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A CHLORATE CANDLE/LITHIUM HYDROXIDE
PERSONAL BREATHING APPARATUS

Frank E. Martin
Westinghouse Ocean Research and Engineering Center
Annapolis, Md.

INTRODUCTION

A major cause of death in coal mine disasters, particularly when underground fires or explosions occur, is the presence of toxic gases in the mine atmosphere. The Coal Mine Health and Safety Act of 1969 was enacted partially to encourage immediate application of current technology toward providing protection from such toxic atmospheres. The March 1970 National Academy of Engineering report, "Mine Rescue and Survival," recommended several alternative techniques for accomplishing such a task. Subsequently, a coal mine rescue and survival system (CMRSS) contract was awarded to Westinghouse to proceed through a process of requirement establishment, concept identification, detail design, procurement, fabrication, assembly, and test of all components necessary to produce survival, communications, and rescue subsystems within an 8-month schedule.

Figure 6.1 provides a brief scenario of the subsystems involved. The communications subsystem consisted of seismic and through-the-earth radio signals, both miner to surface and

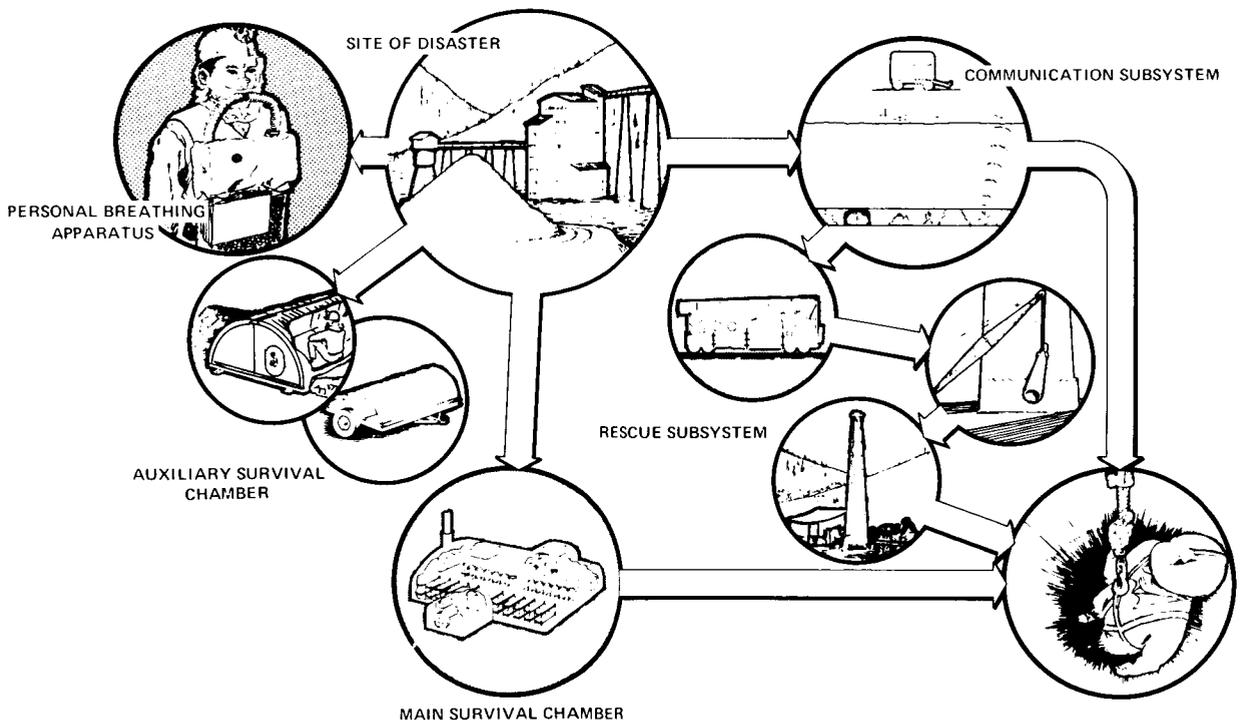


Figure 6.1 Coal mine rescue and survival system.

surface to miner. The rescue subsystem consisted basically of drilling technique development to provide a transportable, high-speed, high-precision drilling capability. Here we are concerned with the survival subsystem and, most particularly in this discussion, the personal breathing apparatus (PBA). The auxiliary survival chamber (ASC) is discussed in paper 9.

DESIGN REQUIREMENTS AND OBJECTIVES

The primary controlling document for breathing apparatus for coal mine use is Code of Federal Regulations, Title 30. To obtain Bureau certification, specific Title 30 requirements must be met dependent upon apparatus classification. With a view toward ultimate certification, Westinghouse design objectives sought to include satisfaction of most Title 30 stipulations. However, as a prototype unit, some Title 30 exceptions were taken while additional requirements outside of Title 30 were imposed.

Basic contract requirements for the PBA were to provide a respirable atmosphere regardless of environment for a 60-min duration at a very high metabolic rate while allowing intermittent voice communication. The NAE report also established a goal of \$50 maximum sell price for the PBA when manufactured in lots of 50,000 to 75,000 units in a 2-year period. From these basic requirements and using Title 30 as a guideline, a complete set of requirements and objectives for the PBA was established.

The PBA offers the following features:

1. Nominal 1-hr endurance at a high work rate during which safe breathing mixtures are provided regardless of ambient atmosphere.
2. Nominal 3 SLPM oxygen generation throughout endurance.
3. Suppression of carbon dioxide level at mouthpiece inhalation side below 1 percent.
4. Breathing resistance maintained at less than 4 in. water total for inhalation and exhalation (generally less than 2 in. water for either).
5. Maximum gas inhalation temperature of 120° F at peak work rates and ambient 50°-60° F coal mine conditions (<120° F at reduced work levels) as per Title 30, table 4, work schedule.
6. Highly intelligible voice communication through man/apparatus interface.
7. Clear vision and environmental protection through man/apparatus interface.
8. Complete fill of 4-liter breathing bags with oxygen in 20-35 sec after actuation.
9. Complete apparatus don time of 60 sec.
10. Long storage life with no maintenance.
11. Minimum size and weight for present state of the art.
12. Estimated production cost of \$50/unit for a volume of 50,000 to 75,000 units over a 2-year period.

SELECTION OF PBA CONCEPT

In this phase, emphasis was on the urgent requirement to meet an early program delivery commitment with a prototype apparatus that would represent current technology and would provide a means for subsequent design evaluation. Consequently, tradeoff analyses concentrated on those systems requiring minimal development and weighted this factor quite heavily. The goal was to give the Bureau of Mines the best possible results in the time available by achieving new applications of proven technology. This attitude is exemplified by the tradeoff most fundamental to design of the entire apparatus—oxygen source.

CRITERION	%	KO ₂ W. Initiator		Chlorate/LiOH		Bottled O ₂ /LiOH	
		Rating	x%	Rating	x%	Rating	x%
I. Reliability	25	705	17,625	690	17,250	605	15,125
II. Portability	20	650	13,000	270	5,400	0	0
III. Cost	25	485	12,125	495	12,375	420	10,500
IV. Schedule	30	360	10,800	690	20,750	800	24,000
TOTALS (high score wins)			53,650		55,775		49,625

Figure 6.2(a) PBA trade-off study on oxygen generators—systems.

