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(REVISION A)

TECHNICAL MANUAL

DESIGN GUIDELINES FOR CARBON DIOXIDE SCRUBBERS

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Design data and guidelines are presented to help predict the performance of axial flow carbon dioxide canister designs using alkali metal hydroxide absorbers. The design data are derived from a large series of laboratory tests conducted at the Naval Coastal Systems Center to isolate the effects of environmental and geometric parameters on canister absorption efficiency. Sample canister designs are considered to demonstrate the use of the derived data to predict effective canister life and pressure drop levels. Alternative techniques for the sorption of carbon dioxide are also reviewed.

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REVISION PAGE

Changes and minor revisions have been made on the following pages.

The changes have not resulted in any technical changes, nor in intent and purpose of the Manual.

Page	Change
v	Change A_F to A_W
2	Add "Text continues..."
3	Box-in Table 1
17	Figure 4 - add grid and change scale
23	Figure 10 - add grid
24	Correct Equation 11
25	Figure 11 - add grid
26	Figure 12 - add grid
27	Figure 13 - add grid
28	Figure 14 - add grid
29	Figure 15 - add grid Change A_F to A_W
31	Correct Equations and values in Steps 4, 5, 6
32	Change e from in. to ft. in Step 6
33	Change A_F to A_W in Steps 13 and 14
34	Change diameter from in. to ft. and A_F to A_W
36	Change diameter to 0.01167 ft. and A_F to A_W
37	Change diameter to 0.01167 ft. Change Re Equation to 0.01167 ft. Change A_F to A_W
38	Change A_F to A_W in two places
42	Change V_o to $\bar{V}$ in three places
43	Change V_o to $\bar{V}$
44	Change V_o to $\bar{V}$ in two places
45	Change e to 0.01167 ft. in two places Change V_o to $\bar{V}$
46	Change e to 0.01167 ft. in Figure 19 Change V_o to $\bar{V}$
47	Change diameter values in Table 3 Change V_o to $\bar{V}$ in three places Insert 0.01167 three places
48	In Δp Equation change divisor to 0.01167

GLOSSARY

Baffle:	An obstructing device within a canister which deflects the flow of gases.
Breakthrough:	The act, result, or time at which the carbon dioxide concentration in the gas stream that exits the canister exceeds the physiological limit for human respiration.
Breathing Resistance:	The impedance to the flow of respired gas, usually expressed in the cm H_2O/l/sec.
Canister Duration:	Useful life of the carbon dioxide absorption system prior to breakthrough.
Causticity:	The ability to burn or destroy living tissue by chemical action.
Contact Time:	The time interval during which the CO_2 laden gas is within the reaction zone of the canister; residence time.
Dead Volume:	The volume within a canister which is not occupied by the solid absorbent; equal to the sum of the interparticle space and the intraparticle space.
Efficiency:	Ratio which is indicative of the canister performance; equal to the capacity of canister CO_2 absorption divided by its theoretical absorption capacity.
Inter-Particle Space:	Dead volume in a canister which is located between the adjacent particles of absorbent material.
Intra-Particle Space:	Dead volume in a canister which is made up of the porous volume within an absorbent particle.
Linear Velocity	Superficial velocity of gas flow through a canister, equal to the product of the canister length and volumetric flow rate divided by the canister dead volume.
Pore:	Microscopic spaces within absorbent particles which provide much of the surface area required for the chemical reactions involved in the absorption of carbon dioxide.
Residence Time:	The mean transit time for a volume of breathing gas between canister inlet and exit.
Respiratory Rate:	Number of breaths per minute.

GLOSSARY (Continued)

Respiratory Cycle:	One complete breath, consisting of an inspiratory and expiratory cycle.
Respiratory Minute Volume:	Volume per minute of gas moved in and out of the lungs.
Respiratory Quotient:	The ratio of the volume of carbon dioxide produced to the volume of oxygen consumed.
Reynolds Number:	A dimensionless quantity expressing the ratio of inertia to viscous forces in a flow system.
Surface Level Equivalent (SLE):	A measure of the partial pressure of CO_2 in a gas mix; equal to the CO_2 percentage by volume in the gas mix multiplied by the total pressure in atmospheres absolute; i.e., $\%\ SLE = \%\ CO_2 \times P$, ata
Tidal Volume:	Volume of gas inspired or expired during a single respiration.
Vital Capacity:	The maximum volume of gas a subject is capable of exhaling after inflating the lungs to their maximum capacity.

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INTRODUCTION

Since World War I, when chemical absorbing agents were being investigated for gas masks,[1] engineers have been asking how the absorption efficiency of their CO_2 scrubbers can be optimized. What are the most favorable environmental conditions for efficient operation of the absorption canister? How does the geometry of the canister affect this efficiency? Can we predict the performance of a CO_2 scrubber under one flow condition based on our observations of its performance under different flow conditions?

This manual has been developed in an effort to help answer these questions as well as help engineers to predict the performance of prototype designs. Most design information in this manual is related to the absorption characteristics of High Performance Sodasorb, manufactured by W. R. Grace Co. This information is derived from a large series of laboratory tests[2] [3] [4] [5] conducted between FY 80 and FY 82 to isolate the effects of various environmental parameters on absorption efficiency. Limited data relating the performances of other absorbents is given in Appendix A. It is the intent of the authors to update this manual with more complete characteristics of other absorbents as this information becomes available.

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[1] Wilson, R. E., "Sodalime as an Absorbent for Industrial Purposes," Journal of Industrial and Engineering Chemistry, Vol. 12, No. 10, pp 1000-1007, October 1920.

[2] Naval Coastal Systems Center Technical Memorandum 349-82, "The Effects of Pressure and Particle Size on CO_2 Absorption Characteristics of High Performance Sodasorb," by A. Purer, G. A. Deaon, B. H. Hammonds, and M. L. Nuckols, June 1982.

[3] Naval Coastal Systems Center Technical Memorandum 327-81, "Carbon Dioxide Absorption Characteristics of High Performance Sodasorb at One Atmosphere," by A. Purer, G. A. Deason, M. L. Nuckols, and J. F. Wattenbarger, October 1981.

[4] Naval Coastal System Center Technical Memorandum TM 364-82, "The Effects of Pulsatile Flow on CO_2 Absorption by High Performance Sodasorb," by A. Purer, G. A. Deason, R. J. Taylor, and M. L. Nuckols, December 1982.

[5] Naval Coastal Systems Center Technical Memorandum TM 363-82, "The Effects of Chemical Hydration Level on CO_2 Absorption by High Performance Sodasorb," by A. Purer, G. A. Deason, and M. L. Nuckols, November 1982.

CARBON DIOXIDE CONCENTRATION AND PHYSIOLOGICAL EFFECTS[6]

In normal breathing, the concentration of oxygen in the breathing gas is reduced and the oxygen is replaced by a nearly equal volume of carbon dioxide. If carbon dioxide is included in the inhaled gas, the partial pressure of carbon dioxide in the blood increases and the respiratory center in the brain increases ventilation rate to restore normal carbon dioxide tension. Excessive amounts of carbon dioxide in the breathing gas result in toxic effects, the severity of which depend upon exposure time and the partial pressure of carbon dioxide.

Carbon dioxide is produced as oxygen is consumed at the rate of 0.8 to 1.0 litre CO_2 per litre of oxygen consumed. This ratio is called the respiratory quotient (RQ) and can be assumed to be about 0.85 for purposes of canister design. Various RQs can be taken from Table 1 for various swimming speeds. To calculate the rate of CO_2 buildup where none is removed, the following equation can be used:

$$\dot{F}_{CO_2} = [(N \cdot \dot{V}_{CO_2})/(V_{CH} \times P_B)] \times 100$$

where

$\dot{F}_{CO_2}$ = Rate of CO_2 buildup (percent/min.)

V_{CH} = Volume of divers helmet or chamber (litres)

N = Number of divers (in a chamber)

P_B = Environmental pressure (ata)

$\dot{V}_{CO_2}$ = Average carbon dioxide generation for each diver, litre/min (STPD) (obtained by multiplying oxygen consumption, $\dot{V}_{O_2}$, by 0.85).

Perhaps of more use in dealing with a one-man life support apparatus is our ability to calculate the CO_2 level in a steady gas stream which carries the diver's exhalation to a scrubber. The inlet CO_2 concentration to the A scrubber can be calculated by:

(Text continues on page 4.)

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[6] NAVMAT P9290 System Certification Procedures and Criteria Manual for Deep Submergence Systems, Appendix E, by CDR E. D. Thalmann, MC, USN, and CDR J. L. Zumrich, MC, USN, August 1981.

TABLE 1
CO_2 PRODUCTION VERSUS O_2 CONSUMPTION FOR VARIOUS SWIMMING RATES

Swim Speed (kt)		O_2 Consumption (lpm)	RMV (lpm)	CO_2 Produced		
				g/min*	lpm**	% CO_2
	Low	0.26	7.0	0.44	0.221	3.57
Rest	Mean	0.34	9.0	0.57	0.289	3.64
	High	0.42	11.0	0.70	0.357	3.68
	Low	0.67	17.0	1.14	0.576	3.84
0.5	Mean	0.82	20.0	1.41	0.714	4.02
	High	1.00	24.5	1.72	0.870	4.05
	Low	0.96	24.5	1.65	0.835	3.87
0.7	Mean	1.14	25.0	1.96	0.991	4.10
	High	1.35	34.0	2.43	1.228	4.50
	Low	1.13	25.0	1.94	0.982	4.19
0.9	Mean	1.53	37.0	2.75	1.391	4.26
	High	1.90	49.0	3.49	1.768	4.45
	Low	1.34	34.0	2.43	1.219	4.03
1.0	Mean	1.83	44.0	3.36	1.701	4.38
	High	2.26	55.0	4.33	2.190	4.51
	Low	1.87	45.0	3.43	1.738	4.39
1.2	Mean	2.50	60.0	4.79	2.425	4.60
	High	3.03	66.0	5.99	3.030	5.21

The data in this table were taken from References 7, 8, and 9.

*Based on density of CO^2 at standard temperature and pressure (STPD) of 1.977 g/litre.

**Based on respiratory quotients ranging from 0.85 to 1.0 where

$$RQ = \frac{\dot{V}CO_2\ (CO_2\ \text{Produced})}{\dot{V}_{O_2}\ (O_2\ \text{Consumed})}$$

NOTE: $\frac{RMV}{\dot{V}_{O_2}} \approx 24$ (RMV = respiratory minute volume

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[7] Donald, K. W. and Davidson, W. M., "Oxygen Uptake of Booted and Fin Swimming Divers," J. of Applied Physiology, Vol. 1, No. 6, pp. 31-37, July 1954.

[8] Goff, L. G., et al, "Oxygen Requirements in Underwater Swimming," J. of Applied Physiology, Vol. 9, No. 2, pp. 219-221, September 1956.

[9] Dwyer, J. V. and Lamphier, E. H., "Oxygen Consumption in Underwater Swimming," US Navy Experimental Diving Unit Formal Report 14-54, December 1954.

$$F_{CO_2} = [(\dot{V}_{O_2} \cdot RQ)/(Q \cdot P_B)]/28.32$$

where

F_{CO_2} = Fractional CO_2 concentration in gas stream

$\dot{V}_{O_2}$ = Diver's oxygen consumption rate, litre/min (Table 1)

RQ = Respiratory quotient, 0.85

Q = Volumetric flow rate to canister (acfm)

Since the usual units for expressing CO_2 partial pressure are mmHg, the fractional increase should be converted to partial pressure increase:

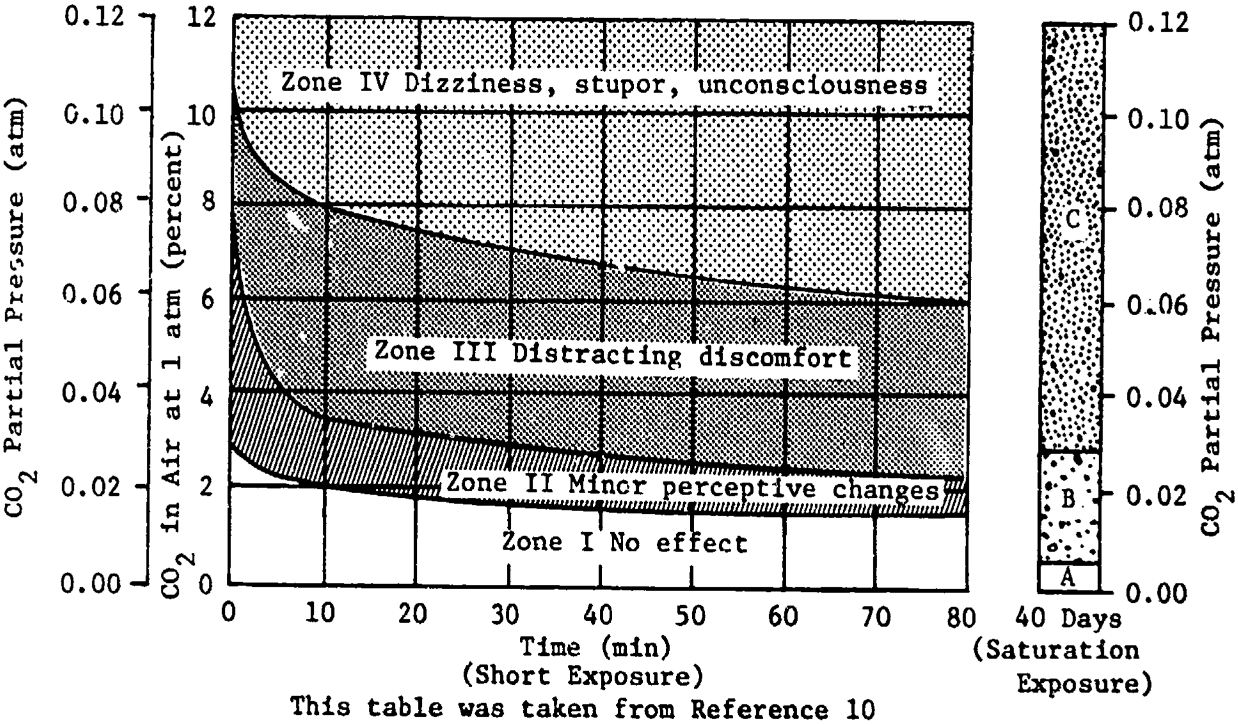
$$P_{CO_2}\ (\text{mmHg}) = F_{CO_2} \times P_B(\text{ata}) \times 760.$$

Thus, for example, 0.5 percent at 3 ata represents a fractional concentration of 0.005 at that depth with the partial pressure being:

$$P_{CO_2} = 0.005 \times 3 \times 760 = 11.40\ \text{mmHg}.$$

It is always desirable to keep the CO_2 level in the breathing gas at 0 mmHg, but this is rarely achieved. Figure 1 shows the physiological effects of carbon dioxide on humans for different concentrations and exposure periods. In Zone I, no perceptible physiological effects have been observed. In Zone II, small threshold hearing losses have been found, and there is a perceptible increase in depth of respiration. In Zone III, the zone of distracting discomfort, the symptoms are mental depression, headache, dizziness, nausea, air hunger and decrease in visual discrimination. Zone IV represents marked physical distress leading to dizziness and stupor with inability to take steps for self-preservation. The final state is unconsciousness.

The bar graph at the right of Figure 1, for exposures of 40 days, shows that concentrations of carbon dioxide in air of less than 0.005 atm partial pressure (Zone A) cause no biochemical or other effects. Concentrations between 0.005 and 0.030 atm partial pressure (Zone B) cause adaptive biochemical changes, which may be considered a mild physiological strain. And concentrations above 0.030 atm partial pressure (Zone C) cause pathological changes in basic physiological functions.



This table was taken from Reference 10

FIGURE 1. RELATION OF PHYSIOLOGICAL EFFECTS TO CARBON DIOXIDE CONCENTRATION AND EXPOSURE PERIOD

For saturation diving (or any long exposure), the CO_2 should be controlled to an upper limit of 3.80 mmHg (0.005 atm) with allowable short peaks up to 6.0 mmHg. For ventilated chambers or open-circuit diving apparatus, an upper limit of 15.0 mmHg (0.02 atm) is acceptable. Both of these limits are safe and have more to do with practical limitations than physiological.

Figure 2 shows CO_2 tolerance zones as a function of percentage CO_2 and depth at partial pressures taken from Figure 1 for a 1-hour exposure period. As with oxygen, the physiological effects of carbon dioxide depend upon its partial pressure in the blood and in the breathing gas. The percentage of carbon dioxide in the breathing gas that can be tolerated while diving decreases with depth, and the respiratory volume required to ventilate the lungs at depth remains approximately equal to that at sea level.

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[10] Roth, E. M., MC, "Space Cabin Atmospheres; Part IV - Engineering Tradeoffs of One - Versus Two - Gas Systems," NASA SP-118.

