifteen years without any protective covering and without undergoing any noticeable change.

APPLICATIONS

Demand Chemicals.—Potassium superoxide has been used in self-contained breathing apparatus for over fifteen years. This apparatus was developed during World War II by Mine Safety Appliances Company for personnel protection on naval vessels. It is now being used by several of the services, industrial companies, fire companies, and in mining operations. Many thousands of canisters employed in this breathing apparatus have been manufactured and successfully used. The canisters have even been used on several mountain climbing expeditions. In a series of recently conducted tests at Mine Safety Appliances Research Corporation,[1,2] it was found that a Chemox canister could be used to control a closed chamber atmosphere. The metabolic requirements of two men were satisfactorily fulfilled for six hours by one canister containing approximately 850 grams KO_2. The canister supplied the oxygen, removed the carbon dioxide and a portion of the water vapor. It is possible to produce oxygen with KO_2 by reacting it with water. An apparatus called an Oxygen Generator was used during World

War II to supply welding oxygen by this method. If breathing oxygen were produced in this fashion the resultant KOH solution could be used for the absorption of CO_2 and the remaining water could be reused or purified for drinking.

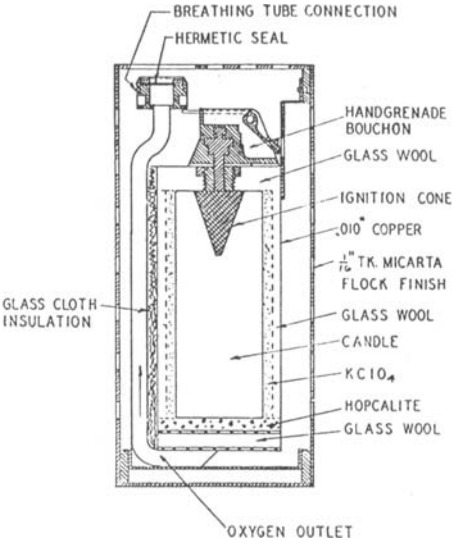

Fig. 1. Emergency candle unit.

Controlled Oxygen Supply. — The sodium chlorate oxygen candle was developed in this country by the Oldbury Electrochemical Company, Naval Research Laboratory and Mine Safety Appliances Company. The first apparatus to use the oxygen candle was a small compact emergency unit that would supply oxygen to a standard high altitude mask at an altitude of 45,000 feet. Extensive chamber tests proved it to be a reliable emergency unit. A small unit similar to this was developed for bailout, with the candle designed to produce a large flow for a few moments and then a gradually decreasing flow. Several small emergency units have been developed for aircraft use. Figure 1 shows the construction of one such unit, which will furnish oxygen for ten minutes. This unit can be fitted with a standard mask for use in commercial jet aircraft or other similar applications.

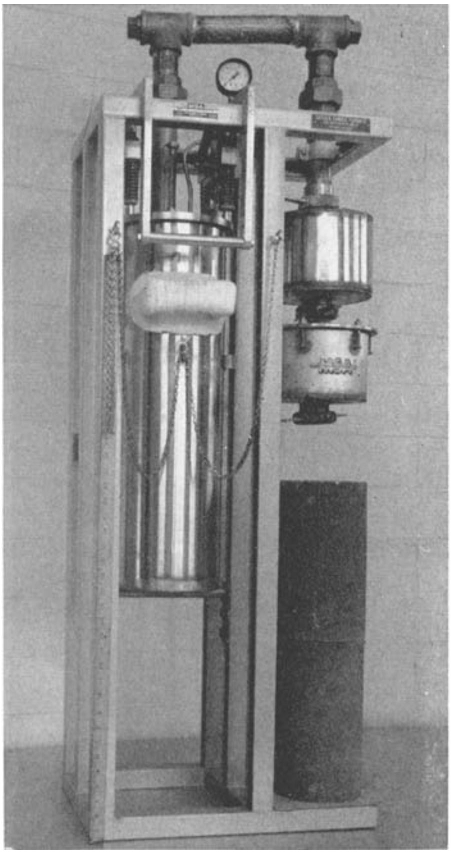

Fig. 2. Oxygen candle burner.

A low pressure burner (Fig. 2) has been developed that will supply over 100 cu. ft. oxygen in fifty minutes. This burner delivers medically pure oxygen through a washable filter.

A portable welding oxygen generator (Fig. 3) was developed for the Army

Corps of Engineers. This unit consists of a burner, a reservoir and a candle producing 35 cu. ft. oxygen. The burner and reservoirs are rated for a pressure of 400 psi. A check valve permits changing candles without affecting the stored oxygen supply.