FACTOR 1 - 10	%	KO ₂ W. Initiator		Chlorate/LiOH		Bottled O ₂ /LiOH	
		Rating	x%	Rating	x%	Rating	x%
A) No. of Seals, Moving Parts and Connections	15	8	120	6	90	4	60
B) Deterioration W. Use (Probable-pos- sible-unlikely)	15	6	90	9	135	9	135
C) Maintenance (daily-monthly-none)	10	9	90	9	90	5	50
D) Durability	15	9	135	9	135	8	120
E) Inhalation Temp. (high - low)	15	4	60	4	60	4	60
F) Flexibility of use (Fixed rate-Demand rate)	10	9	90	1	10	1	10
G) Don Time	10	9	90	9	90	9	90
H) New Designs (complete-none)	10	3	30	8	80	8	80
TOTALS (high score wins)	100		705		690		605

Figure 6.2(b) PBA trade-off study on oxygen generators—reliability.

FACTOR 1-10	%	KO ₂ W. Initiator		Chlorate/LiOH		Bottled O ₂ /LiOH	
		Rating	x%	Rating	x%	Rating	x%
A) Weight (10 lb - 5 lb)	70	5	350	3	210	0	0
B) Volume (200 in ³ -100 in ³)	30	10	300	2	60	0	0
TOTALS (high score wins)	100		650		270		0

Figure 6.2(c) PBA trade-off study on oxygen generators—portability.

The tradeoff study for oxygen generator selection (fig. 6.2) considered three candidate systems: potassium superoxide with a chlorate candle initiator, chlorate candle with a lithium hydroxide carbon-dioxide absorbent, and compressed oxygen with lithium hydroxide absorbent. The chlorate candle lithium hydroxide system prevailed in the tradeoff primarily because of good scores in all areas related to schedule or development requirements while being at least equivalent with the potassium superoxide system in maintenance, durability, heat contribution, and fabrication cost. In addition, it eliminated at least two developmental requirements associated with potassium superoxide—the need for “quick start” capability and minimization of breathing resistance.

Inputs to the portability parameters were updated on the basis of current knowledge. The original inputs were somewhat more optimistic because of some naivete regarding chlorate candle modifications required to suit this application. However, the overall tradeoff result remained unaffected.

While schedule-related parameters were heavily weighted, it is also evident that good scores on these were not in themselves sufficient. This is shown by the fact that a bottled oxygen/lithium hydroxide system, despite its low development requirements, placed third in overall ratings primarily because of poor scores in material cost, portability parameters, and maintenance requirements.

FACTOR 1-10	%	KO ₂ W.		Chlorate/LiOH		Bottled O ₂ /LiOH	
		Rating	x%	Rating	x%	Rating	x%
A) Material (\$25-\$5)	20	8	160	7	140	0	0
B) Fabrication	25	2	50	5	125	8	200
D) Total Estimated Production Cost (>\$50-\$50-<\$50)	55	5	275	6	330	4	220
TOTALS (high score wins)	100		485		495		420

Figure 6.2(d) PBA trade-off study on oxygen generators—cost.

FACTOR 1-10	%	KO ₂ W.		Chlorate/LiOH		Bottled O ₂ /LiOH	
		Rating	x%	Rating	x%	Rating	x%
A) No. Off-the- shelf components (10% - 100%)	30	4	120	8	240	8	240
B) Developmental Risk (High-Low)	30	4	120	7	210	8	240
C) Total Development Required	40	3	120	6	240	8	320
TOTALS (high score wins)	100		360		690		800

Figure 6.2(e) PBA trade-off study
on oxygen generators—contract schedule.

THE CHLORATE CANDLE AS OXYGEN SOURCE

The PBA application requires what probably constitutes the most rigid set of specifications ever imposed on a chlorate candle system. The extremely close working relationship that had been developed with the chlorate candle subcontractor, Arrowhead Products Division of Federal-Mogul Corp., enabled us to participate in all major design decisions, material specifications, developmental testings, and concept selections. Charles Leffler, director of the Arrowhead PBA candle development, was particularly important to this effort.

Configuration

As shown in figure 6.3, the chlorate candle configuration chosen for the PBA is L shaped. This geometry facilitates volume

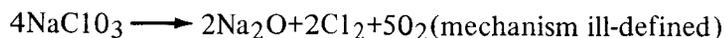
minimization in packaging. Alternate configurations considered included two separate, parallel 30-min duration candle packages and two parallel sodium chlorate segments enclosed within the same envelope but connected by means of a "crossover" mixture. The former was rejected because of increased bulk requirements while the latter required undesirable chemical formulation compensation for complex thermal effects induced by the influence of first segment's decomposition on the burn rate of the second.

A similar situation was also encountered within the L-shaped envelope. The heat produced within the long leg of the L by decomposition would accelerate burn rate of the short leg if a uniform chemical formulation were employed. Consequently, a smaller amount of iron powder fuel was incorporated in the short leg to retain the 3 SLPM nominal rate and 60-min duration requirements. This situation was aggravated by the fact that the burn front area (and therefore burn rate) accelerates as it progresses through the elbow joint of the L shape.

Theory of Operation

The high temperature required to sustain the decomposition of sodium chlorate is obtained in part from the heat of decomposition of the chlorate itself and in part from the oxidation of the metallic fuel (1 μ reduced iron powder), which is also an exothermic reaction. A combined catalyst and gas impurity getter (barium peroxide) is also included in the candle formulation. Its prime purpose in candle formulations is to react with free chlorine, thereby reducing its presence in the generated oxygen. All candles evaluated in this study were produced by the wet pressing technique.

As evidenced by analysis of the ash clinker constituents, many reactions are believed to take place in candle decomposition. The main reactions that illustrate oxygen evolution and chlorine elimination, however, include the following (refs. 1-4):



Free oxygen also combined with the iron fuel in varying degrees of reaction completion to produce various oxides of iron. The main constituents of the ash clinker include sodium chlorate and oxides of iron.

Candle activation is a multiple stage requirement. The first stage includes a modified hand-grenade-type bouchon that uses a munitions primer. Mechanical activation of the primer immediately produces a flash of hot gases releasing about 800 cal of heat. This heat energy is sufficient to ignite a pyrotechnic first-fire composition. The heat energy released by the first-fire reaction (~5000 cal) then ignites a cone portion of the oxygen candle, which is a fuel-enriched composition of chlorate. Enough heat is then finally generated to initiate and sustain the main portion or core composition of the candle. The reaction then proceeds until the supply of chlorate is exhausted. The entire candle is wrapped in layers of a high-temperature-resistant, ceramic type insulation material. The insulation serves to retain sufficient heat within the generator housing to sustain chemical decomposition, and also to help maintain generator wall temperatures within specification (350° F max).

Candle Reliability versus Burn Rate, Duration, and Temperature

This rather fine balance of heat containment (via insulative materials, radiative shields, and air gaps) versus heat dissipation (via skin material selection and surface emissivity) to maintain a 350° F maximum envelope skin temperature played the largest role in the magnitude of development required. Too much heat containment resulted in very rapid decomposition, while too much heat dissipation would result in too slow decomposition and at times premature extinguishment of the reaction. Moreover, the balance that was achieved had to be matched to a chemical formulation with heat content sufficient to guarantee reliability and yet meet the flow rate and duration requirements.

These requirements, as interpreted directly from Title 30, are: whenever oxygen is produced from a nondemand type source, flow rate must be a nominal 3.0 SLPM for a duration not less than the stated apparatus duration (in this case, 60 min). In-house calculations determined that either or both of these requirements could be relaxed (extent dependent on total system volume) and still possess an apparatus that would retain enough residual oxygen in 4-liter breathing bags to sustain comfortable respiration even under high work rate conditions for the 60-min duration. However, the Title 30 requirements were retained as contract objectives.