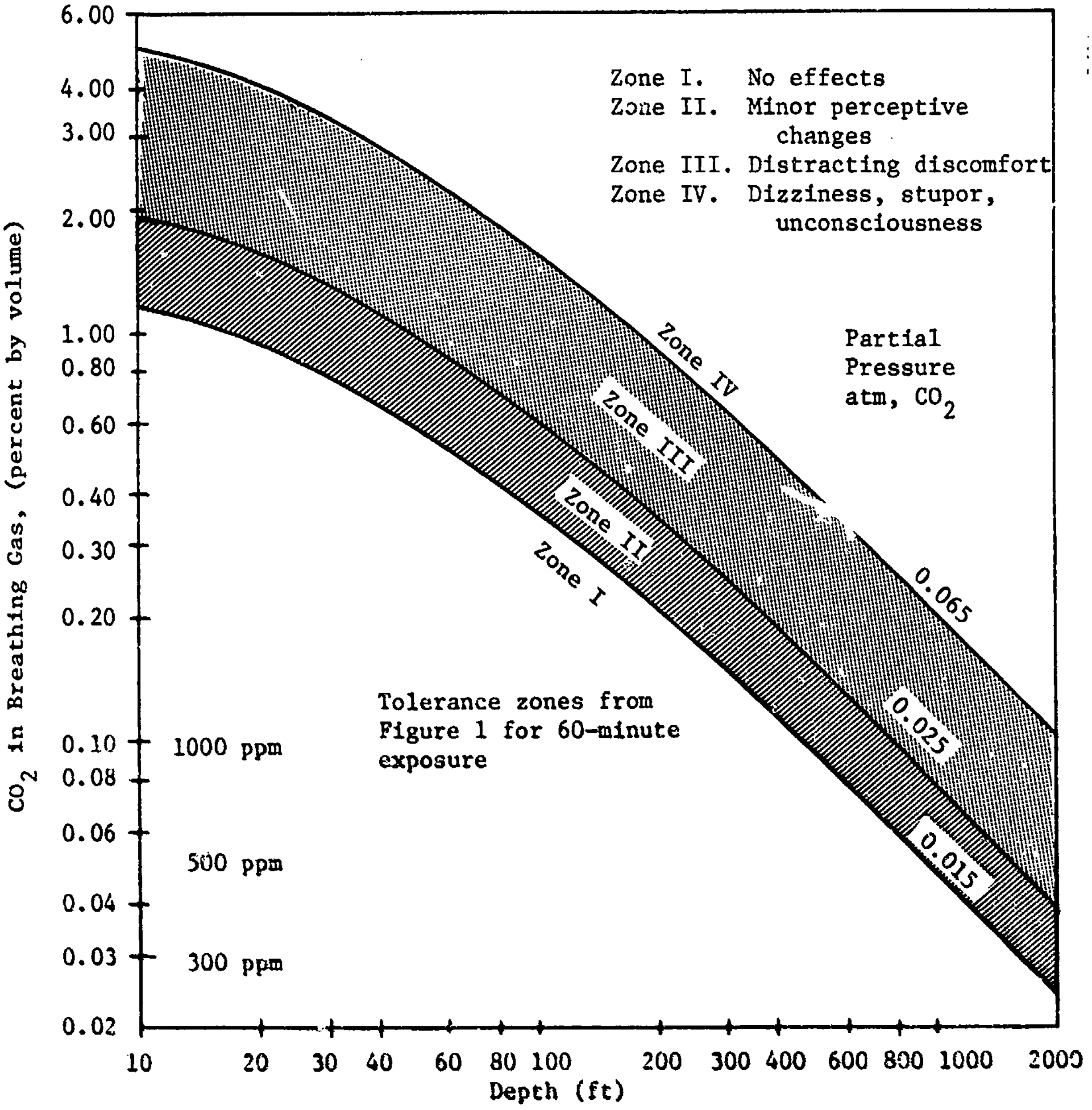


FIGURE 2. RELATION OF CO_2 TOLERANCE ZONES TO DEPTH AND PERCENTAGE OF CO_2 IN BREATHING GAS

If a diver's breathing circuit includes dead space from which he rebreathes exhaled air, this dead space must be ventilated to dilute the carbon dioxide to a nontoxic level. If all of the diver's carbon dioxide production flows into the dead space and is mixed with all of the ventilating gas, the reduction of CO_2 partial pressure depends only upon the ratio of carbon dioxide flow to diluent-gas flow. This ratio must be about 1:100 to limit carbon dioxide to 0.01 atm partial pressure, or similarly 1:50 for 0.02 atm. This range is usual in helmet ventilation.

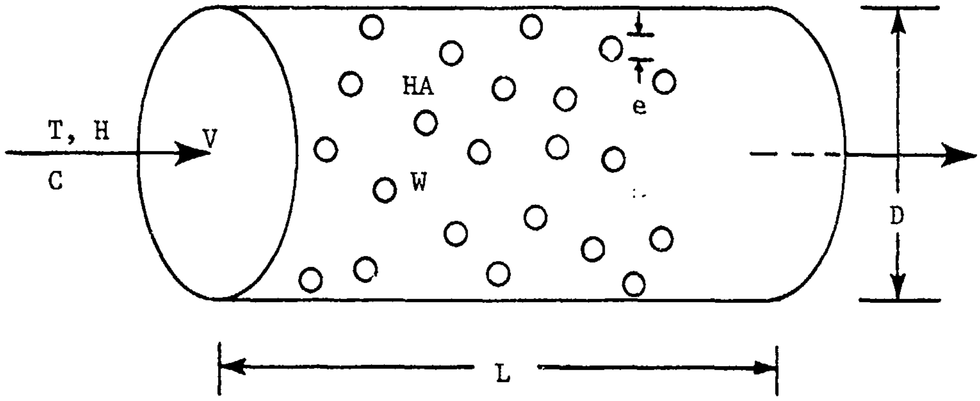
The quantity of ventilation gas can be reduced if the concentration of carbon dioxide can be reduced by other means, such as absorption by a carbon dioxide absorbent. Thus, standard rebreather deep-diving systems have an integral canister of absorbent through which the breathing gas in the helmet is recirculated to reduce carbon dioxide level and hence reduce the quantity of breathing gas required.

In closed-circuit and semiclosed-circuit breathing apparatus, all exhaled gas can be rebreathed. This is made possible by passing all exhaled gas through a canister of carbon dioxide absorber before it is again inhaled. Excess exhaled gas is vented between the mouthpiece and the absorbent canister in semiclosed-circuit apparatus, and incoming gas can be introduced in an ejector to assist in circulation through the canister.

Unventilated dead space has a significant effect on the respiratory volume required for control of carbon dioxide tension. Examples of unventilated dead space are the natural volume of the mouth and throat, the volume of a mouthpiece between nonreturn valves, and the volume of a full face mask. The effect of dead space is to require an increase in the tidal volume, or volume for each inhalation, by the amount of volume of the dead space. Thus, for example, if normal tidal volume is 1 litre and dead space in a full face mask of 0.5 litre is added, the tidal volume needed for equivalent carbon dioxide partial pressure in the blood increases to 1.5 litres. The extra tidal volume needed would reduce maximum work level, increase the quantity of breathing gas needed by 50 percent, and increase the effort of breathing. If a tidal volume of 1.0 litre is maintained, 0.5 litre of gas would be lost to the dead space and only 0.5 litre of fresh gas would be obtained with each inhalation. This would double the diver's respiratory frequency and therefore, his gas consumption. The preceding example demonstrates the desirability of minimizing dead space in any diving equipment to the extent possible while meeting other requirements.

DESIGN CONSIDERATIONS FOR CARBON DIOXIDE SCUBBERS

Many factors affecting the performance of carbon dioxide scrubbers are beyond the control of the designer; for instance, the operational pressure and temperature are usually fixed by the diver's surroundings. Any efforts to operate the scrubber in conditions other than his surroundings would be at the expense of energy, complex designs, and cost.



Refer to Table 2 for nomenclature

FIGURE 3. THE ABSORPTION PROCESS

Typical Chemical Reactions for Sodasorb

1. $CO_2 + H_2O \rightleftarrows H_2CO_3$

2. $2H_2CO_3 + 2NaOH + 2KOH \rightarrow Na_2CO_3 + 4H_2O + K_2CO_3$

3. $2Ca(OH)_2 + Na_2CO_3 + K_2CO_3 \rightarrow 2CaCO_3 + 2NaOH + 2KOH$

Reaction rate, R, is finite.
H_2O is required to initiate reaction.
H_2O is produced as reaction continues.

Controlling Variables (Figure 3)

Residence Time versus Flow Rate. The CO_2 laden gas must reside in the scrubber for a sufficient period of time to allow the absorption process to occur. There is a flow rate beyond which the reaction will not have time to be completed even if all other conditions are satisfactory for the reactions to occur.

Moisture Content.

1. Too little moisture in the incoming gas or in the absorbent will prevent the absorption process from being initiated.

2. Too much moisture in the incoming gas or in the absorbent will cause a blockage of the absorbent pore volume as the reaction progresses and will decrease the absorption capacity.

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[11] Navy Experimental Diving Unit Research Report 9-57, "Canister Design Criteria of Carbon Dioxide Removal From Scuba," by G. J. Duffner, 8 March 1957.

TABLE 2

PARAMETERS OF CANISTER CO_2 ABSORPTION

Parameter	Identification	Dimensions
t_B	Breakthrough time	t
V	Gas stream velocity	L/t
T	Gas temperature	T
ρ	Gas density	m/L^3
μ	Gas viscosity	m/Lt
C	CO_2 concentration	L^3/L^3
H	Gas stream water vapor content	L^3/L^3
HA	Absorbent water content	L^3/L^3
W	Absorbent mass	m
e	Particle size	L
L	Canister length	L
D	Canister diameter	L
D_v	Mass diffusivity	L^2/t
A	Absorption capacity	m/m
R	Reaction rate	m/t

Basic Units

t = Time

m = Mass

L = Length

T = Temperature

Temperature.

1. Reaction rate is dependent upon local temperature.

2. Vapor pressure of gas stream is coupled to local temperature.

3. Too Low Temperature. Insufficient moisture supplied for reaction will produce moisture that cannot be carried away.

4. Too High Temperature. Moisture-carrying capacity of gas will tend to dry out absorbent.

However, maximum efficiency of the carbon dioxide absorbent can be obtained by following several general design guidelines as summarized in Figure 3.[11] They include the following:

1. Maximize the Gas Residence Time Within the Canister. The carbon dioxide in the gas stream has the opportunity to be absorbed by the chemical absorbent. In constant flow systems the residence time can be maximized either by increasing the canister length (a trade-off with canister flow resistance) or by reducing the gas velocity within the canister. The flow velocity can be reduced either by providing a large cross-sectional area within the canister or by controlling the volumetric flow rate actually going through the canister. For example, bypassing a portion of the gas stream around the canister can effectively reduce this flow rate within the canister while still maintaining an acceptable CO_2 level after mixing downstream of the canister.

In intermittent flow systems, such as those using the pumping action of the breathing cycle, the dead volume within the canister should be made as large as the human tidal volume to maximize absorption efficiency. In so doing, the gas from the previous exhalation can reside in the canister during the entire inhalation phase. An intergranular space of approximately 0.5 litre is adequate for resting conditions with up to 3.5 litres required for maximum work rates.

2. Match the Scrubber Duration with the Oxygen Storage Capacity. The scrubber duration should be adequate to match the expected oxygen consumption by the diver as indicated by the diver's respiratory quotient (RQ). For a typical RQ of 0.85, the diver would be required to absorb 0.85 litre of CO_2 for each litre of oxygen consumed. A breathing apparatus designed with a system RQ greater than 0.8 to 1.0, i.e., with an excess scrubber capacity, would deplete its oxygen source prior to canister breakthrough. An apparatus with a system RQ that is too low would cause the diver to carry an unnecessarily large oxygen source.

3. Minimize Canister Flow Resistance. Inhalation during breathing will become more difficult as flow resistance in a breathing apparatus exceeds

7.0 to 7.5 cm H_2O/litre/second.[12] The exhalation resistance should not normally exceed 2.9 cm H_2O/litre/second and should never exceed the inhalation resistance. A further discussion on breathing resistance is given later.

4. Maintain Adequate Moisture Level in the Canister. This factor is more important with Sodasorb and Baralyme than with LiOH. It must be noted that high absorption efficiencies have been observed when LiOH was used in gas streams with relative humidities as low as 5 percent.[13]

The typical three-step reaction involved in the absorption of carbon dioxide by Sodasorb is[14]

1. $CO_2 + H_2O \rightarrow H_2CO_3$
2. $2H_2CO_3 + 2NaOH + 2KOH \rightarrow Na_2CO_3 + 4H_2O + K_2CO_3$
3. $2Ca(OH)_2 + Na_2CO_3 + K_2CO_3 \rightarrow 2CaCO_3 + 2NaOH + 2KOH$.

Note that in this process water is necessary to initiate the CO_2 absorption (Equation 1). Note also that water is a by-product of the absorption process (Equation 2). If the incoming gas stream is saturated with water vapor, the water produced in the absorbent bed may not be picked up. This water will then tend to coat the outer surfaces and pores of the absorbent particles, causing a decrease in absorption efficiency. If the incoming gas stream is too dry, the initiation of the reaction may be inhibited or the absorbent bed may be desiccated once the reaction is initiated, thereby limiting further absorption.

As a general rule, moisture levels of the incoming gas stream should be maintained above 70 percent RH when using Sodasorb or Baralyme.[15]

5. Maintain the Canister Temperature Level Where Possible. The absorption rate of chemical absorbers is directly related to the bed temperature. Scrubber development programs have demonstrated consistently that

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[12] Silverman, L., et al, "Air Flow Measurements on Human Subjects With and Without Respiratory Resistance at Several Work Rates," American Medical Association Archives of Industrial Hygiene and Occupational Medicine, Vol. 3, pp. 461-478, May 1951.

[13] Davis, S. H. and Kissinger, L. D., "The Dependence of the CO_2 Removal Efficiency of LiOH on Humidity and Mesh Size," American Society of Mechanical Engineers Paper No. 78-ENAs-5, Intersociety Conference on Environmental Systems, San Diego, CA 10-13 July 1978.

[14] The Sodasorb Manual of Carbon Dioxide Absorption, W. R. Grace and Co., Library of Congress Catalog Card No. 62-14923, 1962.

[15] US Navy Diving-Gas Manual, NAVSHIPS 0994-003-7010, Second Edition, June 1971.

absorption capacities are reduced in cold environments. The typical exothermic reaction with most chemical absorbers will provide a substantial quantity of heat to the canister bed; e.g., 13,500 calories are released per mole of CO_2 absorbed by Sodasorb[14] and, when properly insulated from the cold surroundings, will contribute to improved absorption efficiency. This factor is somewhat complicated due to the inter-relation of bed temperature and moisture level: a bed temperature that is too high will tend to dry out the absorbent and inhibit the completion of the reactions discussed above.

DIMENSIONAL ANALYSIS OF ABSORPTION PROCESS

The absorption process within a canister involves at least three processes from the time the CO_2 in a gas stream enters until it is chemically absorbed. These may be categorized as the mass transfer of CO_2 from the gas stream to the absorbent surface, adsorption at the surface, and, finally, chemical absorption. Satisfactory conditions must exist in each of these phases for the canister to perform as desired.

In the first process, a continual race is underway between the axial flow of the gas stream and the radial flow (due to convective mass transfer) of the CO_2 molecules toward the absorbent surface. If the axial flow velocity, V, is excessive or if the flow path, L, is too short, the CO_2 molecules will be carried through the canister without having the opportunity to move radially to contact the absorbent surfaces. The radial movement will be influenced by the mass diffusivity of CO_2 in the carrier gas, D_v; the CO_2 concentration of the carrier gas, C; and the path length between the gas midstream and the absorbent surface (related to the absorbent particle size, e, and the canister diameter, D). This radial movement will likewise be influenced by the level of turbulence that exists in the gas stream, a measure of which has been found to be a function of the gas stream density, ρ, and viscosity, μ.

Once the CO_2 molecule has made contact with the surface of the absorbent, it must be noted that water is necessary to initiate the absorption process. This water may be furnished by the vapor present in the carrier gas stream, H, or the water mixed into the absorbent, HA.

Following this initial surface reaction (usually thought of as occurring instantaneously), the CO_2 can be chemically absorbed by the active absorbent. This reaction rate, R, must be sufficient to keep up with the rate at which the CO_2 is being supplied to the chemical surface to maximize absorption. As with most chemical processes, this rate will be influenced by the ambient temperature.

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[14] ibid.

Assuming that the conditions described above have been satisfactory and a sufficient mass of active absorbent, W, is available with adequate absorption capacity, A, the carrier gas stream will be cleansed of the CO_2. When one or several of the above processes are limited, the exit CO_2 level from the canister will rise until it exceeds the physiological limit for safe recirculation, an event commonly referred to as canister breakthrough. The time at which breakthrough occurs is similarly referred to as the breakthrough time, t_B, or canister duration.

From the above discussion we can write a functional expression for the canister breakthrough time as (refer to Table 2):

$$t_B = t_B(V,\ T,\ \rho,\ \mu,\ C,\ H,\ HA,\ W,\ e,\ L,\ D,\ A,\ D_v,\ R).$$

It is not suggested that these parameters are all inclusive; however, it is believed that they have the most influence on the effective canister duration.

The large number of variables shown above (15 parameters) would make any effort to write an explicit expression for canister breakthrough time as a function of all these parameters almost impossible. However, through dimensional analysis and specific observations, we can reduce the number of variables that must be dealt with when attempting to predict the effective duration of canisters.

Note first of all that the absorbent's reaction rate, absorption capacity, and moisture content are beyond our control when dealing with commercial products. Although it would be desirable to understand the relationship that these parameters have on canister duration, their assumed constant behavior for any one absorbent will allow us to remove them from this analysis. We are then left with

$$t_B = t_B(V,\ T,\ \rho,\ \mu,\ C,\ H,\ W,\ e,\ L,\ D,\ D_v). \tag{1}$$

A Buckingham Pi[16] dimensional analysis of the above relationship will allow us to form a minimum number of independent dimensionless groups that can be used to describe the above functional relationship. Rewriting the above relationship, while substituting the basic dimensions given in Table 2 for the various parameters, we get

$$t = \left[\frac{L}{t}\right]^a [T]^b \left[\frac{m}{L^3}\right]^c \left[\frac{m}{Lt}\right]^d \left[\frac{L^3}{L^3}\right]^e \left[\frac{L^3}{L^3}\right]^f [m]^g [L]^h [L]^i [L]^j \left[\frac{L^2}{t}\right]^k . \tag{2}$$

---

[16] Shames, I, H., Mechanics of Fluids, McGraw-Hill Book Co., New York, 1962.

The exponent of the basic dimensions m, L, t, and T on both sides of the equation may be, respectively, equated according to the law of dimensional homogeneity to form the following simultaneous equations:

for m: $0 = c + d + g$

for L: $0 = a - 3c - d + 3e - 3e + 3f - 3f + h + i + j + 2K$

for t: $1 = - a - d - K$

for T: $0 = b$.