Combinations. — Various apparatus has been designed around a combination of KO_2 and oxygen candles. Such a candle-KO_2 unit was used to fill the needs of the medium bomber in World War II. Three small candles were inbedded in KO_2, the oxygen from the candle filling the breathing bags and helping to warm the KO_2 for a rapid start. A self rescuer was designed to give respiratory protection when escaping from any toxic atmosphere. This has been suggested for use in large ships and coal mines. Small candles have been added to the bottom of a Chemox canister to give it quick starting features.[3,4] Again the oxygen from the candle fills the breathing bags and helps to warm the KO_2 to enable the canister to be started after being stored in the cold (Fig. 4).

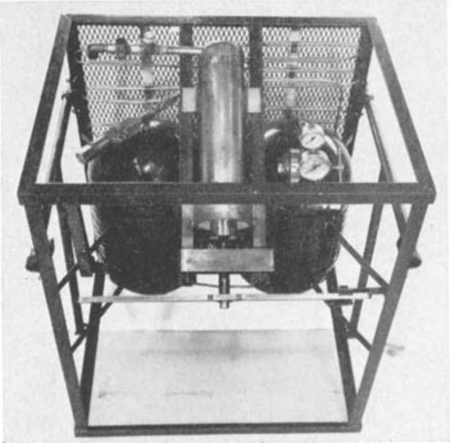

Fig. 3. Portable oxygen generator.

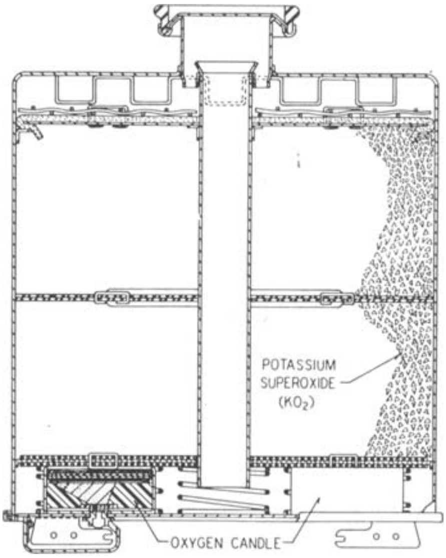

Fig. 4. Quick start canister.

Handling of KO_2 and Candles.— The same precautions that are taken when handling liquid and gaseous oxygen should be followed when handling oxygen producing chemicals. Potassium superoxide is a strong alkali and should not come into contact with the skin. Tons of it have been handled in a dry room by men wearing rubber gloves and dust respirators—there is very little reaction under these conditions. The dust is irritating to the mucous membranes, but is not as severe as lithium hydroxide. Chlorate candles received a bad reputation during World War II because of reported explosions, probably due to impure chlorate and perchlorates used by the Germans in their candles. A percussion cap and 15 grams of tetryl booster were used to shock test the sodium chlorate candles. These tests, conducted by the Bureau of Mines, proved the candles to be stable to shock and detonation. Supply lines must be maintained as with pressurized oxygen to prevent the candle from building up pressure while burning. Thousands of candles have been manufactured and used without a single incident.

After use, a KO_2 canister may be destroyed by perforating the can and immersing it in water. A spent chlorate candle is completely inactive.

SUMMARY

Tests recently conducted have shown that two relatively new oxygen sources, potassium superoxide and sodium chlorate candles, could be used as a means of controlling a closed chamber atmosphere. Potassium superoxide, a demand chemical, has the unique property of releasing oxygen when it reacts with exhaled moisture and carbon dioxide. This was demonstrated in a 7 cu. ft. chamber and a 210 cu. ft. chamber closed atmosphere test. The metabolic requirements of a small animal (7 cu. ft. chamber) and that of two men (210 cu. ft. chamber) were satisfactorily fulfilled by circulating the atmosphere through a potassium superoxide canister. The potassium superoxide adequately supplied the oxygen, removed the carbon dioxide, odors and a portion of the water vapor. Data collected on the chemical behavior of potassium superoxide in these applications are compared with lithium hydroxide and other carbon dioxide adsorbers. Potassium superoxide is presently used in the Chemox self-breathing apparatus which has been approved by the Bureau of Mines for forty-five minutes of strenuous work.

Sodium chlorate candles are a solid oxygen source that contain a volume equivalent oxygen density equal to liquid oxygen. A portable oxygen generator has previously been built around the oxygen candles. They also have been used as a quick start means for the potassium superoxide canisters. The oxygen candle fills the breathing bag with oxygen and warms the canister to initiate the reaction of the potassium superoxide. This same combination has been used in a small rescue canister. The possibility of using sodium chlorate candles as an emergency source of a surge of oxygen in conjunction with the potassium superoxide system has been demonstrated.

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