The maximum envelope skin temperature of 350° F was derived from a worst-case analysis of coal dust autoignition in which it was assumed that a coal dust layer composed exclusively of particles <75 μ diam with 52 percent volatiles content has collected on the candle surface. Even though it is recognized that this constitutes a highly improbable situation, this specification also was retained as a design objective.

To satisfy these multiple requirements and yet retain reliability, a wide assortment of chemical formulations was evaluated. These included mixtures of low fuel with catalyst, mixtures with potassium perchlorate, and mixtures with silicon dioxide inert and several permutations thereof.

The addition of silicon dioxide inert (40-mesh granules) constitutes a unique method of stabilizing the decomposition front, thus controlling burn rate. Visual examination of spent clinkers and burns-in-progress confirmed that silicon dioxide maintained the front in an attitude transverse to the candle axis. Without silicon dioxide, the front often progressed in a random fashion, producing large variations in burn rate and consequent loss of duration. The formulation that ultimately displayed the greatest reliability under design constraints gave reproducible burn rate profiles with no chemical failures over 26 candle decompositions.

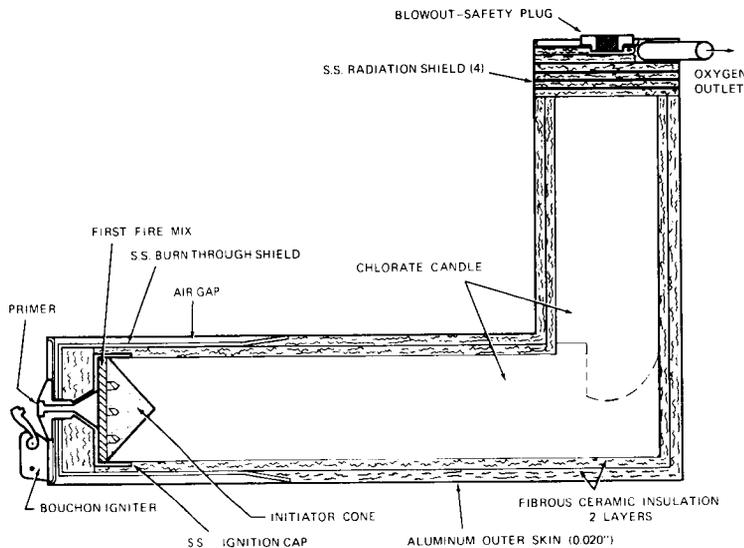
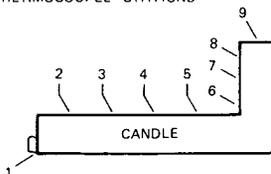


Figure 6.3 PBA chlorate candle.

Ambient Test Temperature: 51 - 77°F
 Time for 4 liters (STP) Delivery: 22 - 35 seconds
 Decomposition Duration: 56.75 - 64.0 min.
 Maximum Tube Wall Temperatures:

THERMOCOUPLE STATIONS



- | | | |
|----------------|----------------|----------------|
| 1) 275 - 330°F | 4) 286 - 316°F | 7) 303 - 346°F |
| 2) 285 - 322°F | 5) 273 - 294°F | 8) 328 - 368°F |
| 3) 289 - 327°F | 6) 285 - 310°F | 9) 315 - 360°F |

Results were obtained while candle was subjected to multi-orientational movements.

Figure 6.4 PBA chlorate candle final test data range.

It had earlier been established that the preferable container material was black anodized aluminum due to its preferred heat dissipation qualities as contrasted with stainless steel, the more conventional candle container material. The combination of this container with the proper insulative materials and candle formulation produced the construction shown in figure 6.3 and the qual test results in figures 6.4 and 6.5.

These results show that all the design objectives have been successfully approximated; however, surface temperature of 350° F and duration of 60 min can not be reliably specified as minimum values without further development.

These two parameters can be met by a relatively simple redesign of the container with little or no additional development of the chlorate mix. In fact, solving the temperature problem, which calculations have shown can be accomplished by the addition of fins to the aluminum casing, may also solve the duration problem since the burn rate of the candle is partially a function of heat dissipation. The more efficient the dissipation, the slower the burn.

Should the duration not be achieved with the lower surface temperature, the case could be increased slightly to accommodate increased length of the candle.

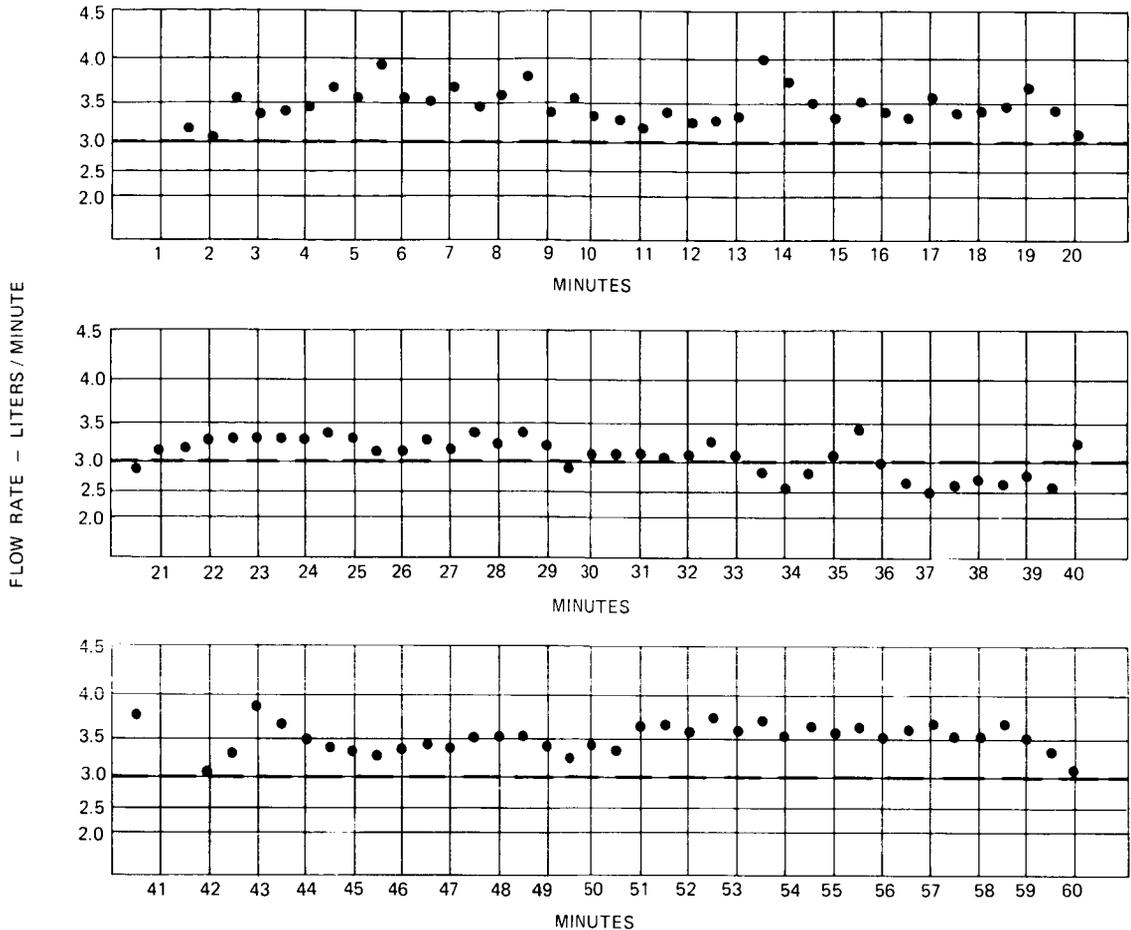


Figure 6.5 Qualification test flow rate data.