Note that we now have 11 quantities related by four equations. We can thus solve any four quantities in terms of the other seven. By solving for b, c, d, and j we obtain

$$b = 0$$

$$d = - a - K - 1$$

$$c = a + K + 1 - g$$

and

$$j = a + 2 - 3g - h - i \ .$$

By returning to Equation (2) with the dimensions replaced by the parameters and replacing b, c, d, and j by the above relations, we get

$$t_B = V^a \, T^o \, \rho^{a + K + 1 - g} \, \mu^{- a - k - 1} \, C^e \, H^f \, W^g \, e^h \, L^i \, D^{a + 2 - 3g - h - i} \, D_v^k .$$

After regrouping all parameters which have the same exponents, the above equation can be written

$$\frac{t_B \, \mu}{\rho \, D^2} = \left[\frac{\rho \, V \, D}{\mu}\right]^a [T]^o [C]^e [H]^f \left[\frac{W}{\rho \, D^3}\right]^g \left[\frac{e}{D}\right]^h \left[\frac{L}{D}\right]^i \left[\frac{\rho \, D_v}{\mu}\right]^k$$

or, returning to the functional representation given initially and noting that the first and last groupings on the right of the equation are the dimensionless Reynolds, Re_D, and Schmidt, Sc, numbers.

$$\frac{t_B \, \mu}{\rho \, D^2} = f\left[Re_D, \frac{W}{\rho \, D^3}, T, C, H, \frac{e}{D}, \frac{L}{D}, Sc\right] . \qquad (3)$$

Note that the group $t_B\mu/\rho D^2$ can be written $T_BV/D(\mu/\rho\ VD)$ or $t_BV/D(1/Re_D)$. Since we have already indicated the functional relationship of Re_D exists, we can say

$$\frac{t_B\ V}{D} = f[Re_D, \frac{W}{\rho\ D^3}, T, C, H, \frac{e}{D}, \frac{L}{D}, Sc]. \qquad (4)$$

Also, note that even though the mass diffusivity of respirable gases will decrease with pressure, the dimensionless Schmidt number has been shown to remain near constant over the operational pressure range of concern;[17] we can thus eliminate this group from the above functional representation.

Now, we define a canister efficiency as

$$\eta = \frac{t_B}{t_{TH}} \qquad (5)$$

where t_{TH} is the theoretical time to consume all active absorbent. This time can be computed by dividing the absorption capacity of the chemical by the rate of CO_2 delivered to the canister as follows:

$$t_{TH} = \frac{A \cdot W}{\frac{\pi}{4} D^2\ V\ C\ \rho_{CO_2}} . \qquad (6)$$

Rewriting Equation (5) while substituting for t_{TH} we get

$$\eta = \frac{\pi\ t_B\ D^2\ V\ C\ \rho_{CO_2}}{4\ A\ W}$$

or lumping dimensionless groups we have

$$\eta = \frac{[\frac{t_B\ V}{D}]\ C}{[\frac{W}{\rho\ D^3}]\ A} \cdot \frac{\frac{\pi}{4}}{\rho/\rho_{CO_2}} . \qquad (7)$$

---

[17] Naval Coastal Systems Center Technical Report NCSC TR 364-81, "Heat and Water Vapor Transfer in the Human Respiratory System at Hyperbaric Conditions," by M. L. Nuckols, September 1981.

By the previous definition we are able to lump four of the dimensionless groups into one to simplify the functional representation so that

$$\eta = f[Re_D, T, H, \frac{e}{D}, \frac{L}{D}] \ . \tag{8}$$

Note that we have been able to reduce the 15 original functional parameters into six dimensionless groups. In so doing we have been able to reduce the imponderable mathematics of Equation (1) to a more manageable characterization of six dimensionless groups.

CANISTER DESIGN DATA

Data from a large series of carefully controlled laboratory tests[2] [3] [4] [5] were handled in the manner described in the previous section and plotted in Figures 4 through 9. These data show the effects of particle Reynolds number, temperature, moisture level, and canister geometry on the efficiency of a canister to absorb carbon dioxide. All data are based on steady flow through axial canisters. A discussion of the relative efficiencies for canisters with intermittent flow will be given later. Refer to Appendix B for symbols and parameters used in the figures.

To use these data to design new canisters or to predict the life of present canisters in varying environmental conditions, enter Figure 10 on the abscissa or ordinate depending on the constraining conditions being put on the design. If the system flow rate is known at the depth of interest, the Reynolds number (based on absorbent particle diameter) can be calculated. This Reynolds number can then be used to obtain a canister efficiency, η, corresponding to the appropriate operating pressure. The theoretical bed life can then be read from Figure 10, for a specific weight of absorbent, to allow us to calculate a predicted canister life as

$$t_B = t_{TH} \eta \ . \tag{9}$$

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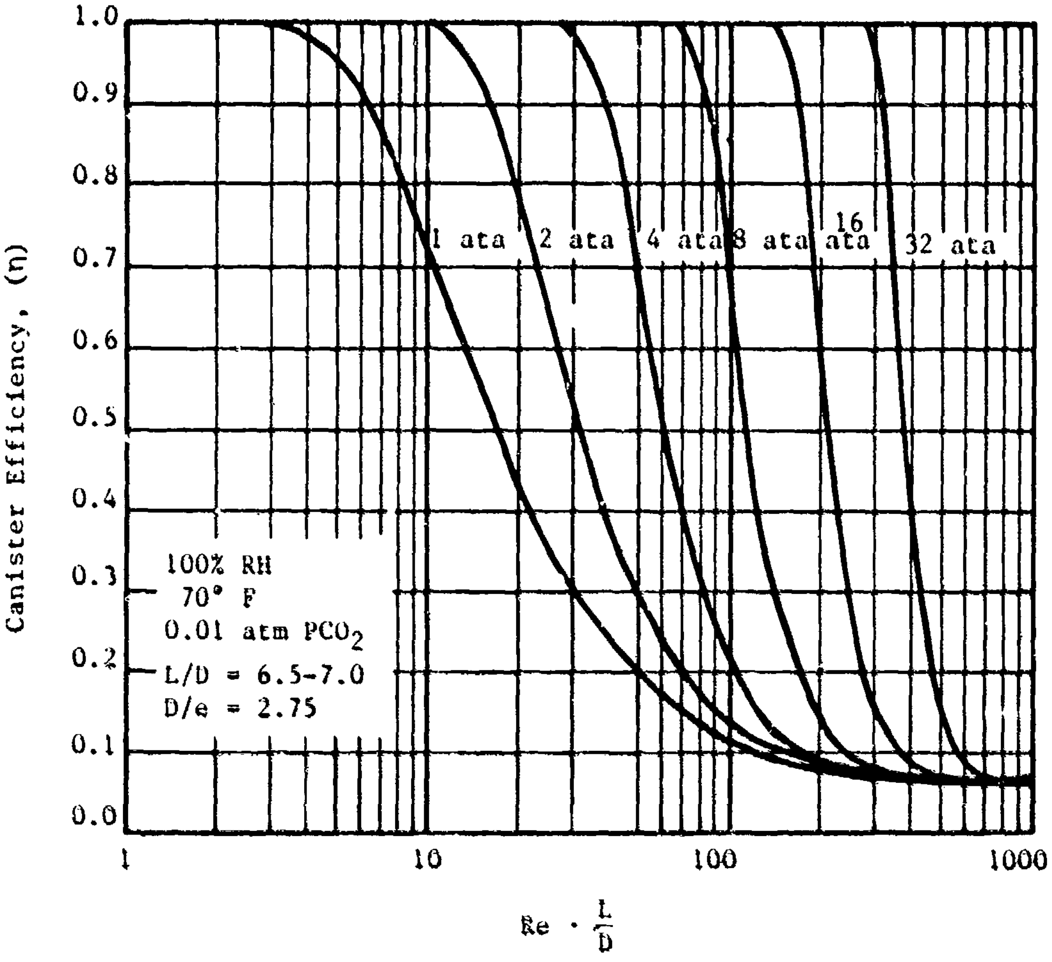
[2] ibid.

[3] ibid.

[4] ibid.

[5] ibid.



A

FIGURE 4. CALCULATED EFFICIENCY OF STANDARD TEST CANISTER AT VARYING PRESSURES

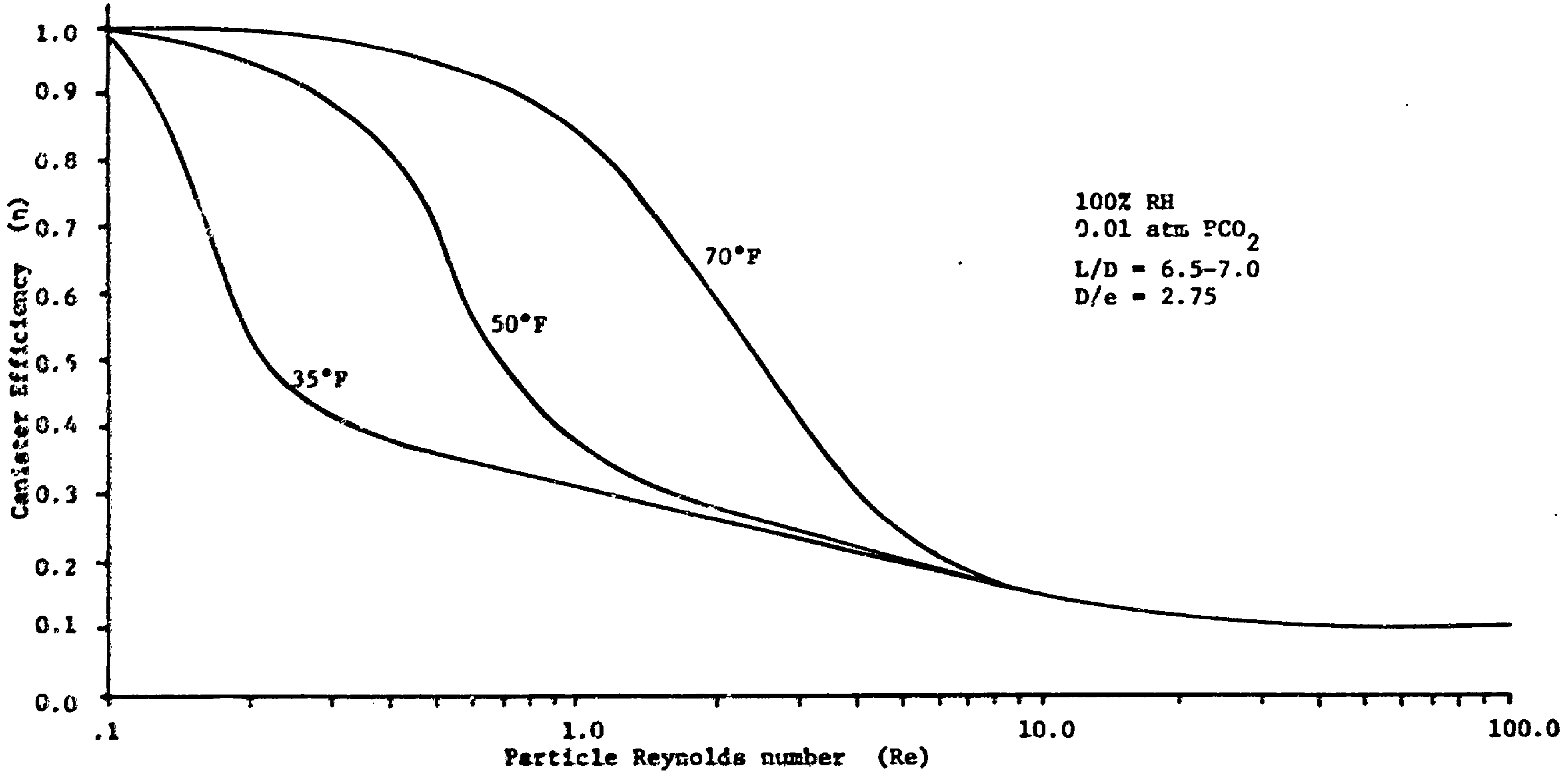


FIGURE 5. EFFECT OF GAS STREAM TEMPERATURE ON CANISTER EFFICIENCY AT 1 ATA
(FOR STANDARD CANISTER)

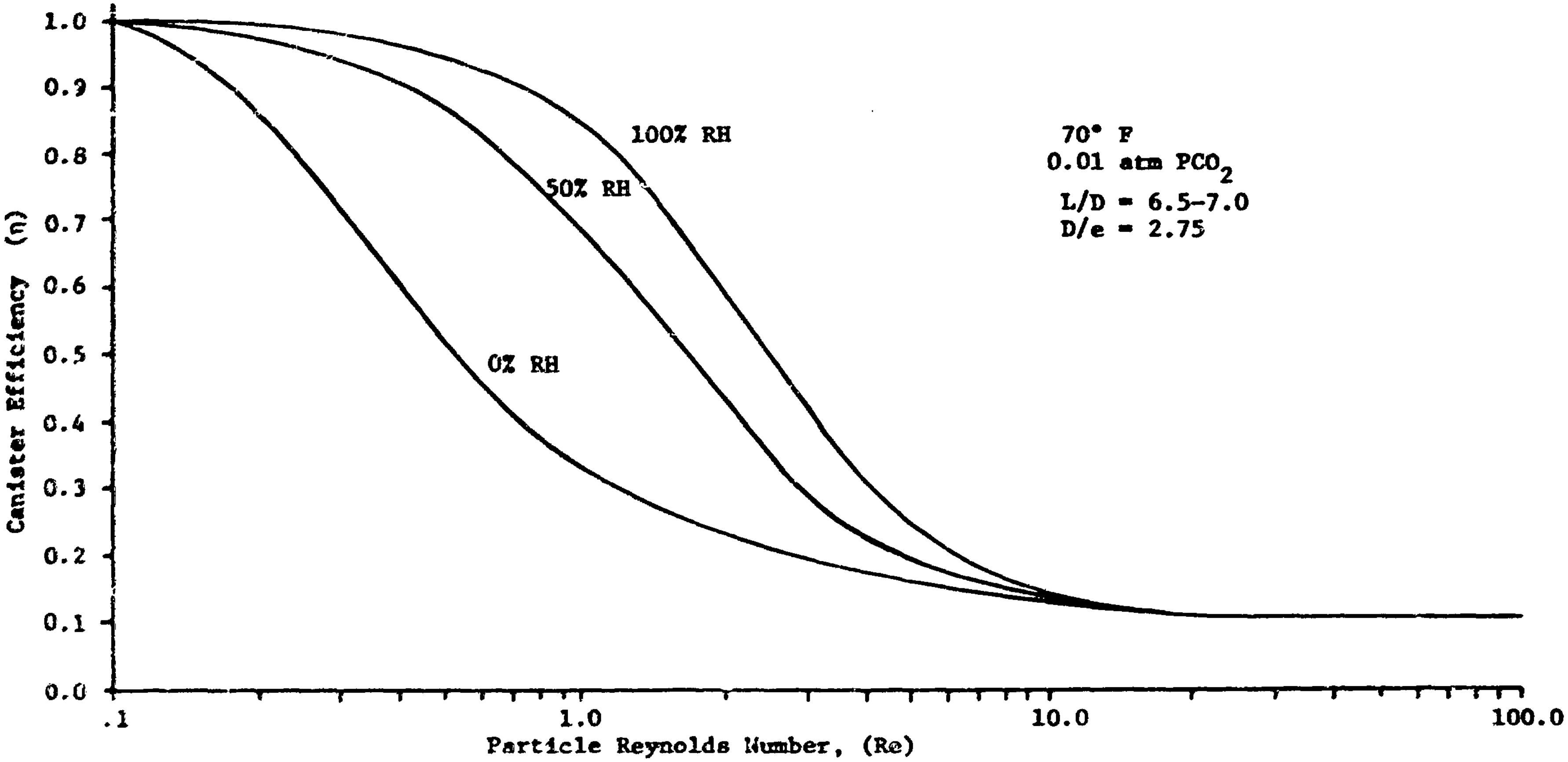


FIGURE 6. EFFECT OF GAS STREAM HUMIDITY ON CANISTER EFFICIENCY AT 1 ATA
(FOR STANDARD CANISTER)

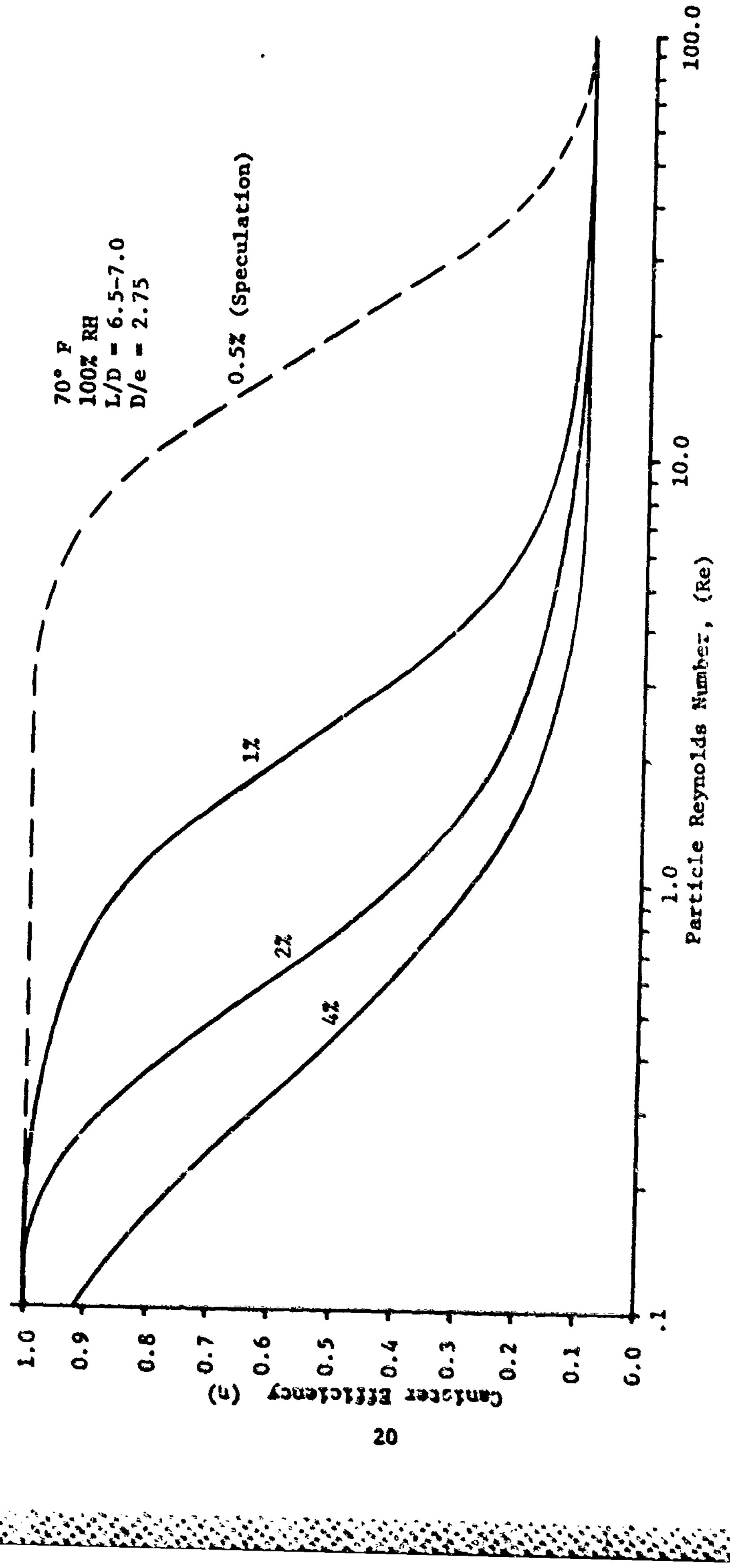


FIGURE 7. EFFECT OF GAS STREAM CO_2 CONTENT ON CANISTER EFFICIENCY AT 1 ATM
(FOR STANDARD CANISTER)