Candle Ignition Design

The multiple-stage sequence involved in candle ignition has previously been described; however, it was not then emphasized that critical requirements determined its design. These requirements are ignition reliability, production of 4 liters oxygen within the first 20 to 35 sec, prevention of burn-through to the aluminum casing, and maintenance of the 350° F surface temperature specification. The bulk of these requirements are satisfied by proper sizing and formulation of the cone material. The cone must both provide the initial 4 liters of oxygen and initiate sustained decomposition while itself decomposing in a minimally exothermic manner. As was revealed by the qual test data (figs. 6.4 and 6.5) and by the reliability shown over 26 qual and prequal runs, this balance of properties was successfully achieved.

Reliability was significantly enhanced by design of an intimate cone/first fire interface. The most successful such interface design involved drilling five 3/16" D holes to a depth of 5/8 in. into the cone and then packing these tightly with first fire. Additional first fire was then applied uniformly over the cone face before carefully inserting the candle into its stainless steel ignition cap (fig. 6.3).

This cap was designed to contain molten sodium chloride produced from the violent cone decomposition and prevent it from traveling to the package perimeter. This was further prevented by welding of the bouchon ignition channel and ignition cap into an integral part and by selection of high melting point refractory material as insulation. Finally, a stainless steel burn-through shield, lining the entire ignition end of the package, assures that molten material will not contact the aluminum exterior even if it does manage to travel to the perimeter.

Purity of Generated Oxygen

The normal exit path for oxygen generated by the chlorate candle is through flexible tubing attached at the far end of the short leg. Also located in this vicinity is a pressure-relief assembly provided for the event that gas pressure buildup occurs through any possible exit path blockage.

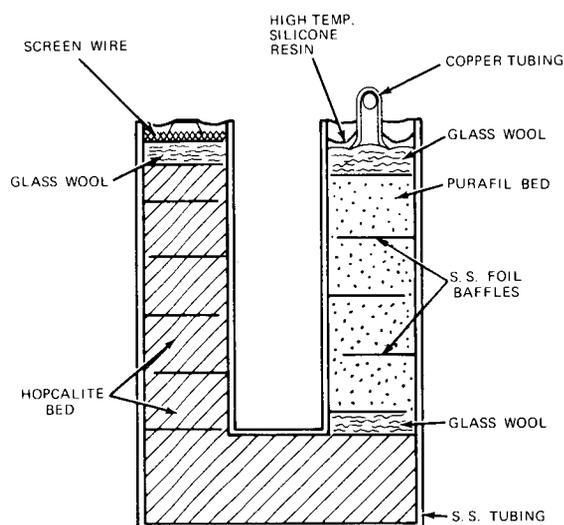


Figure 6.6 Gas scrubbing unit for PBA chlorate candle.

The flex tubing attaches to a separate U-shaped gas impurity scrubbing cartridge, designed for installation within the inlet plenum of the PBA carbon dioxide removal canister. This scrubbing unit (fig. 6.6) contains baffled beds of Purafil and hopcalite for removal of chlorine and carbon monoxide, respectively. Its performance has proven quite efficient as shown by gas analysis data in figure 6.7. The impurity levels of all gases are well within standards applicable to breathing mixtures with the exception of carbon dioxide. No provision was made within the gas scrubbing cartridge for carbon dioxide removal under the rationale that the lithium hydroxide bed downstream of the cartridge could readily accomplish this task.

LITHIUM HYDROXIDE CANISTER DESIGN

Carbon Dioxide Absorbent Selection

Three state-of-the-art chemical absorbents applicable for PBA use, lithium hydroxide, baralyme, and sodasorb, were evaluated on the criteria shown in figure 6.8. Lithium hydroxide is by far the most efficient absorbent of carbon dioxide by weight. Its theoretical absorption capacity is 0.92 lb CO₂/lb LiOH as opposed to a capacity of 0.50 lb CO₂/lb of baralyme (ref. 5). Its density, however, is quite low, giving it slightly less efficiency than baralyme in terms of volume.

It has slight defects also in its comparative cost effect on the PBA and in the amount of heat liberated; however, these are compensated by the assignment of less development risk. The lower development risk rating was achieved primarily because of preliminary testing by Foote Mineral Co. This testing produced an experimentally derived figure for the amount of lithium hydroxide required to meet PBA input conditions.

Sample Time (min)	O ₂ (%)		CO ₂ (%)		CO (ppm)		H ₂ O (ppm)		Hydrocarbons (ppm CH ₄)		Cl ₂ (ppm)
	A	B	A	B	A	B	A	B	A	B	A&B
5	99.90	99.93	0.10	0.07	0.60	0.55	0.0	15.0	2.5	6.4	< 0.1
10	99.89	99.92	0.11	0.08	0.65	0.60	5.0	20.0	3.2	6.1	"
15	99.86	99.90	0.14	0.10	0.70	0.70	14.0	35.0	4.2	6.0	"
20	99.86	99.89	0.14	0.10	0.75	0.75	30.0	55.0	4.7	6.3	"
25	99.84	99.87	0.15	0.12	0.90	0.90	60.0	90.0	5.6	6.6	"
30	99.67	99.84	0.32	0.14	1.05	1.10	110	150	6.4	7.3	"
35	99.52	99.77	0.46	0.20	1.30	1.40	190	245	7.4	11.0	"
40	99.52	99.70	0.44	0.26	1.65	1.75	420	405	8.6	11.7	"
45	99.46	99.57	0.46	0.37	2.15	2.30	800	615	9.9	13.5	"
50	99.32	99.40	0.62	0.52	2.95	3.15	630	820	12.2	15.7	"
55	99.12	99.15	0.86	0.75	4.85	4.75	200	915	15.0	18.6	"
60	Candle out		Candle out		Candle out		Candle out		Candle out		

Oxygen by Beckman O₂ Analyzer, Model E2.

Carbon Monoxide by Beckman Model GC-5 Gas Chromatograph
(helium ionization detector).

Water Vapor by Beckman Trace Moisture Analyzer P₂O₅ Electrolytic Cell.

Chlorine by General Electric Halogen Detector, Type H.

Hydrocarbons by Beckman Model 109 Flame Ionization Total Hydrocarbon Analyzer.

Carbon Dioxide by Beckman IR 20.

Figure 6.7 PBA chlorate candle gas analyses.

CRITERION 1-5-10	%	LiOH		Baralyme	
		Rating	%	Rating	%
1) Sensible heat BTU/ft ³ CO ₂ absorbed	10	7	70	9	90
2) Cost Effect on PBA	20	4	80	6	120
3) Non Operational Reliability	15	9	135	9	135
4) Theoretical Weight req'd for 1 hour mission	20	9	180	5	100
5) Theoretical Bulk volume req'd for 1 hour mission	15	7	105	9	135
6) Development Risk (high low)	20	10	200	8	160
TOTALS	100%		770		740

NOTE: Sodasorb comparable to Baralyme in all parameters

Figure 6.8 Carbon dioxide canister absorbent
trade-off study.

Even so, the tradeoff overall results were very close. As noted in figure 6.8, sodasorb is comparable in all parameters to baralyme. All other conventional carbon dioxide absorbent systems were considered either less efficient or not applicable to PBA use without entailing undue development risk. Accordingly, lithium hydroxide was selected as the absorption material, primarily because of higher probability of successful development.

Lithium Hydroxide Canister Design Requirements

In contrast to the chlorate candle, which must generate oxygen at a fixed rate based on highest expected workload, the carbon dioxide absorbent is sized to accommodate

fluctuations in workload and the total amount of carbon dioxide produced. Accordingly, the amount of carbon dioxide liberated during a 60-min high-work-rate program was estimated as shown in figure 6.7. This was accomplished by estimating from (ref. 6) the oxygen expenditure per activity, totaling the result, and applying an average respiratory quotient value of 0.85 to arrive at 82 liters carbon dioxide.

A safety factor of nearly 25 percent above this was included in our design considerations to cover the following:

1. The stated oxygen consumption rates are estimated for specific tasks and do not account for recovery time required in progressing from greater to lesser work rates.
2. Simulation of table 4 (Title 30) work tasks was accomplished on a bicycle-type ergometer (see fig. 6.9 for ergometer settings). Since the ergometer requires continual use of the same musculature, recovery times are yet more difficult to estimate.
3. Respiratory quotient (RQ) may reach values of 0.9 - 1.0 at high work rates.
4. Respiratory quotient may vary depending on the individual test subject. Therefore, in consultation with Westinghouse Physiology Department, a figure of 102 liters (0.41 lb) of carbon dioxide was estimated as the worst-case amount the canister would have to accommodate.

Activity	Time (min)	SLPM O ₂	Total O ₂ (ℓ)	Total CO ₂	Ergometer Setting (Kiloponds)
1) Sampling & reading	2	0.7	1.4		0
2) Walk at 3 mph	2	1.2	2.4		1.5
3) Climb 75° treadmill	1	2.5	2.5		3.5
4) Walk at 3 mph	2	1.2	2.4		1.5
5) Pull 45 lb. wt. 5 ft. 60 times	5	2.1	10.5		3.0
6) Walk at 3 mph	3	1.2	3.6		1.5
7) Carry 50 lb. wt. over overcast 4 times	8	1.9	15.2		2.75
8) Sampling & reading	2	0.7	1.4		0
9) Walk at 3 mph	4	1.2	4.8		1.5
10) Runs at 6 mph	1	2.7	2.7		3.75
11) Carry 50 lb. wt. over overcast 6 times	9	1.9	17.1		2.75
12) Pull 45 lb. wt. 5 ft. 36 times	3	2.1	6.3		3.0
13) Sampling & reading	2	0.7	1.4		0
14) Walk at 3 mph	6	1.2	7.2		1.5
15) Pull 45 lb. wt. 5 ft. 60 times	5	2.1	10.5		3.0
16) Carry 45 lb. wt. walking at 3 mph	3	1.9	5.7		2.75
17) Sampling & reading	2	0.7	1.4		0
TOTAL	60		96.5	82 liters	

Figure 6.9 Oxygen consumption
CO₂ liberation estimate for Title 30, Test 4, Table 4 work schedule.

Pressure drop across the canister was another important design parameter. The theoretical plate area based on a 4 by 14 mesh size reactant material computed to be 15 in.² based on an flowrate of 85 SLPM air and a pressure drop not exceeding 2 in. water. The bed depth, given an experimentally derived figure for required lithium hydroxide volume, was computed to be 6 in. By adopting a canister geometry within these dimensions, we were confident of maintaining

pressure drop below 2 in. water at even the highest work rate called out by Title 30 (at which a velocity of 40 SLPM could occur).

Finally, a circle-flow breathing circuit was selected over pendulum flow, and axial flow through the canister was selected over radial flow. Since some problem was anticipated in dissipating the heat of reaction generated with the lithium hydroxide bed (sensible heat = 875 Btu/lb CO₂), circle flow appeared preferable because of greater opportunity for heat transfer as contrasted to the reduced circuitry of pendulum flow.

In addition, pendulum flow would have presented an opportunity for formation of depleted reactant dead spaces within the canister. Axial flow through the canister was chosen primarily because it afforded fewer fabrication difficulties, minimal bulk, and greater opportunity for internal canister modification. Some canister modification in the form of internal finning was contemplated, once again, because of anticipated heat transfer difficulties.

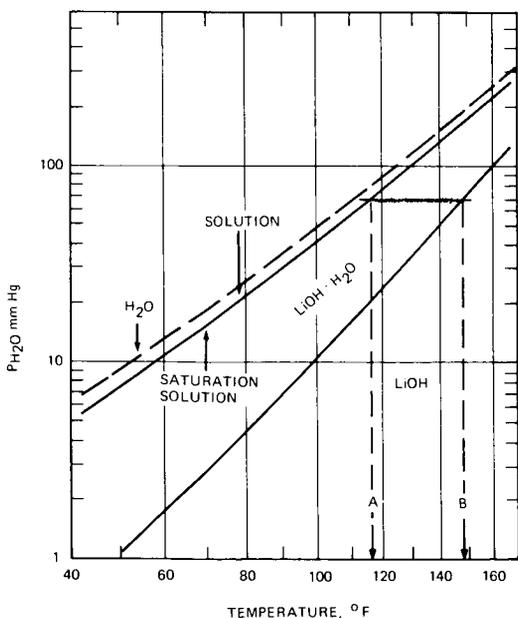
Preliminary Unmanned Testing

Concurrent with the formation of our design decisions, Foote Mineral Co., agreed to conduct some preliminary performance evaluations on lithium hydroxide based on input conditions. We are especially indebted to Dr. Dan Boryta and Dr. Wm. Hart of Foote for their valuable cooperation in this test. The test was run by open-circuit flow of 100 percent RH air containing 4.3 percent carbon dioxide at 90° F through a quartz tube filled with 1 lb sm 4 by 14 LiOH and at a flow rate of 0.40 lb CO₂/hr. Breakthrough (rapid increase of carbon dioxide in effluent above 0.5 percent) did not occur until some 35 to 40 min into the test.

This result appeared quite encouraging in view of the fact that it was achieved in spite of low thermal conductivity of the quartz container. Thermocouple probes within the bed indicated

that bed center temperature was in excess of the optimum operating range for our particular input conditions within 5 to 6 min. Thereafter, most of the bed was operating at greatly reduced efficiency because of steadily increasing thermal rise to a maximum of 284° F. According to a Foote Mineral Co., phase diagram (fig. 6.10), the optimum operating range for this application falls between 116° and 149° F.

This diagram is based on experimental and literature evidence that the most efficient route for formation of lithium carbonate from lithium hydroxide proceeds through a lithium hydroxide monohydrate (LiOH • H₂O) intermediate (ref. 7):



A - B = OPTIMUM OPERATING RANGE FOR PBA

Figure 6.10 Vapor pressure
LiOH-H₂O (ref. 7)

In figure 6.10, the lower curve represents the dissociation vapor pressure of lithium hydroxide monohydrate while the upper solid curve is LiOH • H₂O saturated solution vapor pressure. Poor absorption of carbon dioxide occurs when either dry

conditions (such as caused by excessive bed temperature) prevent formation of $\text{LiOH} \cdot \text{H}_2\text{O}$ or when excessive moisture causes formation of a saturated solution. Therefore, maximum utilization occurs when bed temperature is maintained between the two curves at the level determined by "effective" vapor pressure. Effective vapor pressure is defined as the sum of input water partial pressure and the partial pressure of input carbon dioxide converted to water. Under input PBA conditions, this works out to 68.2 mm Hg effective vapor pressure, thus establishing optimum range at 116° to 149° F.