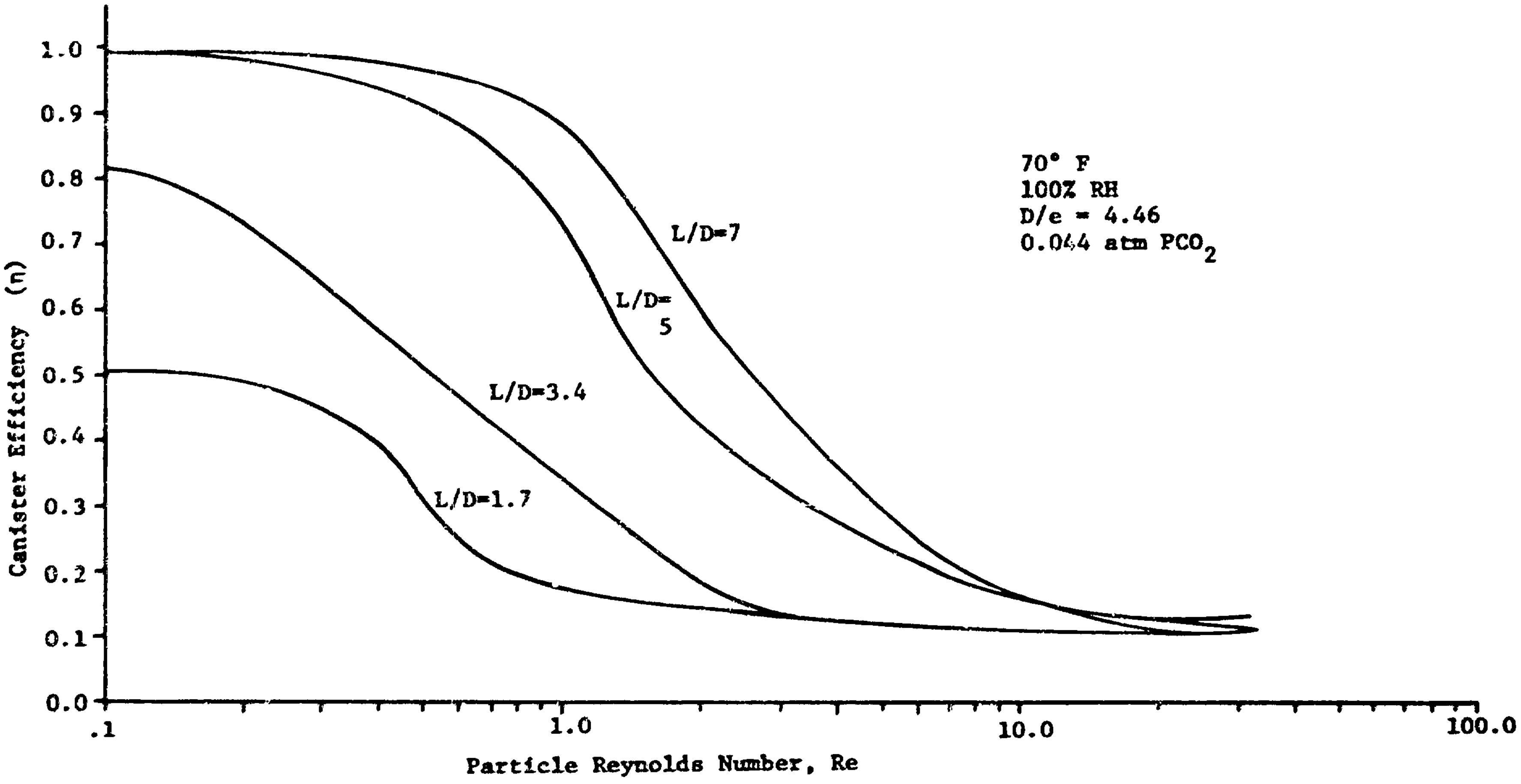


FIGURE 8. EFFECT OF CANISTER L/D RATIO ON ITS EFFICIENCY AT 1 ATA

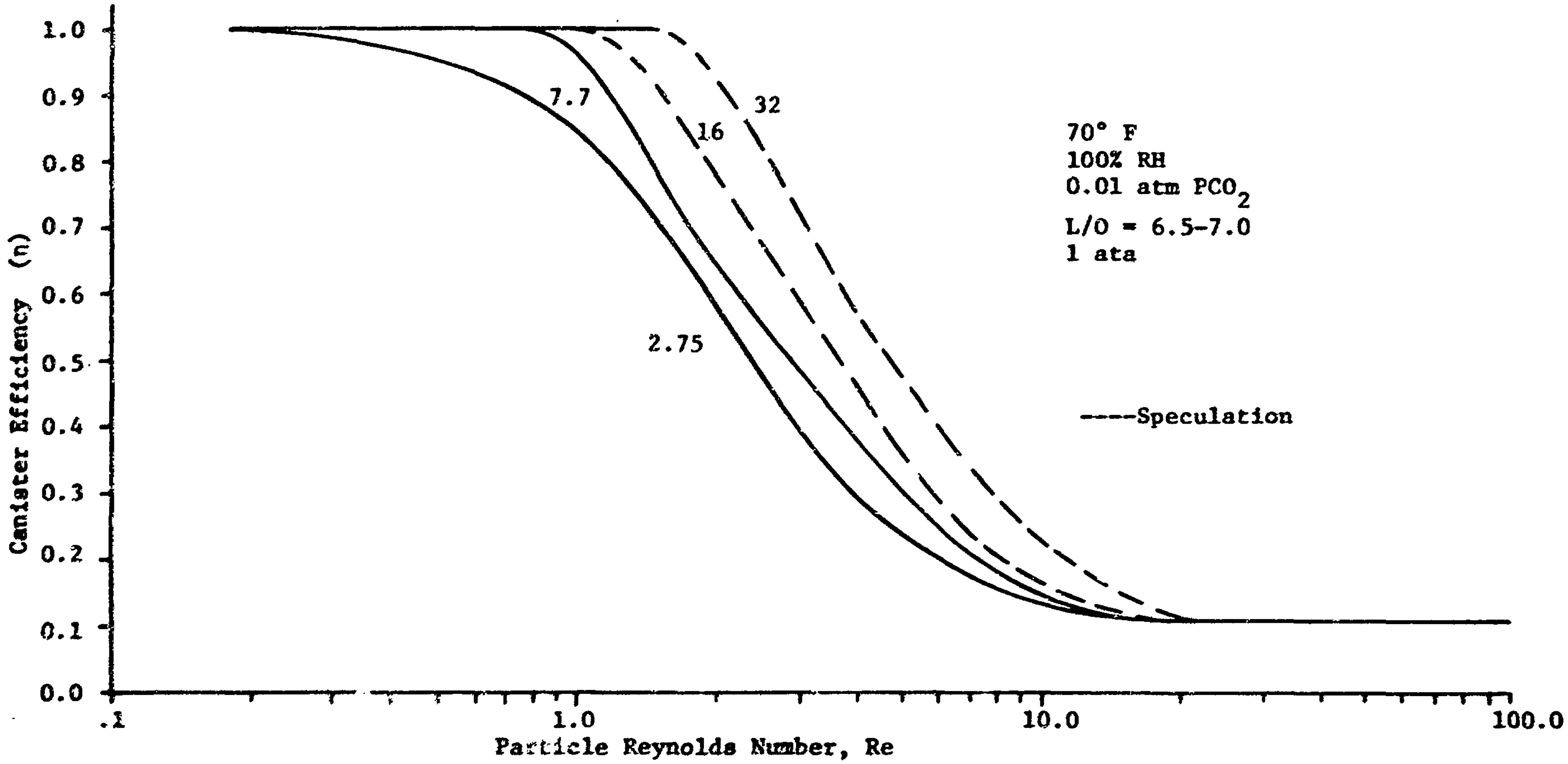


FIGURE 9. EFFECT OF D/e RATIO ON CANISTER EFFICIENCY

For CO_2 concentrations diff from 1%

Divide theoretical bedlife from chart by % CO_2 (SLE)

Bedlife based on 0.01 ata (1% SLE) CO_2 in system flow

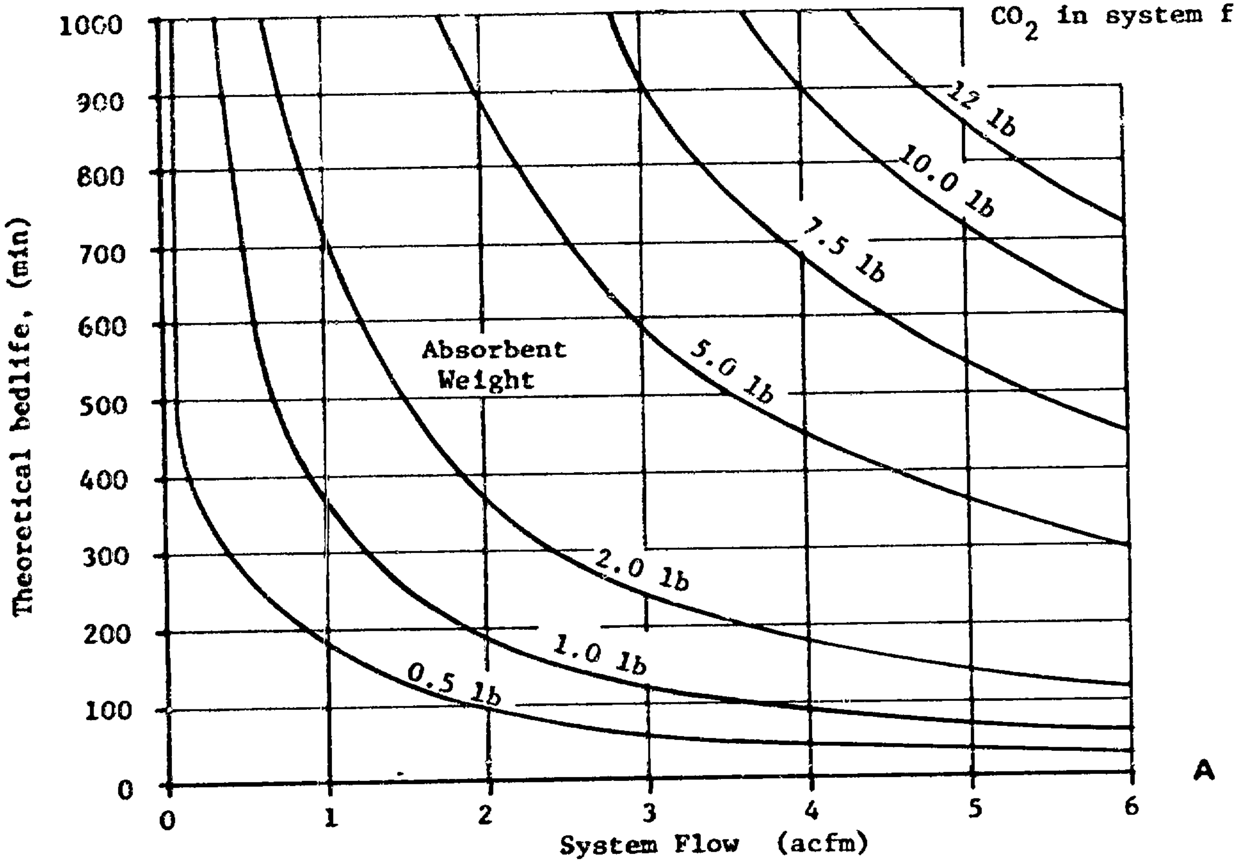


FIGURE 10. THEORETICAL BEDLIFE FOR SODASORB CANISTERS

On the other hand, if a specific canister life is desired, the previously obtained value of η can be used to calculate the necessary theoretical bed life as

$$t_{TH} = t_B/\eta \ . \qquad (10)$$

Figure 10 can then be used to determine the mass of absorbent required for this canister life requirement.

The empirical relationship for the efficiency of a standard canister

A

$$\eta_{STD} = 1 - 0.94\text{EXP}\left[-\left(\frac{P+1}{\left(\frac{Re \cdot L/D}{7P}\right)^{1.3\sqrt{P}}}\right)\right] \qquad (11)$$

where

P = environmental pressure (ata)

Re = Reynolds number based on absorbent particle diameter

has been found to closely represent the data in Figure 4. This equation can be used to derive a canister efficiency once the Reynolds number of the system flow and the ambient pressure is known. Note that this derived efficiency is for a saturated gas stream at 70°F with a canister length-to-diameter ratio and diameter-to-mesh ratio of 7 and 2.75. For conditions and canister geometries other than these, modifying coefficients, as shown in Figures 11 through 15, must be considered to calculate the canister efficiency under actual flow conditions. Detailed procedures for using this design information are given in the next section.