Clearly, some measure of additional cooling capacity beyond that inherent to the packed quartz tube would be required for the PBA canister. It remained, however, to determine whether the use of more conductive canister material alone could accomplish this task because of the possibility that heat capacity of the bed itself was the limiting factor. Foote could offer no reliable estimate as to the actual thermal conductivity of the bed while in PBA use (consisting, as it would, of a complex mixture of H_2O , LiOH , $\text{LiOH} \cdot \text{H}_2\text{O}$, Li_2CO_3 and LiHCO_3). It was decided to defer a decision on the necessity for internal cooling fins until data were available from actual manned testing.

However, Foote was able to estimate the amount of lithium hydroxide required under the assumption that bed temperature could be controlled. Comparison of the unmanned testing data (which used a developmental grade of lithium hydroxide with background comparative runs and extrapolation of results under more suitable thermal conditions led Foote to conclude that a minimum of 1.36 lb standard Navy grade 4 by 14 mesh lithium hydroxide would be sufficient.

Developmental Lithium Hydroxide Canister

The canister designed to contain the lithium hydroxide is an axial flow type consisting of standard perforated brass screens at each end for retention of the lithium hydroxide charge (fig. 6.11). The body of the canister is made of red brass having a thermal conductivity of 92

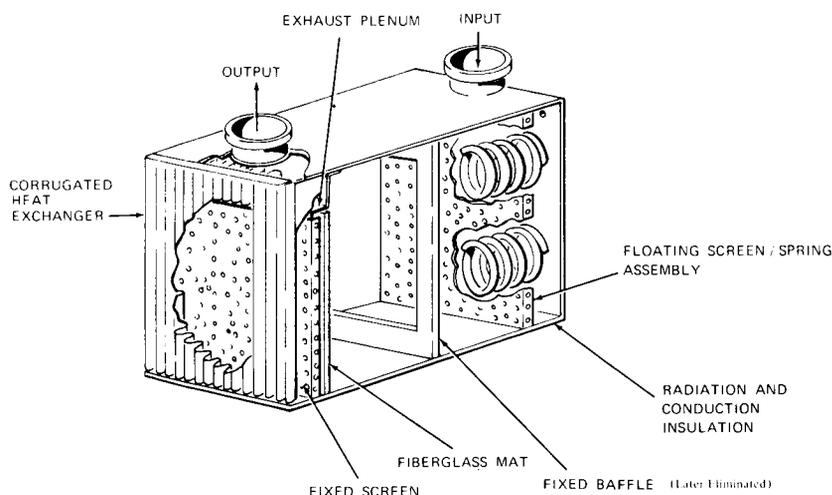


Figure 6.11 Developmental LiOH canister.

Btu/hr-ft²-°F. The amount of heat that will be generated by a man working to table 4 Title 30 work schedule computes to be approximately 357 Btu/hr. Considering the worst case of laminar flow convection cooling, which would be the case if the miner were not moving but standing in a stagnant air environment, the exposed surface area of the body of the canister is not enough to transfer this quantity of heat. Therefore, a corrugated heat exchanger surface affording

additional surface area was built into the output end of the canister housing to help cool the effluent breathing gas.

Two plies of Air-Mat No. 12 fiberglass mat were installed over the stationary output end screen. The canister was charged and closed up, thus compacting the input screen against the bed

by means of springs (2-3 psi pressure), and was then ready for pressure-drop and dust testing at 85 SLPM flow.

The canisters were first blown through with dry nitrogen at a flow rate of 85 SLPM and pressure drop measured across the inlet and outlet ports (~ 1.5 in. H₂O). The dust test was performed by placing a virgin piece of No. 12 Air-Mat filter material over the outlet port of the canister and purging the canister with 85 SLPM nitrogen introduced at the inlet port for 3 sec. The sample piece of filter material along with a nonexposed piece of same was subjected to titration pH analysis and the values compared. Both samples consistently registered the same pH. Therefore, the test was negative and the filter design acceptable.

Manned Testing and Heat Transfer Analysis of Developmental Canister

The next test was a manned test of the canister. The final breathing bags, man/apparatus interface, and chlorate candle, not yet delivered, were simulated with comparable in-house components.

A candle simulator was built to the same configuration as the deliverable unit and was fitted with two electric-resistance heaters that would bring the surface temperature up to and beyond 350° F. The breathing bags consisted of two rubber anesthesiology bags, and man/apparatus interface was a standard scuba-type mouthpiece. Aside from these developmental modifications, the experimental setup was as shown in figure 6.12, with oxygen and carbon dioxide being monitored continuously and then returned to the system. Breathing resistance and gas inhalation temperature were also continuously monitored. Temperatures of the canister wall and lithium hydroxide bed were spot checked. The test subject was simulating the work schedule of figure 6.9 by riding a bicycle ergometer throughout the test at various kilopond settings.

The data in figure 6.13 (runs 1, 2, and 3) on inspired gas temperature versus test duration show that the canister as then constructed possessed inadequate heat transfer characteristics.

The first man test, which ran for 33 min and 45 sec, was aborted because the inhalation temperature exceeded 115° F.

The second man test was run the same way as the first except that the candle simulator was not energized. This run lasted 34 min and was aborted, again because the inhalation temperature exceeded 115° F. Comparing the two sets of data showed that the heat generated by the candle simulator contributed little to the overall heat load of the canister and that the exothermic reaction and conductivity of the lithium hydroxide had to be determined.

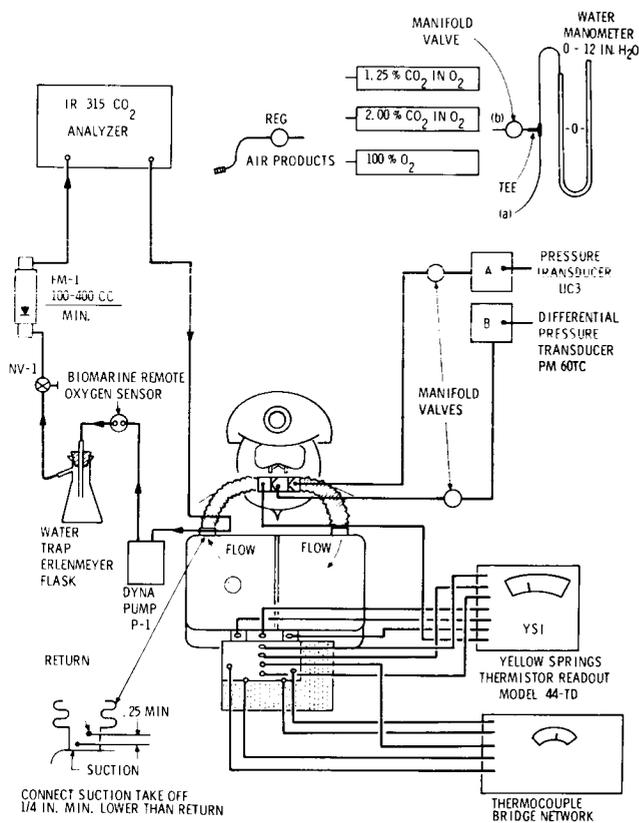


Figure 6.12 Developmental test setup schematic.