SCRUBBER DESIGN PROCEDURE

STEP 1: Determine inlet CO_2 concentration to canister

$$C = \frac{\dot{V}_{O_2} * RQ * 100}{Q * P * 28.32}$$

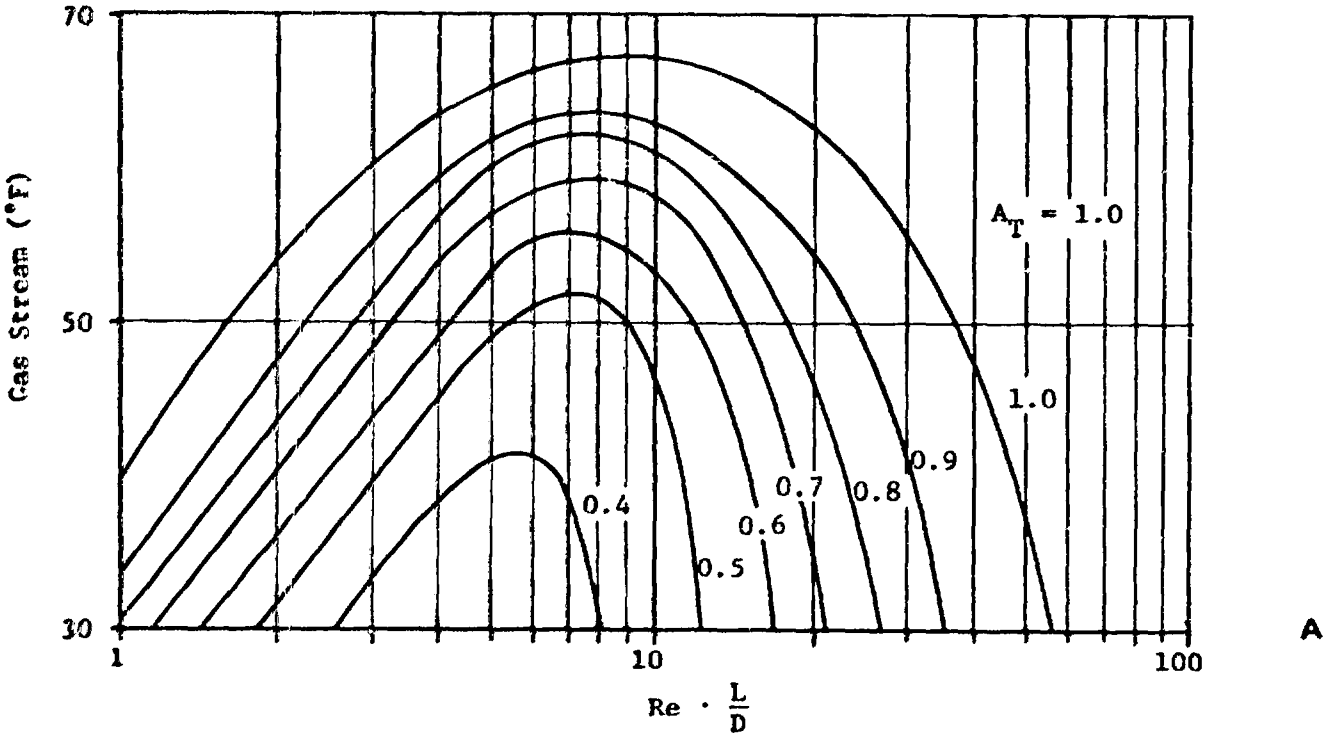


FIGURE 11. TEMPERATURE EFFECT FACTOR, A_T

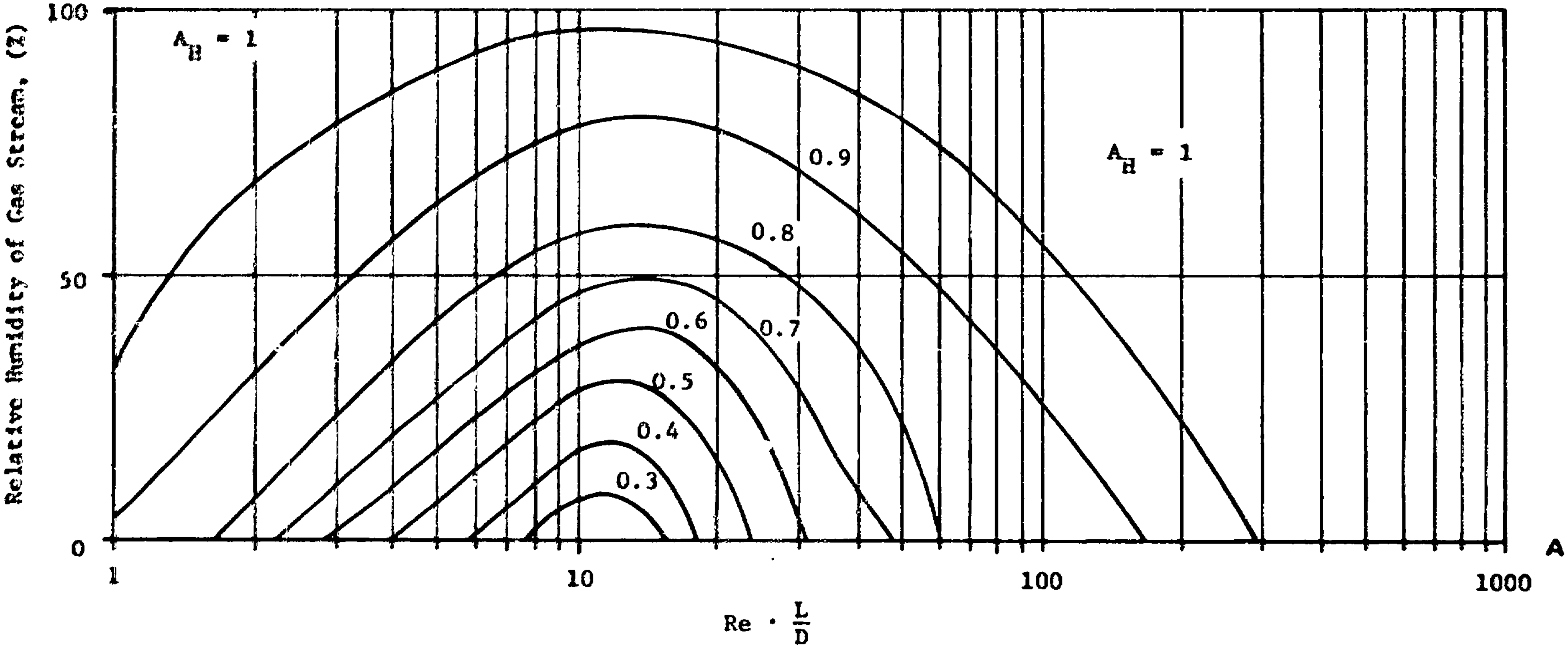


FIGURE 12. HUMIDITY EFFECT FACTOR, A_H

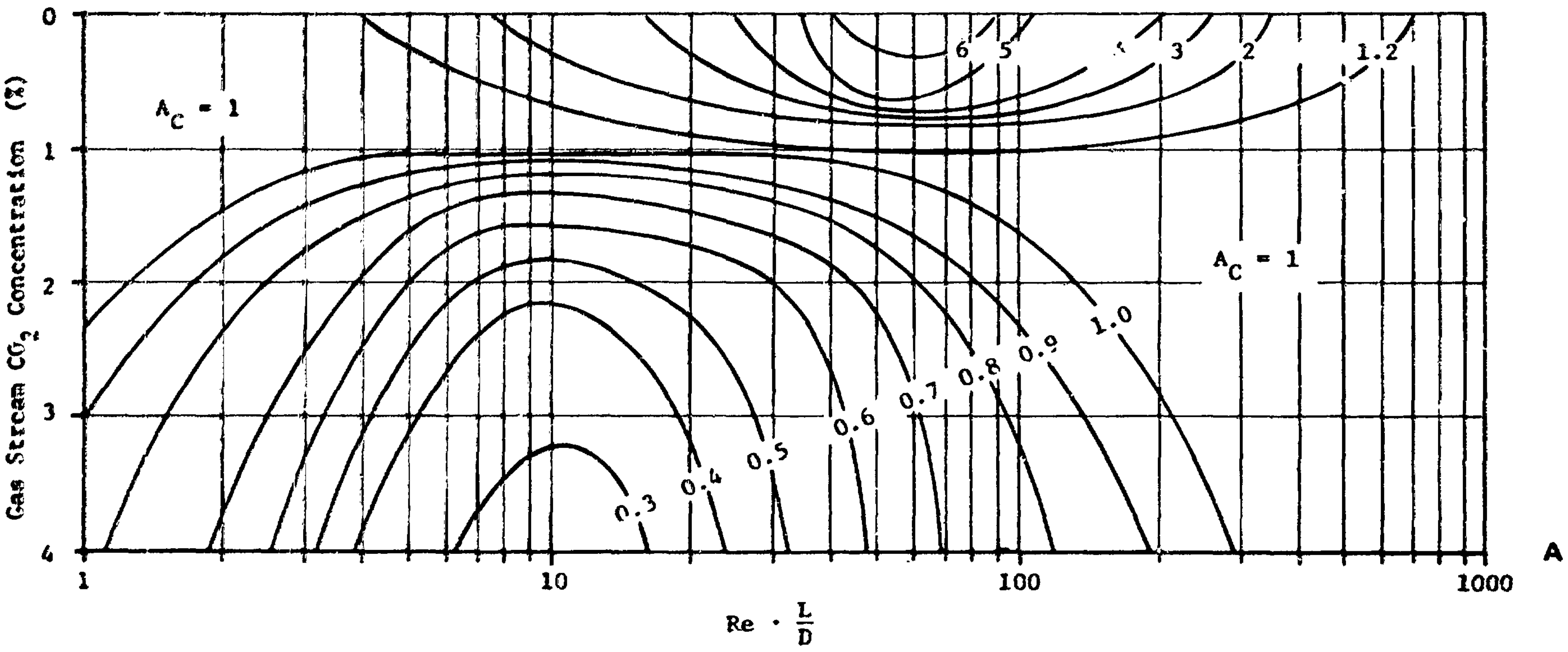


FIGURE 13. CO_2 INJECTION RATE FACTOR, A_C

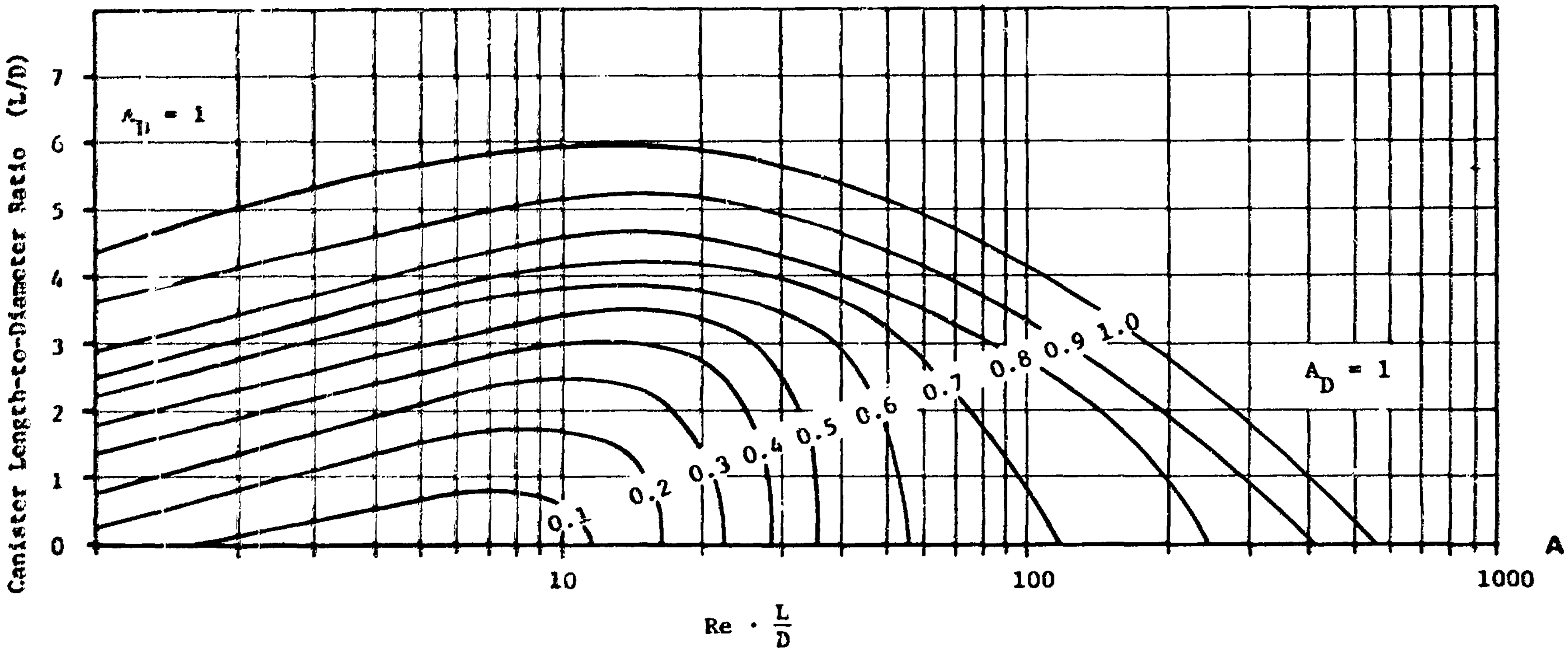


FIGURE 14. LENGTH-TO-DIAMETER EFFECT FACTOR, A_D

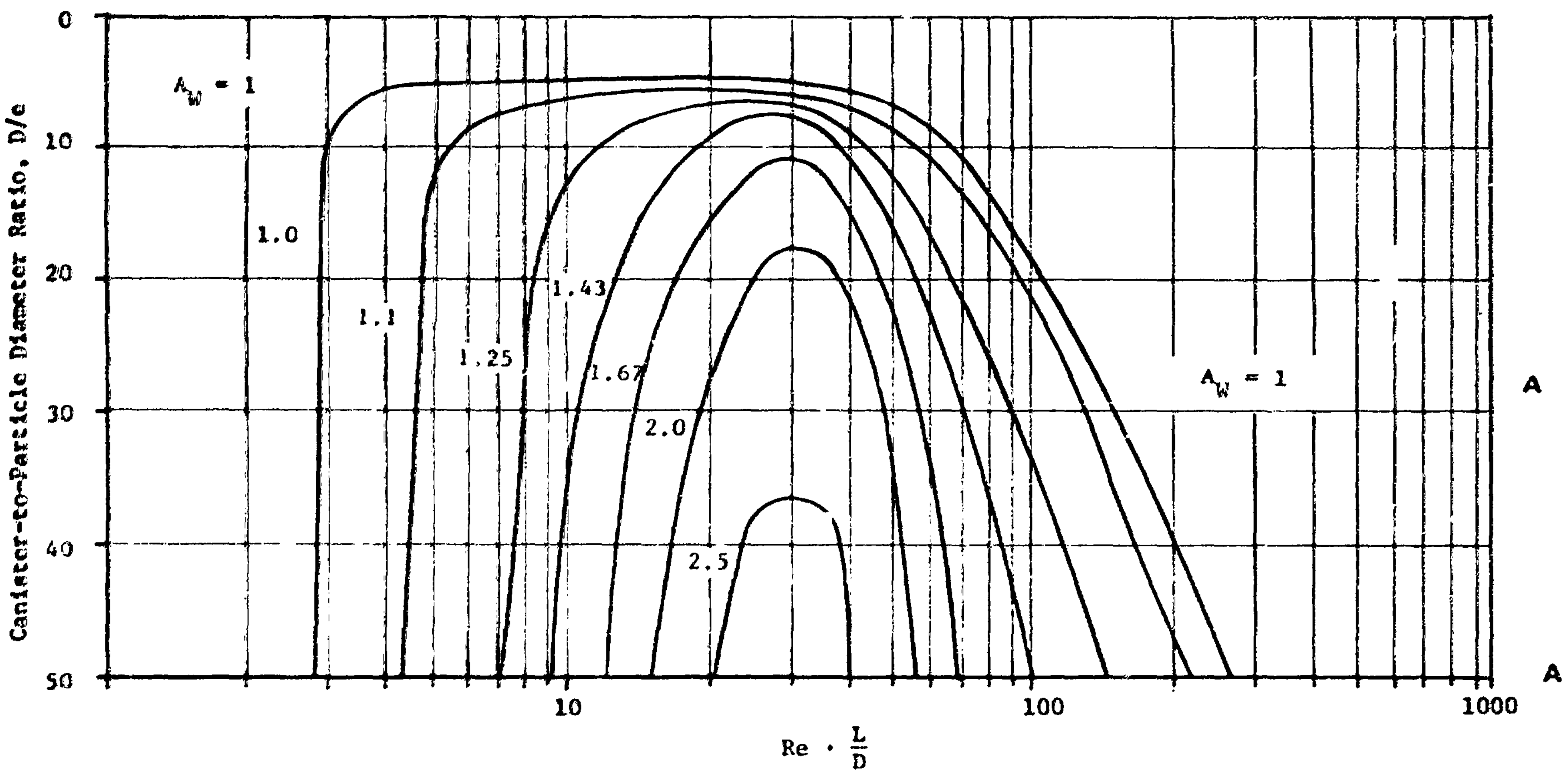


FIGURE 15. WALL EFFECT FACTOR, A_W

where:

$\dot{V}_{O_2}$ = Diver's oxygen consumption (litre/min.) (Table 1)

RQ = Respiratory quotient (varies between 0.8 to 1.0)

Q = Volumetric flow rate to canister (acfm)

P = Ambient pressure (ata)

C = CO_2 concentration in gas stream (percent)

NOTE: Surface Level Equivalent (SLE) Concentration

$$C\ (SLE) = C * P$$

STEP 2: Determine absorbent weight, W

$$W = VOL * \rho_{BULK} * 0.0361$$

where:

W = Absorbent weight (lbm)

VOL = Canister empty volume (in.^{3})

ρ_{BULK} = Bulk density of absorbent (g/cc) (page A-2)

STEP 3: Obtain tht theoretical bed life by.

a. Using Figure 10, enter at bottom at system flow rate. Move vertically upward until intersecting curve showing absorbent weight (interpolate if necessary). Move left, horizontally to read the theoretical bed life for a 1 percent SLE CO_2 level. Divide this value by actual CO_2 concentration in percent to obtain actual theoretical bed life (TBL).

b. Or calculate theoretical bed life from the following:

$$t_{TH} = \frac{A\ W}{Q\ C\ \rho_{CO_2}}$$

where

A = Absorbent capacity (mass of CO_2 absorbed per mass of absorbent)

= 0.41 lbm CO_2/lbm Sodasorb

W = Mass of absorbent (lbm)

Q = Volumetric flow rate through canister (acfm)

C = CO_2 volume fraction in gas stream (percent CO_2/100)

ρ_{CO_2} = Density of CO_2 at operating pressure (lbm/ft^3)

t_{TH} = Minutes

STEP 4: Calculate superficial velocity through canister

$$\bar{V} = \frac{Q}{60A_{CS}}$$ A

where

$\bar{V}$ = Superficial gas stream velocity (ft/sec)

Q = Volumetric flow rate (acfm)

A_{CS} = Cross sectional area of flow path in canister (ft^2)

STEP 5: Find mean particle diameter for absorbent, e

Tyler Mesh Range	Mean Particle Diameter (ft.)
4 - 8	0.01167
8 - 20	0.00525
10 - 20	0.00417
20 - 60	0.00183
32 - 60	0.00125

A

STEP 6: CALCULATE PARTICLE REYNOLDS NUMBER, Re

$$Re = \frac{\rho \bar{V} e}{\mu}$$ A

where ρ = Gas stream density (lbm/ft^3)

μ = Gas stream viscosity (lbm/ft-sec)

$\dot{v}$ = Superficial gas stream velocity (ft/sec)

A e = mean absorbent particle diameter (ft.)

STEP 7: Calculate length-to-diameter ratio for canister.

NOTE: For noncylindrical canisters use the hydraulic diameter, D_H

$$D_H = \frac{4\,A_{CS}}{P_W}$$

A_{CS} = Cross sectional area (ft^2)

P_W = Wetted perimeter (ft)

L = Canister length (ft)

STEP 8: Enter Figure 4 at bottom with product Re · L/D.

Move vertically upward until intersecting curve showing ambient pressure (interpolate if necessary). Move left, horizontally, to read the efficiency, η, of a canister with standard conditions of

100% RH - Gas stream humidity level

70°F - Gas stream temperature

0.01 atm P_{CO_2} - Inlet CO_2 level

L/D = 6.5-7.0 - Length-to-diameter ratio

D/e = 2.75 - Canister-to-absorbent particle diameter ratio

STEP 9: For temperatures less than 70°F enter Figure 11 at bottom with the product RE · L/D.

Move vertically upward until intersecting the horizontal line showing actual gas stream temperature. Read the temperature effect factor, A_T (interpolate if necessary). A_T = 1.0 if 70°F.

STEP 10: For humidity levels less than 100% RH enter Figure 12 at bottom with the produce Re · L/D.

Move vertically upward until intersecting the horizontal line showing actual humidity level. Read the humidity effect factor, A_H (interpolate if necessary). $A_H = 1.0$ if 100% RH

STEP 11: For CO_2 injection concentrations other than 1% (SLE) enter Figure 12 at bottom with the product Re · L/D.

Move vertically upward until intersecting the horizontal line showing actual CO_2 concentration. Read the CO_2 injection rate factor, A_C (interpolate if necessary). $A_C = 1.0$ if 1% CO_2 (SLE).

STEP 12: For length-to-diameter ratios other than 6.5 to 7.0 enter Figure 14 at bottom with the product Re · L/D.

Move vertically upward until intersecting the horizontal line showing actual value of L/D. Read the L/D effect factor, A_D (interpolate if necessary). $A_D = 1.0$ if L/D = 6.5 to 7.0.

STEP 13: For canister-to-absorbent particle diameter ratios other than 2.75 enter Figure 15 at bottom with the product Re · L/D.

Move vertically upward until intersecting the horizontal line showing the actual value of D/e. Read the wall effect factor, A_W (interpolate if necessary). $A_W = 1.0$ if D/e = 2.75. A

STEP 14: Calculate the actual canister efficiency by multiplying efficiency found in Step 8 by factors found in Steps 9 through 13.

$$\eta_{ACTUAL} = \eta_{STD} \cdot A_T \cdot A_H \cdot A_C \cdot A_D \cdot A_W$$ A

STEP 15: Calculate the predicted canister life as the product of the efficiency term from Step 14 by the theoretical bed life found in Step 3.

$$t_B = t_{TH} \cdot \eta_{ACTUAL}$$

The worksheet which follows can be used to assist in arriving at canister life predictions.

CANISTER DESIGN WORKSHEET

CANISTER DESIGN

Length, L ________________ ft
Diameter, D ________________ ft
L/D Ratio ________________

FLOW CONDITIONS.

Depth, ________________ fsw
Pressure, P ________________ ata (Depth/33 + 1)
Flow Rate, Q ________________ acfm

Diver O_2 Consumption, $\dot{V}_{O_2}$ ________________ lpm

Respiratory Quotient, RQ 0.85
Inlet CO_2 Concentration, C ________________ %
C (SLE) ________________ % SLE

THEORETICAL BED LIFE

Canister Volume, VOL ________________ in^3
Absorbent Weight, W ________________ lbm
Theoretical Bed Life, t_{TH} ________________ minutes

PARTICLE REYNOLDS NUMBER

Superficial Gas Stream Velocity, $\bar{V}$ ________________ ft/sec
A Mean Particle Diameter, e ________________ ft
Gas Density, ρ ________________ lbm/ft^3
Gas Viscosity, μ ________________ lbm/ft-sec
Reynolds Number, Re ________________
Re · L/D ________________

CANISTER EFFICIENCY

Standard Efficiency, η_{STD} ________________

Temperature Correction, A_T ________________

Humidity Correction, A_H ________________

Injection Rate Correction, A_C ________________

L/D Ratio Correction, A_D ________________

A Wall Factor, A_W ________________

Actual Canister Efficiency, η_{ACTUAL} ________________

PREDICTED CANISTER LIFE

____
____

The following sample problem demonstrates the use of this worksheet when used in conjunction with the charts of test data and modifying coefficients.

Sample Calculations

An axial flow canister 14.75 inches long by 6-inch inside diameter is filled with 12 pounds of 4-by-8 mesh High Performance Sodasorb. What is the predicted life of this canister when 5.4 acfm of a heliox mix with 0.58 percent SLE carbon dioxide flows through at an ambient pressure equivalent to 390 feet of seawater?

The predicted life of this canister can be arrived at by multiplying the theoretical canister life, t_{TH}, by the canister efficiency, η, as

$$t_B = t_{TH} \cdot \eta \, .$$

From Figure 10, we can find the theoretical life of a canister with 12 pounds of High Performance Sodasorb which sees 5.4 acfm of 1-percent CO_2 laden gas to be approximately 790 minutes (13.2 hours). As directed in this figure, divide the bed life by the actual percent concentration of CO_2 for CO_2 levels other than 1 percent. Thus, the actual theoretical bed life will be

$$t_{TH} = \frac{790 \text{ minutes}}{0.58} = 1362 \text{ minutes (22.7 hours)}.$$

We arrive next at the expected canister efficiency through the use of Figures 4 through 9 and 11 through 15. To enter these charts first determine the mean particle Reynolds number, Re, for the canister absorbent material where

$$Re \equiv \frac{\rho \bar{V} e}{\mu}$$

$\bar{V}$ superficial gas stream velocity in the canister (ft/sec)

e mean absorbent particle diameter (feet)

ρ, μ the gas stream density and viscosity, respectively.

From the US Navy Diving-Gas Manual,[15] an acceptable breathing mixture at 390 fsw (12.8 atm) would be 84 percent helium/16 percent oxygen with the following gas properties

$$\rho = 0.26 \text{ lb/ft}^3$$

$$\mu = 1.43 \times 10^{-5} \text{ lb/ft-sec.}$$

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[15] ibid.

CANISTER DESIGN WORKSHEET
(Sample)

CANISTER DESIGN

Length, L 1.23 ft
Diameter, D 0.50 ft
L/D Ratio 2.46

FLOW CONDITIONS

Depth, 390 fsw
Pressure, P 12.8 ata (Depth/33 + 1)
Flow Rate, Q 5.4 acfm
Diver O_2 Consumption, $\dot{V}_{O_2}$ --- lpm
Respiratory Quotient, RQ 0.85
Inlet CO_2 Concentration, C --- %
C (SLE) 0.58 % SLE

THEORETICAL BED LIFE

Canister Volume, VOL --- in^3
Absorbent Weight, W 12.0 lbm
Theoretical Bed Life, t_{TH} 790.0 minutes

PARTICLE REYNOLDS NUMBER

Superficial Gas Stream Velocity, $\overline{V}$ 0.46 ft/sec
A Mean Particle Diameter, e 0.01167 ft
Gas Density, ρ 0.26 lbm/ft^3
Gas Viscosity, μ 1.43×10^{-5} lbm/ft-sec
Reynolds Number, Re 97.6
Re · L/D 240

CANISTER EFFICIENCY

Standard Efficiency, η_{STD} 0.23
Temperature Correction, A_T 1.0
Humidity Correction, A_H 1.0
Injection Rate Correction, A_C 1.9
L/D Ratio Correction, A_D 1.0
A Wall Factor, A_W 1.0
Actual Canister Efficiency, η_{ACTUAL} 0.437

PREDICTED CANISTER LIFE

595 min. (9.9 hr)

Gas properties for other gas mixes can be obtained from the Navy Diving-Gas Manual[15] or from the methods described in Appendix C.

The superficial gas stream velocity is determined by dividing the gas flow rate by the canister cross-sectional area

$$\bar{V} = \frac{5.4\ \text{ft}^3/\text{min}}{\frac{\pi}{4}\left(\frac{6}{12}\right)^2\ \text{ft}^2} \times \frac{1\ \text{min}}{60\ \text{sec}} = 0.46\ \frac{\text{ft}}{\text{sec}}\ .$$

The mean particle diameter of 4-by-8 mesh Sodasorb (Table 3) is 0.01167 ft. We can now calculate the particle Reynolds number according to the above definition to get A

$$\text{Re} = \frac{0.26\ \text{lb/ft}^3 \times 0.46\ \text{ft/sec} \times 0.01167\ \text{ft}}{1.43 \times 10^{-5}\ \text{lb/ft-sec}}$$ A

$$\text{Re} = 97.6$$

and $$\text{Re} \cdot \frac{L}{D} = 97.6 \times \frac{14.75}{6.0} = 240.$$

We can now enter the bottom of Figure 4 with a value of Re · L/D of 240 to arrive at a value for the canister efficiency at 12.8 atm under the standard conditions shown in the legend; i.e.,

100% RH incoming gas humidity
70°F incoming gas temperature
1% CO_2 level in incoming gas
6.5 to 7.0 length-to-diameter ratio of canister
2.75 canister-to-particle diameter ratio.

For this value of Re · L/D we get approximately $\eta = 0.23$.

For this example assume that the incoming gas stream is 60°F and saturated with water vapor. The canister L/D ratio is 2.5; the canister-to-particle diameter ratio, D/e, is 43; and as stated previously, CO_2 concentration is 0.58 percent SLE.

The canister efficiency under these conditions is found by multiplying the standard canister efficiency, η, by the correction factors from Figures 11 through 15 for conditions which vary from the standard; i.e.,

$$\eta_{ACTUAL} = \eta_{STD} \cdot A_T \cdot A_H \cdot A_C \cdot A_D \cdot A_W$$ A

where

A_T = Temperature Effect Factor

A_H = Humidity Effect Factor

A_C = CO_2 Injection Rate Factor

A_D = Length-to-Diameter Effect Factor

A A_W = Wall Effect Factor.

A_T for 60°F and Re · L/D of 240 is 1.0 (Figure 11). A_H is also 1.0 since it is identical to the standard canister (Figure 12). A_C is approximately 1.9 A for a CO_2 level of 0.58 percent SLE (Figure 13). A_D and A_W are seen to be 1.0 in Figures 14 and 15 for Re · L/D = 240. Therefore,

$$\eta_{ACTUAL} = 0.23\ (1.0)(1.0)(1.9)(1.0)(1.0)$$

$$= 0.437,$$

and the predicted canister life will be

$$t_B = t_{TH} \cdot \eta_{ACTUAL}$$

$$= 1362 \text{ min.} \times 0.437 = 595 \text{ min.}\ (9.9 \text{ hr}).$$

The canister and flow conditions described in the previous example are similar to those seen by the Navy's MK 12 Surface Supported Diving System. This system is designed to operate at a maximum depth of 390 fsw while supplying 6 acfm to the diver's helmet (5.4 acfm recirculated through the CO_2 canister). A system duration in excess of 10 hours for the MK 12 CO_2 scrubber at 390 fsw when the inlet gas temperature was maintained above 60°F was reported in Reference 18. During these unmanned tests a diver work cycle was simulated by a 6-minute injection of CO_2 into the canister at 0.75 percent SLE

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[18] Naval Coastal Systems Center Technical Report NCSC TR 353-80, "MK 11 and MK 12 CO_2 Scrubber Development," by R. Dowgul, March 1980.

(moderate work rate) followed by a 4-minute injection of CO_2 at 0.33 percent SLE (rest). This gave a mean injection rate over a 10-minute period of

$$\% \ CO_2 \text{ mean} = \frac{6 \times 0.75\% + 4 \times 0.33\%}{10}$$

$$= 0.582\% \ .$$

The close agreement between the predicted canister life and the experimentally recorded duration of the MK 12 canister under similar operational conditions is encouraging. A shortcoming of this predictive method, however, is seen when we attempt to look at how the canister life will drop off as the gas stream temperature is decreased (a phenomenon recorded experimentally for the MK 12 canister). Figure 11 shows a decreasing temperature effect factor, A_T, as temperature is decreased when values of Re · L/D are less than approximately 56. This would suggest that the effect of temperature is minimal when Re · L/D is greater than a value of 56 (sample canister had a value of 240). The shortcoming of this design data is not really understood. However, it could result from the use of data derived from small, isothermal canisters to predict the performance of relatively large canisters with known bed temperature variations. Further experience with the use of these charts will be necessary before it can be determined whether this shortcoming is universal or only peculiar to the MK 12 design.

PULSATILE VERSUS STEADY FLOW IN CANISTERS

The data shown in Figures 4 through 9 and 11 through 15 were generated from laboratory testing where steady flow gas streams travelled through cylindrical canisters. This flow behavior is typical of continuous flow systems such as the MK 12 SSDS, the MK 14-1 Emergency Backpack, and the hyperbaric chamber environmental control systems. Certain other human-propelled breathing systems, such as the MK 11 UBA, have cyclical flow patterns which can be represented by pulses of gas flow (during diver exhalation) followed by a short dwell time when canister flow stops (during diver inhalation). The effects of this pulsatile flow behavior on the carbon dioxide absorption efficiency of High Performance Sodasorb were reported in Reference 4. In that study the test beds having pulsatile flow patterns were seen to have up to 30 percent longer durations than with constant flow where a dry (RH = 0%) carrier gas was introduced. This increase in bed life was attributed to a

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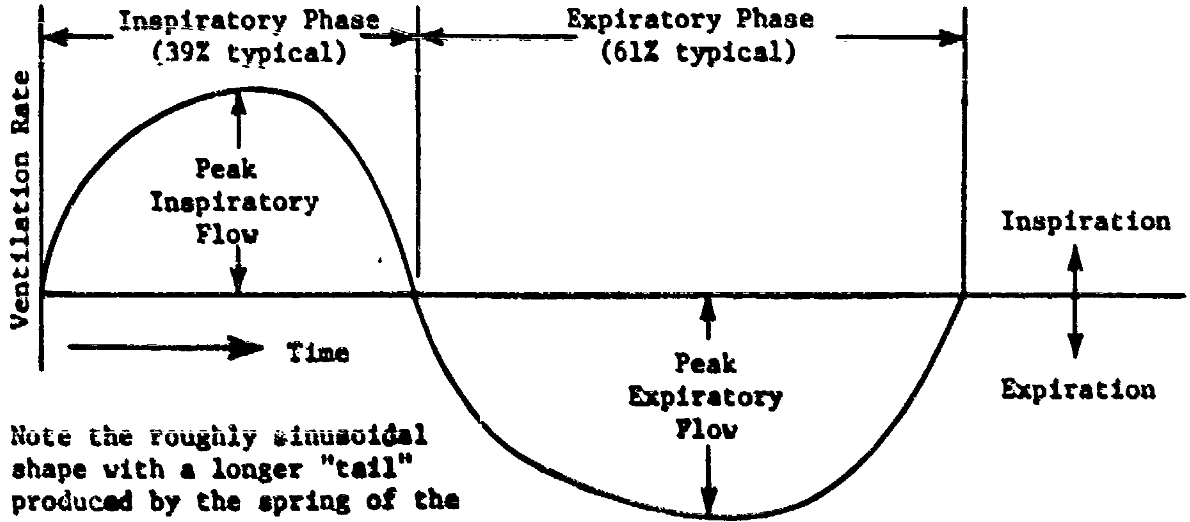
[4] ibid.

lower absorbent use in the early life of the canister when pulsatile flow was present. A larger amount of CO_2 exited the test bed at the start of gas flow for pulsatile flow than for continuous flow (although the exit CO_2 level remained below 0.5 percent SLE). Thus, the absorbent in the continuous flow canister was consumed at a higher rate initially, and the breakthrough level of 0.5 percent in the exit gas occurred sooner. Even though the total amount of CO_2 absorbed by the canister with steady flow could be higher than with pulsatile flow, its efficiency (defined as breakthrough time divided by theoretical bed life) was lower.

When a water saturated gas stream was introduced, the continuous flow canisters had up to 100 percent longer durations than the pulsatile flow canisters. This reversal in relative canister efficiencies with gas stream water content was primarily caused by the large effect of water vapor during the continuous flow testing and the relatively small effect of water vapor on canister efficiency during the pulsatile flow studies. The reason for this water vapor insensitivity during pulsatile flow is not understood. Until further investigation of this phenomenon is accomplished, predictions of durations for canisters with pulsatile flow will necessarily be speculative.

CANISTER FLOW RESISTANCE AND ITS INFLUENCE ON HUMAN BREATHING CHARACTERISTICS

Another major consideration in the design of CO_2 scrubbers is the resistance of the scrubber to system flow and the effect of this resistance on the diver's breathing. The following briefly discusses the effects of this resistance and a general approach to estimating the pressure drop through a canister (Figure 16).



Note the roughly sinusoidal shape with a longer "tail" produced by the spring of the chest wall

FIGURE 16. TYPICAL BREATHING PATTERN FOR MAN

Cain and Otis[19] found in general that the time durations of the inspiratory and expiratory phases were 39 percent and 61 percent of the total respiratory cycle. Additionally, they found that a relationship generally exists between RMV and maximum rate of flow as:

$$\frac{\text{Maximum Flow Rate}}{\text{RMV}} = \begin{matrix} 3.53 \text{ (inspiration)} \\ 2.59 \text{ (expiration)} \end{matrix}$$

NOTE: $\frac{\text{Maximum Flow Rate}}{\text{RMV}} = 3.14159$ or π for both inspiration and expiration if a sinusoidal wave form is assumed

Due to the highly variable behavior of the breathing pattern, a sinusiodal pattern is generally assumed as a first approximation.

Breathing patterns are highly variable among individuals under various activity levels. Additionally, breathing patterns are strongly influenced by the inherent resistance of the breathing apparatus.

Cain and Otis[19] found that as the breathing resistance of the apparatus increases the following modifications to the breathing pattern occur:

1. The total time of each phase of respiration increases
2. Maximum rate of flow decreases
3. Time required to reach maximum flow rate decreases
4. Mean rate of air flow decreases
5. Peak inspiration and expiration pressures increase
6. The breathing pattern becomes more rectangular, especially during the expiration half-cycle.

PRESSURE DROP THROUGH CANISTERS

When carbon dioxide canisters are used in a closed or semiclosed breathing circuit, it is necessary to minimize the added breathing resistance caused by the added energy the diver will need to expend in breathing. Flow resistances in canisters will become subjectively discomforting during inhalation

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[19] Cain, C. C. and Otis, A. B., "Some Physiological Effects Resulting From Added Resistance to Respiration," J. Aviat. Med., 20 (1949), pp. 149-160.

at magnitudes exceeding 7 to 7.5 centimetres H_2O per litre per second.[12] Likewise, exhalation resistance should not exceed 2.9 centimetres H_2O per litre per second, and in no case should exhalation resistance exceed inhalation resistance.

The pressure drop through an absorbent bed will depend upon the rate of gas flow, bed length, absorbent particle size, and the physical properties of the gas stream. A satisfactory level of success has been obtained in predicting this pressure drop by treating the canister as being made up of uniform solid particles. In such a treatment, modified friction factors, f, have been derived from a correlation of available pressure drop data for flow through solid granular beds.[20] Figure 17 presents the correlation of available data on pressure drop through beds of solid particles in the format of bed friction factors versus a modified Reynolds number.

A

$$Re = \frac{\rho \bar{V} e}{\mu}$$

where

ρ = gas stream density (lbm/cu ft)

μ = gas viscosity (lbm/ft-sec)

e = mean absorbent particle diameter (ft)

and

A $\bar{V}$ = flow velocity based on the cross section of an empty canister (ft/sec).