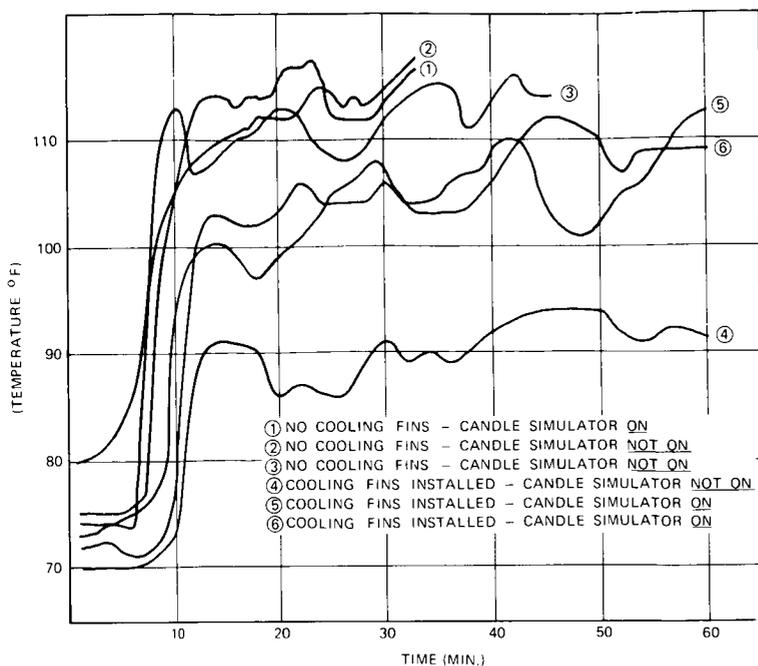


Figure 6.13 Inspired gas temperature versus canister finning.

temperature would be only 85° F above a 60° F ambient air temperature for a total hot spot temperature of 145° F (just within optimum operating range). This value, however, was predicted on laminar-free convection and radiation cooling with the additional presence of external cooling fins, spaced along the canister front and back faces.

At the high work rates associated with maximum heat generation, it is a reasonable assumption that an individual using the PBA would be disturbing ambient air at an equivalent velocity of 1 to 3 mph and thereby inducing turbulent cooling air flow. On this premise, subject to additional testing, it was proposed that similar thermal control be achieved without requiring external fins, which would have had significant impact on already-frozen packaging considerations.

As can be seen in figure 6.13, further manned testing after internal fin modification verified the efficiency of this construction. Test 4 was performed without energizing the candle simulator. A lithium hydroxide bed temperature of 187° F was achieved and maximum inspired gas temperature was 94° F, as opposed to 270° F and 116° F, respectively, for an unfinned canister. For tests 5 and 6, the presence of an energized candle simulator had a pronounced effect; nevertheless, peak inspired gas temperatures below 115° F still were obtained.

Further evidence that the internal cooling fins did indeed maintain bed temperature much closer to the optimum operating range was produced from the carbon dioxide analyses. For tests 1 through 3 (no fins), carbon dioxide breakthrough occurred at a 1.0 percent level within 30 to 40 min into the test. By contrast, tests 4 through 6 (with fins) maintained carbon dioxide below 1.0 percent for the entire 60 min.

Further evidence of design efficiency of the modified canister was obtained as follows. The canister was vibrated according to MIL-STD-810 method 514, procedure X, figure 514-6, curve AB modified. It was vibrated in all three X, Y, Z axes; Z was the vertical axis, X was sideways

The third test was conducted like the second, except that thermocouples were strategically imbedded into the lithium hydroxide charge. This test lasted 40 min. The data showed center bed temperatures as high as 270° F, while canister wall temperature remained typically 180° F.

From these data, heat transfer calculations were run that established thermal conductivity of the absorbent bed at 0.465 Btu/hr-ft-°F. Further calculations determined that, by internal addition of copper fins, a ΔT of 19° F could be established between the hottest spot in the lithium hydroxide bed and the canister wall. Additional calculations showed that the canister wall could be modified to dissipate heat efficiently enough so that overall rise of the center bed

along the short axis, Y was longitudinally along the long axis. The input acceleration in all three axes was from 2 to 5 G wherein the frequency ranged from 2 to 500 Hz. The fundamental resonant frequency at which the canister had the highest output acceleration was 115 Hz and 36 G; this frequency was noted to exist in the X axis. Following vibration testing, the canister was x-rayed, dust tested, and carbon dioxide tested. The x-rays showed no lithium hydroxide settling, and the dust test proved negative. Lastly, 2.25 percent carbon dioxide in oxygen was caused to flow through the canister at 300 cc/min for 6 min. The effluent gas was monitored with a Beckman 315 carbon dioxide analyzer. The effluent gas read zero carbon dioxide.

PBA COMPONENT INTEGRATION

Chlorate Candle Lithium Hydroxide Canister Interface

Figure 6.14 shows the internally finned canister just discussed and its interface with the chlorate candle. The candle is hung under the canister and is thermally insulated from the canister by the Teflon cradle and hanger strap assemblies (two each) and by urethane foam and Mystik reflective tape radiation and conduction insulation (located on the candle sides of the canister). The candle's exit gas filter cartridge is contained within the canister's exhalation plenum.

A perforated polycarbonate shroud covers the candle assembly, offering protection against possible contact burns while still providing convection cooling for the candle assembly. There is a polycarbonate standoff (not visible in the figure) on the back face of the canister to protect the wearer against canister surface temperatures.

Figure 6.15 shows the entire portable breathing apparatus.

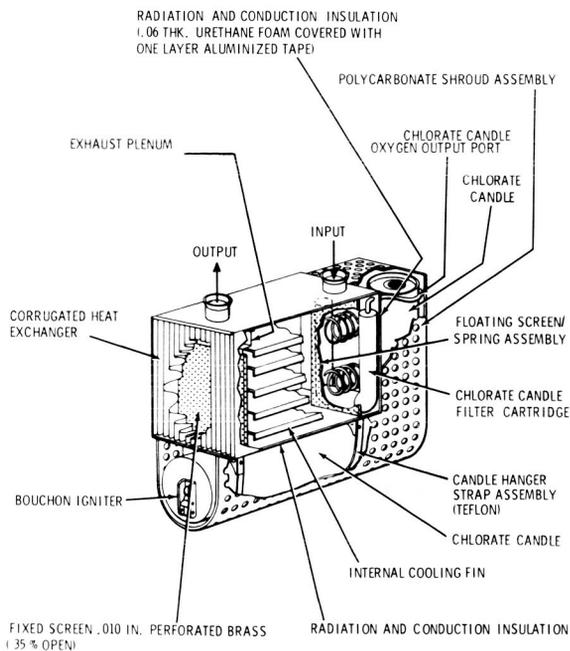


Figure 6.14 PBA canister candle assembly.

of open-cell foam along the gas exit path from the canister, which ensures gas flow even in the event of bag collapse under external force.

General requirements for the bags were that they be light weight, gas-tight, able to withstand long-term folding, and capable of folding into a compact storage configuration. The vendor selected for bag fabrication was the G. T. Schjeldahl Co. The material chosen for the prototype was nylon impregnated with polyurethane with cemented seams. The bags can be produced from a number of materials and by processes that are more cost-effective, such as blow molding and heat sealing.

Breathing Bags

The initial design decision for circle flow dictated the use of a split breathing bag with one compartment for exhalation and the other for inhalation. Title 30 specifies that the pressure relief valve must be located on the inhalation side. It is set to relieve at 1 in. water column overpressure.

The inhalation compartment also contains a strip



Figure 6.15 PBA as worn.

Man/Machine Interface

For the PBA application, interface requirements included not only the means to conduct breathing gas to and from the man but also to allow communication, provide eye protection, and prevent inhalation through the nose. The trade-off study considered six different interface means: mouthpiece, smoke hood, oral mask, oro-nasal mask, full face mask, and fright mask. The study showed that for the PBA application the smoke hood is the best choice.

The vendor selected to manufacture the PBA hood was, again, the Schjeldahl Co., which had previous experience in this type of product and had worked with the FAA on hood developments. The PBA hood differed from earlier ones in the requirements for incorporation of

a mouthpiece and means to prevent fogging. The original approach to the fogging problem was incorporation of an eyepiece of CR-39 allyldiglycolcarbonate into the hood and application of the antifogging compound DeMist manufactured by AID, Ltd. This combination was the result of an extensive literature search and contacts with NASA and the U.S. Army. However, difficulties were encountered in applying DeMist to the selected standard MSA lenses. To meet delivery commitments, an alternative compound, Hydrazorb (also from AID), was selected for application on cellulose acetate butyrate lenses; this coating ranks right behind DeMist in NASA ratings.

Other hood materials selected included a 1.5-mil laminated construction of Mylar[®] for the hood proper and a polyurethane elastomer for neck seal. The eyepiece was laminated to the inside surface of the hood so that all hood materials in direct contact with ambient atmosphere are self-extinguishing. The nosepiece is designed as an integral part of the lens and is constructed of nylon, while the mouthpiece is constructed of polyvinylchloride.

Acceptance testing performed on the hood included bond strength of lens, bond strength of mouthpiece, haze of lens, luminous transmittance of lens, pressure drop through mouthpiece, and leak integrity of neck seal. All specifications were met.

PROTOTYPE PBA MANNED TESTING

Manned testing on the completely fabricated PBA prototypes was conducted to the work schedule shown in figure 6.9 and in the manner shown in figure 6.12 except that no thermocouple taps were made into the canister. After running five such tests, the following observations were made.

1. The lithium hydroxide canister as coupled with the chlorate candle possesses heat transfer characteristics sufficient for a coal mine environment (50°-60° F) so long as high work rates in a stagnant air flow situation are not encountered. Under conditions of 50°-60° F ambient and average air velocities of 2 mph across the canister during high-work rate activities, the PBA can assure peak inspired gas temperatures no greater than 115°-120° F.
2. It was shown that the hood could be easily donned and doffed, provides an adequate seal without discomfort, does not interfere with the wearing of a hard hat, and allows good communication. However, light fogging of the lens was experienced after about 20 min into the tests. This light fog continued for about 5 min and then cleared somewhat by drainoff. Approximately a cupful of perspiration collected within the hood during this time. It is felt that use of DeMist antifog on CR-39 lenses as originally planned would alleviate this problem.
3. Although chlorate candle duration cannot be specified at 60 min minimum, the total PBA easily achieves this duration. Even at the end of 60 min of high-work-rate testing, the PBA breathing bags remained 60 to 70 percent filled with oxygen.
4. No additional qualifications need be taken to the design requirements and objectives previously listed.

PBA STORAGE AND DEPLOYMENT

It is obvious that, to supply the greatest degree of safety to the user, the PBA must be close to the user at the instant of the emergency. Ideally, the miner would have the PBA attached to his person. To be acceptable to the user and to be carried during his normal work day, the PBA must be of the minimum weight and size. As can be seen in the tradeoffs, these factors were heavily weighted. It was the design goal to make the PBA of such weight, bulk, and configuration that the miner would accept the hindrance. It was felt that the initial designs

would meet the criteria, and the carrying case was planned for wearing the PBA on the miner's belt. However, weight and bulk on several components had to be increased because of developmental problems in pushing current state-of-the-art. It became apparent that the prototype PBA would probably not be well suited to continuous carry by most miners without undergoing major redesign (see component and overall weights in fig. 6.16). Therefore, the carrying case configuration shown in figure 6.17 was adopted for at least intermittent carry by miners.

<u>Item</u>		<u>Actual Weight</u>	<u>Estimated Weight</u>
<u>Canister Assembly:</u>	(1)	6.200	--
Body	(1)		0.520
Cooling Fins	(5)		0.416
Exhaust Plenum	(1)		0.018
Exhaust Screen	(1)		0.051
Intake Screen	(1)		0.057
Heat Exchanger	(1)		0.210
Ports	(2)		0.054
End Closure	(1)		0.071
LiOH	-		1.480
Candle and Filter	(1 each)		3.100
Heat Shroud	(1)		0.102
<u>Carrying Case</u>	(1)	1.440	--
Carrying Case (Redesign)	(1)		1.437
Straps	(1)		0.060
<u>Man-Apparatus Interface</u>	(1)	0.120	0.120
<u>Breathing Bags and Hoses</u>	(1 set)	0.450	0.400
<u>Barrier Bag</u>	(1)	0.070	0.063
<u>Solder and Shroud Assembly Clips</u>			0.300
TOTALS:		8.280	8.459

Figure 6.16 Overall PBA weight (lb).



Figure 6.17 PBA, stowed configuration.

The next step was to select suitable materials for the case. This study considered not only material weight but manufacturing processes, strength (dent resistance), cost, process development, and number of fabrication steps. Both metals and plastics were con-

sidered. Plastics, although much better for dent resistance, are inherently porous. The study considered metalizing the inside of the case to eliminate the porosity, of the use of a very thin (0.005 in.) metal foil liner. It was learned that metalizing was not to be recommended, and the foil liner would complicate the manufacturing process and require much development. However, it was found that newly developed package material (using heavier foil) will provide the necessary seal.

The combination of a fiberglass case and heat-sealed packing bag (fig. 6.18) results in the best strength, weight, cost, and development combination.

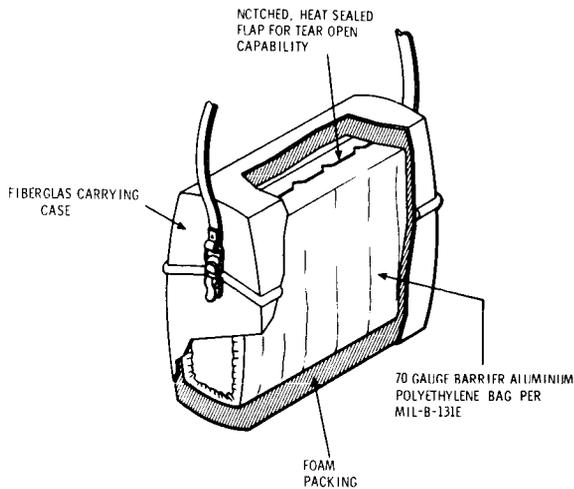


Figure 6.18 PBA packaging.

The PBA is contained within the hermetically sealed barrier bag. Notches along the top edges of the bag provide an easy tear-open unit. The sides of the case are slightly bowed to add deflection resistance; the two halves are joined together by a tongue-and-groove joint and secured by quick-action snaps. As shown, the PBA is supported within the case by foam rubber padding.

In addition to carrying case design and development, a system analysis study was conducted to determine criteria, recommendations, and guidelines for deployment of PBAs in strategically located caches proximal to major work areas.

CONCLUSIONS

This work has demonstrated that it is well within the reach of today's technology to produce a 1-hr closed-circuit, no-maintenance breathing apparatus

that provides good voice communications and is inexpensive enough for widespread use in coal mines. Approach feasibility has been proven, and with improvements in technology, such as the chlorate candle improvements described by Dr. Malich in paper 25, the package weight and volume can be reduced. The only discomfort factor—high inhalation gas temperature—becomes prohibitive only during improbable operation at peak work rates in stagnant ambient air. Improvement of heat transfer characteristics to render the concept capable of broader application and use at higher ambient temperatures is readily achievable.

ACKNOWLEDGEMENT

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