Using the modified friction factors of the figure, the pressure drop across an absorbent canister can be predicted as

A

$$\Delta p = \frac{4fL\rho \, \bar{V}^2 A_f}{2g_c \, e} \tag{12}$$

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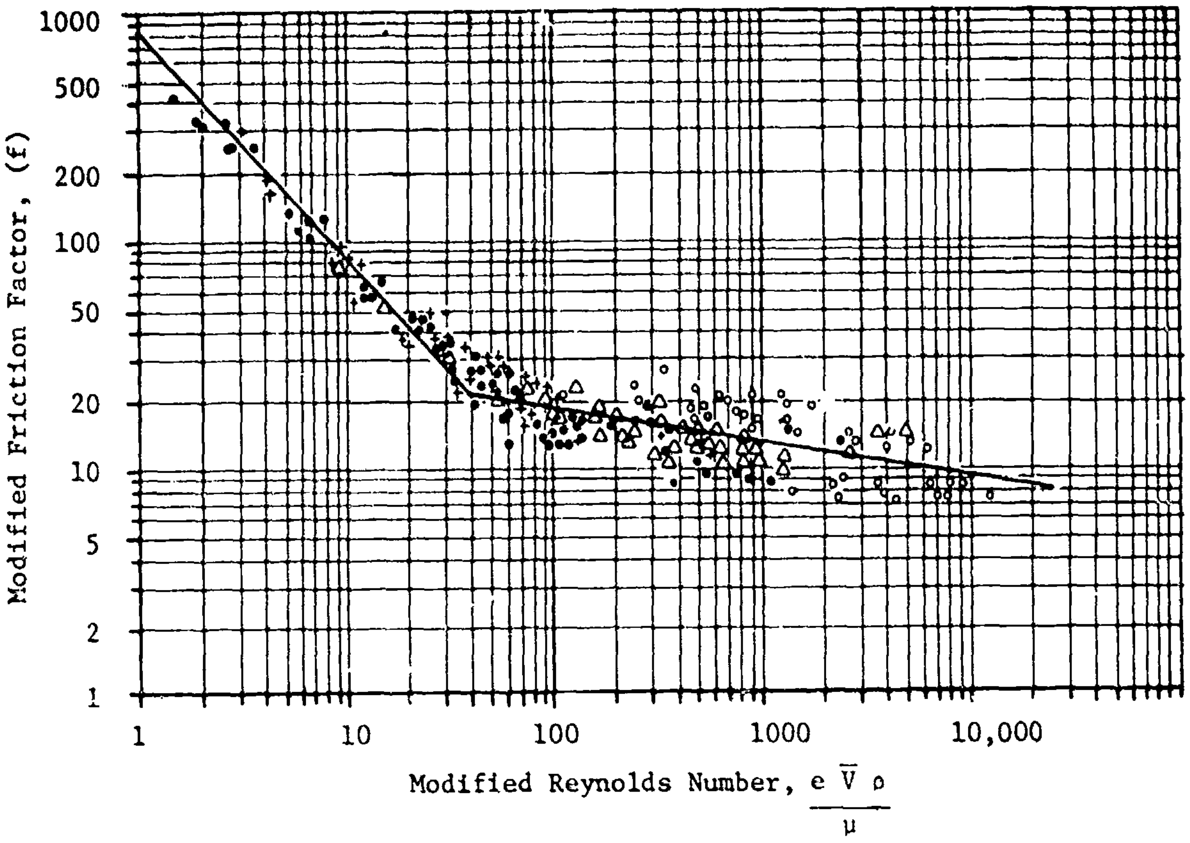
[12] ibid.

[20] Perry, R. H., and Chilton, C. H. (Editors), Chemical Engineers' Handbook, Third Edition, McGraw-Hill, New York, 1973.



A

FIGURE 17. CORRELATION OF DATA ON PRESSURE DROP THROUGH BEDS OF SOLIDS

where

Δp = canister pressure drop (lbf/ft^2)

L = canister bed length (ft)

A_f = a dimensionless wall effect factor which depends on the ratio of the particle diameter to the canister diameter (Figure 18)

and g_c = 32.174 lbm-ft/lbf-sec^2.

The modified friction factors can be taken from Figure 17 once the Reynolds number is known, or they can be calculated from two expressions covering the laminar and turbulent flow regions of this curve. For Re < 40

$$f \approx 850/Re \tag{13}$$

and for Re > 40

$$f \approx 38/Re^{0.15} . \tag{14}$$

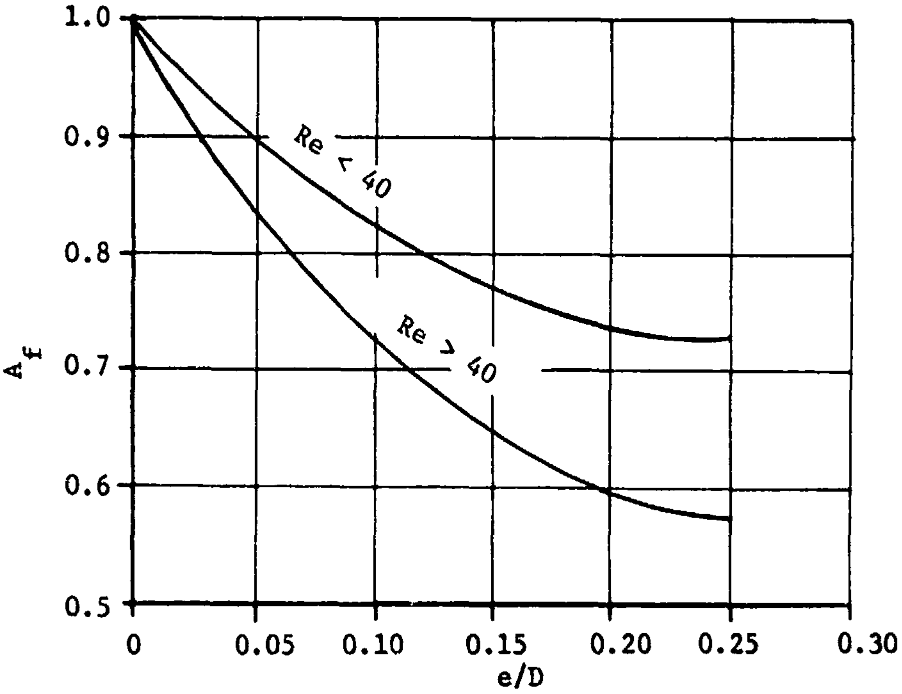


FIGURE 18. WALL EFFECT FACTOR

By obtaining the above two curve fits for the data of Figure 17, we can now calculate the canister pressure drop directly by substituting Equations (13) and (14) into Equation (12), giving

A $$\Delta p = \frac{53 \mu L \bar{V} A_f}{e^2} \quad \text{for Re} < 40 \qquad (15)$$

A and $$\Delta p = \frac{2.36\, \mu^{0.15} L \rho^{0.85} \bar{V}^{1.85} A_f}{e^{1.15}} \quad \text{for Re} > 40\,. \qquad (16)$$

NOTE: For most canisters with internal diameters greater than 6 inches, A_f ranges from 0.9 to 1.0.

Riegel and Caudy[21] showed that the above expressions gave satisfactory
agreement with pressure drop recordings across Baralyme canisters (where e is
approximately 0.01167 feet) in hyperbaric environments varying from 1 to 8 atmos- A
pheres with air. Figure 19 shows the relation of pressure drop to superficial
velocity, pressure, and bed depth for air and helium passing through a bed of
4 to 8 mesh absorbent particles (e = 0.01167 feet; Table 3) as predicted by Equa- A
tions (15) and (16). They can likewise be used to predict canister pressure
drops when using other gases at varying ambient conditions.

When only air is being considered, Riegel and Caudy[21] have proposed a simplified, empirical relationship which can likewise be used for predicting canister pressure drop across 4 to 8 mesh particles. This expression

$$\Delta p = 0.965P^{0.393}\bar{V}^{1.39}$$ A

where P is the ambient pressure (ata)

showed good agreement with their experimental recordings across Baralyme beds at ambient pressures between 1 to 8 atmospheres.

One other consideration that must be included when predicting canister flow resistance is how this resistance will vary as the absorbent bed is being depleted of active chemical. Absorption by-products including carbonates and water could tend to increase the flow resistance of the bed as the reactions progress.

Purer et al[2] observed less than 5 to 10 percent increase in bed resistance at canister breakthrough when water saturated, CO_2 laden gases were tested. During dry gas runs, pressure increases of less than 5 percent were observed. Riegel and Caudy[21] also observed negligible changes in flow resistance during their experiments. Both investigations used particle mesh sizes of 4 to 8 Tyler. For this size particle, the added resistance due to chemical by-products can usually be ignored. However, as absorbent particles become smaller, it is conceivable that this added flow resistance could become appreciable.

Sample Calculation

An axial flow canister 10 inches long with a 6-inch diameter is filled with 4 to 8 mesh Sodasorb. What will be the pressure drop across this canister when 6 acfm of 97 percent helium/3 percent oxygen flows through this canister at an ambient pressure of 650 feet of seawater?

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[2] ibid.

[21] Riegel, P. S. and Caudy, D. W., "Air Flow and Pressure Drop in Hyperbaric Baralyme Beds," The Characterization of Carbon Dioxide Absoring Agents for Life Support Equipment, Edited by M. L. Nuckols and K. A. Smith, American Society of Mechanical Engineers, New York, 1982.

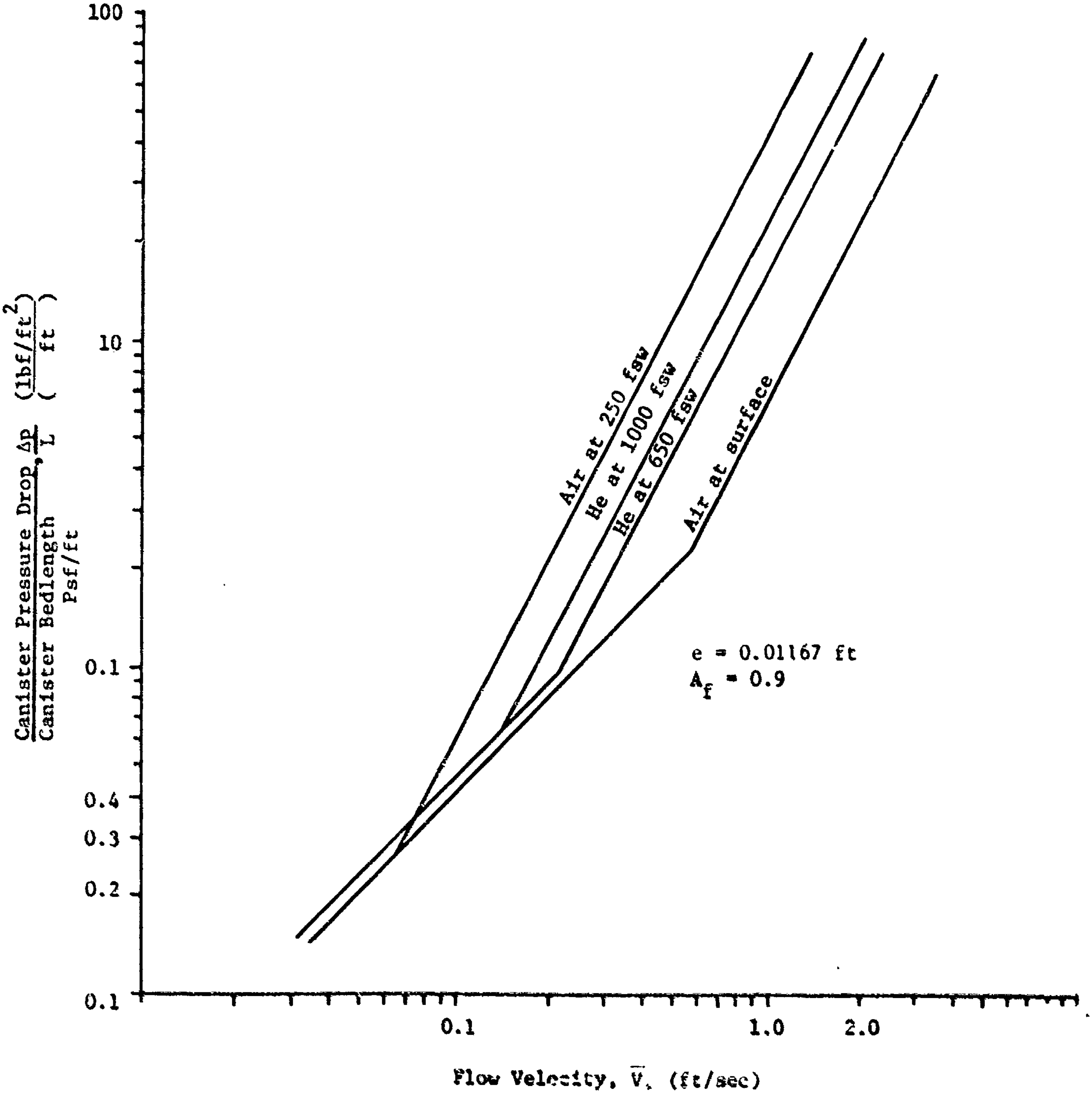

FIGURE 19. PRESSURE DROP ACROSS ABSORBENT CANISTERS AT VARIOUS DEPTHS

TABLE 3

PARTICLE MESH SIZES

A

Tyler Mesh Range	Mesh Opening (in.)	Mean Particle Diameter (ft.)
4 - 8	0.187 - 0.093	0.01167
8 - 20	0.093 - 0.033	0.00525
10 - 20	0.067 - 0.033	0.00417
20 - 60	0.033 - 0.010	0.00183
32 - 60	0.020 - 0.010	0.00125

A

At 650 fsw, the above gas mix has the properties (Appendix C):

$\rho = 0.256$ lbm/cu ft
$\mu = 1.359 \times 10^{-5}$ lbm/ft-sec.

The mean flow velocity (based on empty canister) is now calculated by dividing the volumetric flow rate by the cross-sectional area of the empty canister:

$$\overline{V} = \frac{6\ \text{ACFM}}{\text{AREA}} = \frac{6}{\frac{\pi}{4}(0.5)^2}\ \frac{\text{ft}}{\text{min}} = 30.56\ \frac{\text{ft}}{\text{min}}$$

A

$$\overline{V} = 0.51\ \text{ft/sec.}$$

Based on a mean particle diameter of 0.01167 ft for 4 to 8 mesh Sodasorb (Table 3), the modified Reynolds number can be calculated as A

$$\text{Re} = \frac{\rho \overline{V} e}{\mu} = \frac{0.256(0.51)(0.01167)}{1.359 \times 10^{-5}}$$

A

$$\text{Re} = 111.9.$$

The modified friction factor of 18.7 can be obtained from Equation (14) or read directly from Figure 17 for this corresponding Reynolds number. Equation (12) can then be used to calculate the pressure drop with $A_f = 0.9$ (Figure 18).

$$\Delta p = \frac{4(18.7)(10/12)(0.256)(0.51^2)(0.9)}{2(32.174)(0.01167)}$$

A

$$\Delta p = 4.98\ \text{lbf/ft}^2 = 0.035\ \text{psi.}$$

An alternative approach would be to go directly to Equation (16) ($Re > 40$) to get

A

$$\Delta p = \frac{2.36(1.359 \times 10^{-5})^{0.15}(10/12)(0.256)^{0.85}(0.51)^{1.85}(0.9)}{(0.01167)^{1.15}}$$

$$= 4.98 \text{ lbf/ft}^2 = 0.035 \text{ psi.}$$

ALTERNATIVE CARBON DIOXIDE REMOVAL METHODS

The conventional methods used for removing carbon dioxide from diving gases, and the methods for which most data are presented here, deal with the chemical absorption of carbon dioxide with alkali metal hydroxides; i.e., calcium hydroxide, sodium hydroxide, lithium hydroxide, and barium hydroxide. However, there are numerous other techniques which the designer of carbon dioxide scrubber systems should be aware. These techniques can be divided into two fundamental groups; i.e., chemical and physical removal methods[22] [23] as outlined in Tables 4 and 5.

CHEMICAL REMOVAL OF CARBON DIOXIDE

The entire family of alkali and alkaline earth metal hydroxides, peroxides, superoxides, and ozonides react chemically with carbon dioxide and water to form carbonates, bicarbonates, or hydrates of either.[22] These chemical processes are normally thought of as irreversible, the chemical absorbent being replenished with a fresh supply after a predetermined interval. On the other hand, various metal oxides and organic amines have been used as regenerative absorbent systems in atmopheres which remain sealed for prolonged durations; e.g., submarines and submersibles.

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[22] Wang, T. C., "Carbon Dioxide Scrubbing Materials in Life Support Equipment," The Characterization of Carbon Dioxide Absorbing Agents for Life Support Equipment, Edited by M. L. Nuckols and K. A. Smith, American Society of Mechanical Engineers, New York, 1982.

[23] Anthony, T. C., "Improved Methods of Absorbing Carbon Dioxide," Proceedings of Diveteck 1981, Society of Underwater Technology, London, 24-26 November 1981.

TABLE 4

CHEMICAL REMOVAL OF CARBON DIOXIDE

- Metal Hydroxides
  - Alkali Metal Hydroxides
  - Alkali Earth Hydroxides

- Oxygen Generators
  - Metal Peroxides
  - Metal Superoxides
  - Metal Ozonides

- Regenerative Absorbents
  - Metal Oxides
  - Amines

- Miscellaneous
  - Sabatier Process
  - Bosch Reactor

TABLE 5

PHYSICAL SYSTEMS FOR THE REMOVAL OF CARBON DIOXIDE

- Molecular Sieve
- Membrane Separation
- Cryogenic Removal (Freeze Out)
- Electrochemical Removal

NOTE: M in the following equations represents an alkali metal from Group 1A or 2A of the Periodic Table of Elements.

Hydroxides

Because of the ease in handling and low cost, this group of absorbents is the most commonly used in diving systems. Their overall chemical reaction, as typified by the following equations,

$$2MOH^* + CO_2 \longrightarrow M_2CO_3 + H_2O \qquad \text{(alkali metal)}$$

or

$$M(OH)_2 + CO_2 \longrightarrow MCO_3 + H_2O \qquad \text{(alkali earth)}$$

is exothermic and requires that the carbon dioxide is initially dissolved in water to produce carbonic acid before absorption will occur. Table 6 lists the absorption capacities and relative causticities for common metal hydroxides. Note that the alkali metal hydroxides, as a rule, have higher absorption capacities than the alkali earth hydroxides. However, as a rule, this advantage is offset somewhat by the relatively high causticity inherent with the alkali metals. Also, the apparent advantage of LiOH in absorption capacity over sodalime (primarily $Ca(OH)_2$) is lost when determined on a volumetric basis.

TABLE 6

PROPERTIES OF METAL HYDROXIDES

Compound	Chemical Formula	Molecular Weight	CO_2 Capacity, $gmCO_2$/100 gm	Causticity*
Postassium Hydroxide	KOH	56.1	39.2	1.00
Sodium Hydroxide	NaOH	40.0	55.0	0.95
Lithium Hydroxide	LiOH	23.9	91.9	0.11
Barium Hydroxide	$Ba(OH)_2$	171.4	25.7	0.05
Calcium Hydroxide	$CA(OH)_2$	74.1	59.4	0.0015
Magnesium Hydroxide	$MG(OH)_2$	58.3	75.5	0.0000007

*Causticity based on relative solubility in water.

When low operating temperatures are a concern, as is usually the case in diving applications, LiOH has a decided advantage over other common absorbents. At temperatures as low as 5°C, LiOH has been shown to undergo only small reductions in efficiency, while sodalime and other alkali earth hydroxides suffer major reductions.[24]

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[24] Wang, T. C., "Temperature Effects on Baralyme, Sodasorb, and Lithium Hydroxide," Ind. Eng. Chem., Process Des. Dev., Vol. 14, No. 2, 1975, pp. 191-193.

Peroxides

Alkali metal peroxides have found use as carbon dioxide absorbents, but unlike the hydroxides, release oxygen concurrently according to the general reaction

$$M_2O_2 + CO_2 \xrightarrow{H_2O} M_2CO_3 + 0.5O_2 \ .$$

The most common compound in this category, lithium peroxide (Li_2O_2), can theoretically remove 0.96 kg of CO_2 with each kilogram of lithium peroxide, while at the same time, release 0.35 kg of oxygen. Its respiratory quotient, (RQ), defined as the ratio of volume of CO_2 absorbed to O_2 produced, equals 2.0 as can be seen from the above reaction. This RQ would require that an additional source of oxygen be used to meet the desired human RQ of approximately 0.8. However, the theoretical absorption capacity of lithium peroxide is approximately 4 percent greater than lithium hydroxide. On this basis Li_2O_2 is an attractive chemical for consideration in a mixed, active chemical system where its high CO_2 absorption capacity could be used while supplemented with an auxiliary O_2 supply. Table 7 lists typical metal peroxides used in air revitalization systems.

TABLE 7

CAPACITIES OF SUPEROXIDE COMPOUNDS

Compound	Chemical Formula	Molecular Weight	CO_2 Capacity $gmCO_2/100gm$	Available Oxygen $gmO_2/100gm$
Lithium Superoxide	LiO_2	38.9	56.6	61.7
Sodium Superoxide	NaO_2	55.0	40.0	43.6
Potassium Superoxide	KO_2	71.1	30.9	33.8
Lithium Peroxide	Li_2O_2	45.8	96.0	34.9
Sodium Peroxide	Na_2O_2	78.0	56.4	20.5

Superoxides

Like peroxides, superoxides release oxygen concurrently with the absorption of carbon dioxide. However, unlike the peroxides, the reactions with superoxides potentially can be controlled to match the human respiratory quotient of approximately 0.8. The generalized equation governing superoxide reactions with water vapor and carbon dioxide into a carbonate and oxygen

$$2MO_2 + CO_2 \xrightarrow{H_2O} M_2CO_3 + 1.5O_2$$

yields a respiratory quotient of 0.67. A competing reaction of carbon dioxide with a hydroxide, formed from an intermediate reaction in the superoxide evolution, forms a bicarbonate

$$MOH + CO_2 \longrightarrow MHCO_3$$

$$2MO_2 + H_2O + 2CO_2 \longrightarrow 2MHCO_3 + 1.5O_2 \ .$$

Here the RQ is 1.33. It can be seen that by properly controlling the proportion of carbonate and bicarbonate formation, the respiratory quotient can be made to approach that required for human metabolism. Past studies[25] have indicated that the superoxide reactions potentially can be controlled to produce RQs equal to 0.8 by controlling the inlet CO_2/H_2O mole ratio at 2/1. Other studies have indicated that the desired formation of carbonates and bicarbonates can be controlled by accurately maintaining the proper bed temperature (bicarbonate formation is favored if bed temperature is kept low.)[26] In practice however, the accurate control of these reactions has been found to be extremely difficult. Systems in the past have opted for parallel canisters of potassium superoxide and lithium hydroxide to remove CO_2 to avoid over-producing oxygen.

Table 7 lists the theoretical CO_2 absorption capacity and O_2 generation capacity for various superoxide compounds. Lithium superoxide has not been successfully manufactured and is probably unstable.[27] The high temperature and pressure at which sodium superoxide must be produced makes its cost unattractive. The most commonly used compound, potassium superoxide, has found applications in USSR manned spacecraft flights,[28] submersibles,[29] [30] and multiperson environmental control systems.[31]

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[25] Kunard, D. H. and Rogers, S. J., "Exploratory Study of Potassium and Sodium Superoxide for Oxygen Control in Manned Space Vehicles," N62-11082, MSA Research Corporation, Callery, PA, 1962.

[26] Melnikov, A. K., Firsova, T. P., and Molodkina, A. N., "Raction of Potassium Superoxide with Water Vapor and Carbon Dioxide," Russian Journal of Inorganic Chemistry, (English Translation), Vol. 6, No. 6, 1962, pp. 633-637.

[27] Mausteller, J. W., "Review of Potassium Superoxide Characteristics and Applications," The Characterization of Carbon Dioxide Absorbing Agents for Life Support Equipment, Edited by M. L. Nuckols and K. A. Smith, American Society of Mechanical Engineers, New York, 1982.

[28] Bovard, R. M., "Oxygen Sources for Space Flights," Aerospace Medicine, Vol. 31, No. 5, 1960, pp. 407-412.

[29] Li, Y. S., "A Potassium Superoxide Life Support System for Deep Quest," Biotechnology, Lockheed Missiles and Space Co., Sunnyvale, CA, undated.

[30] Presti, J., Wallman, H., and Petrocelli, A. W., "Superoxide Life Support System for Submersibles," Undersea Technology, June 1967, pp. 20-21.

[31] McGoff, M. J. and King, J. C., "Superoxide Configurations for Atmosphere Control Systems," AMRL-TR-66-167, Aerospace Medicine Research Laboratory, Wright Patterson AFB, Ohio, 1966 (AD647135).

Ozonides

Ozonides (Table 8) have the highest theoretical oxygen release capacities of all known carbon dioxide absorbents. Like the superoxides, competing reactions between carbonate formation

$$2MO_3 + CO_2 \xrightarrow{H_2O} M_2CO_3 + 2.5O_2$$

and bicarbonate formation

$$2MO_3 + H_2O + 2CO_2 \longrightarrow 2MHCO_2 + 2.5O_2$$

produce system respiratory quotients between 0.4 and 0.8. Notice that if bicarbonate formation could be forced continually when using this chemical, a RQ compatible with the normal human metabolic needs could be met without the need for dual canister systems that are required in superoxide applications.

TABLE 8

CAPACITIES OF OZONIDE COMPOUNDS

Compound	Chemical Formula	Molecular Weight	CO_2 Capacity $gmCO_2/100gm$	Available Oxygen $gmO_2/100gm$
Lithium Ozonide	LiO_3	54.9	40.1	72.9
Sodium Ozonide	NaO_3	71.0	31.0	56.3
Potassium Ozonide	KO_3	87.1	25.3	45.9

Unfortunately, these materials are difficult to synthesize, making their costs excessive. Additionally, they are likely to ignite and even explode when put in contact with many materials. Exposure to an excessive supply of water will cause a violent reaction, with generation of a large quantity of oxygen and toxic byproducts.

Oxides

Metal oxides received some attention during the early 1970s as carbon dioxide absorbents with regenerative capability.[22] [23] Silver oxide, the most

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[22] ibid.

[23] ibid.

popular of these compounds, was first investigated by the US Navy in the 1940s as a reversible CO_2 absorbent.[22] Absorption efficiencies of better than 60 percent were reported[23] when silver oxide was present in a form that displayed a large surface area. In fact, it appears that the large surface area requirement, due to the limited rate of diffusion of CO_2 gas through a silver carbonate surface layer, is the primary obstacle to making this a viable alternative. The metal oxide can easily be regenerated by heating the carbonate byproduct to 185°C or prolonged heating at 99°C[22] with no caustic or toxic effects reported.

Table 9 lists various metal oxides and their respective absorption capacities. The metal oxide possessing the highest capacity for carbon dioxide, lithium oxide, is extremely unstable in the presence of water.

TABLE 9

ABSORPTION CAPACITIES OF METAL OXIDES

Compound	Chemical Formula	Molecular Weight	CO_2 Capacity $gmCO_2/100gm$
Lithium Oxide	Li_2O	29.8	147.7
Sodium Oxide	Na_2O	62.0	71.0
Potassium Oxide	K_2O	94.2	46.7
Silver Oxide	Ag_2O	231.8	19.0
Magnesium Oxide	MgO	40.3	109.2
Calcium Oxide	CaO	56.1	78.4
Strontium Oxide	SrO	103.6	42.5
Barium Oxide	BaO	153.3	28.7
Zinc Oxide	ZnO	81.4	54.1

Amines

Another class of carbon dioxide absorbents with regenerative capability is represented by aqueous solutions of ethanolamines. The most common of these liquid amines, monoethanolamine (MEA), is used extensively in industrial applications and on submarines.[22] [23] These solutions readily absorb carbon dioxide when cooled and are easily reversed by boiling to give up CO_2.[32] The major shortcoming of these systems deals with the tendency for the aqueous

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[22] ibid.

[23] ibid.

[32] Carey, R., Comezplata, A., and Sarich, A., "An Overview into Submarine CO_2 Scrubber Development," Proceedings of American Society of Mechanical Engineers Symposium, The Characterization of Carbon Dioxide Absorbing Agents for Life Support Equipment, Phoenix, AZ 15-16 November 1982.

solutions to release toxic gases such as ammonia during operation. This, along with the requirement for a substantial power supply to repeatedly heat and cool the liquid, limits these applications to large, multiperson environmental control systems.

The use of solid amines for submarine CO_2 removal systems has recently been proposed.[33]

Miscellaneous

Two additional chemical processes used in industry to remove carbon dioxide from gas mixtures are referred to as the Sabatier process and the Bosch reactor. In the Sabatier process, carbon dioxide is mixed with hydrogen at a $H_2:CO_2$ molar ratio of approximately 4.35:1[34] and passed over a ruthenium-on-alumina catalyst at 400 to 700°C. Methane and water vapor are the reactants.

Water at high pressure is used commercially in a Bosch reactor to absorb carbon dioxide. Unfortunately, the efficiency of this process is reduced considerably at low pressures and low CO_2 concentrations.

PHYSICAL SYSTEMS FOR THE REMOVAL OF CARBON DIOXIDE

Molecular Sieve

Molecular sieves, normally consisting of synthetic crystalline zeolites, are the most commonly used physical means for the removal of carbon dioxide from a life support system. The molecular sieve, in the form of pellets or beads, is formed by bonding the zeolite, in the form of a fine white powder, with 20 percent clay. The pore size of the molecular sieve is selected to adsorb carbon dioxide and toxic impurities from the breathing gas onto the large surface areas of the pellets or beads. The zeolites have a relatively high affinity for CO_2 but, unfortunately, a still higher affinity for water. Thus, the air stream is commonly dried by passing it through silica gel prior to being introduced into the zeolite beds. When exhausted, the molecular sieve can be regenerated either by the application of a vacuum to the sieve bed or by increasing the bed temperature. In addition to the zeolites, silica gel, activated charcoal, and alumina can be used for adsorbing carbon dioxide from breathing gases. However, these materials are far less efficient than the zeolites.

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[33] "Proposal for A Solid Amine CO_2 Removal Prototype," Hamilton Standard, Windsor Locks, CT, 13 January 1981.

[34] Yakut, M. M. and Barker, R. S., "Parametric Study of Life Support Systems," National Aeronautics and Space Administration, Washington, DC, NASA-CR-73283, 1969.

Membrane Separation

The use of semipermeable membranes has been proposed to enrich various components of breathing gas mixtures by allowing selective diffusion between the breathing gas and the surrounding seawater.[22 23 35] By so doing, carbon dioxide can diffuse across the membrane to be expelled into seawater while oxygen is diffused into the breathing gas. Cascade systems have been proposed[35] to complete this diffusion process in a multistage operation with each step further enriching or depleting the gas stream of the selected component.

The major shortcomings of such systems pertain to the fragility of the thin membrane films and to the large surface areas required to meet the gas diffusion needs (it has been calculated that 35 m^2 of dimethyl silicone membrane 0.025 mm thick would be required to supply 2.0 slpm of oxygen to a diver and remove his exhaled carbon dioxide.[35] However, the recent advances in thin membrane technology are moving this separation technique into the realm of being feasible.

Cryogenic Removal (Freeze Out)

Carbon dioxide can be selectively removed from exhaled gases by lowering the gas stream below the freezing point of CO_2 (-78°C) while remaining above the freezing points of the other constituents (O_2, N_2, and He all freeze at temperatures below -180°C). The most attractive system freezes both CO_2 and water, which are then removed by sublimating the solids in a vacuum.[22] Similar systems for the recovery of helium in saturation diving are presently operational. These systems require a substantial power supply to produce the cold temperatures and are thus limited in application.

Miscellaneous

Various electrochemical systems have been proposed for the removal of carbon dioxide from respiratory gases.[23] However, discussions are limited in the technical literature for these methods. They require a large power source, limiting their potential applications to situations where such energy sources are available.

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[22] ibid.

[23] ibid.

[35] Sarich, A. J., "Permeable Membrane Removal of Carbon Dioxide from Diving Gas," The Characterization of Carbon Dioxide Absorbing Agents for Life Support Equipment, Edited by M. L. Nuckols and K. A. Smith, American Society of Mechanical Engineers, New York, 1982.

APPENDIX A

PROPERTIES OF CO_2 ABSORBENTS

CAUSTICITY

Certain of the carbon dioxide absorbents of the metal-hydroxide group are noted for dual properties of CO_2 removal efficiency and causticity. The most effective of these carbon dioxide absorbers are also the most caustic.

Causticity and reaction rate of the absorbent with CO_2 from an airstream are in part influenced by the solubility in water of the absorbent.

WATER SOLUBILITY AND CAUSTICITY OF METAL-HYDROXIDES

Hydroxide	Solubility in Water gm/100cc	Causticity* Relative to KOH
Potassium Hydroxide KOH	115	1.000
Sodium Hydroxide NaOH	109	0.95
Lithium Hydroxide LiOH	13	0.11
Barium Hydroxide $Ba(OH)_2 \cdot 8H_2O$	5.6	0.05
Calcium Hydroxide $Ca(OH)_2$	0.183	0.0015
Magnesium Hydroxide $Mg(OH)_2$	0.0009	0.0000007

*Based on relative solubility in water

PROPERTIES OF HYDROXIDES USED IN CO_2 SCRUBBERS

Name	Molecular Weight	CO_2 Capacity $gmCO_2/100gm$	Solubility in Water gm/100cc
Potassium Hydroxide KOH	56.10	47	115 @ 20°C
Sodium Hydroxide NaOH	40.01	54	109 @ 20°C
Lithium Hydroxide LIOH	23.95	92	13 @ 20°C
Barium Hydroxide $Ba(OH)_2 \cdot 8\ H_2O$	315.51	-	5.6 @ 15°C
Calcium Hydroxide $Ca(OH)_2$	74.10	59	0.183 @ 10°C
Magnesium Hydroxide $Mg(OH)_2$	58.34	76	0.0009 @ 18°C

TYPICAL CO_2 ABSORBENT COMPOSITIONS

Name	Composition		Bulk Density (g/cc)	ABS Density (g/cc)	Mesh
HP Sodasorb	$CA(OH)_2$	80%	0.745	2.49	4-8
	NaOH KOH $Ba(OH)_2 \cdot 8\ H_2O$	5%			
	H_2O	14-19%			
Granular Baralyme	$CA(OH)_2$	74%	0.94-1.04	1.91-2.15	4-8
	$Ba(OH)_2 \cdot 8\ H_2O$	11%			
	KOH	5%			
	H_2O	10%			

APPENDIX B

CALCULATIONS OF DIMENSIONLESS GROUPS

CALCULATIONS OF DIMENSIONLESS GROUPS

L/D = Length-to-diameter ratio of canister

D/e = Canister diameter-to-absorbent particle diameter ratio

Re = Absorbent particle Reynolds number

$$= \frac{\rho_{mix} \bar{V} e}{\mu_{mix}}$$

where

ρ_{mix}, μ_{mix} are the gas stream density and viscosity

e is the absorbent particle diameter

$\bar{V}$ is the superficial gas stream velocity

$$\eta = \frac{\text{Recorded Breakthrough Time}}{\text{Theoretical Bed Life, TBL}}$$

where

$$TBL = \frac{\text{Total Theoretical Absorption Capacity}}{\text{CO}_2 \text{ Input Rate}}$$

$$= \frac{A\ W}{Q\ C\ \rho_{CO_2}}$$

A = Absorbent capacity (mass of CO_2 absorbed per mass of absorbent)

W = Mass of absorbent

Q = Volumetric flow rate through canister

C = Carbon dioxide volume fraction in gas stream (percent $CO_2/100$)

ρ_{CO_2} = Density of carbon dioxide at operating pressure.

APPENDIX C

GAS STREAM PROPERTIES

GAS STREAM PROPERTIES

DENSITY

$$\rho = \frac{M_w P}{RT} \times 144$$

where

ρ = lbm/ft^3

P = Pressure (absolute) (lbf/in^2)

R = Universal gas constant
= 1544 ft-lbf/mole-°R

M_w = Gas molecular weight

T = Temperature (°R)

and

$$\rho_{mix} = \sum_{i=1}^{N} x_i \rho_i$$

where

x_i = Volume fraction of gas constituent
= Percent/100

N = Number of constituents.

VISCOSITY

$$\mu = A \left(\frac{459.67 + T}{529.67}\right)^b$$

where (derived from US Navy Diving Gas Manual)

Gas	A	b
O_2	202.99	0.784
He	196.89	0.664
CO_2	147.48	0.999
Air	180.37	0.710

μ = Micropoise
T = °F.

NOTE: lb/ft-sec x 14.882 = Poise

and

$$\mu_{mix} = \sum_{i=1}^{N} \frac{x_i \, \mu_i}{\sum_{j=1}^{N} x_j \, \Phi_{ij}}$$

where

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \left[1 + \frac{M_i}{M_j}\right]^{-\frac{1}{2}} \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}} \left(\frac{M_j}{M_i}\right)^{\frac{1}{4}}\right]^2$$

x_i = Volume fraction of gas constituent

N = Number of constituents

M_i = Molecular weight of gas constituent

μ_i = Viscosity of gas constituent.

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