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AD A116903 **TECHNICAL MEMORANDUM** NCSC TM 349-82

**JUNE 1982** 

# THE EFFECTS OF PRESSURE AND PARTICLE SIZE ON CO<sub>2</sub> ABSORPTION **CHARACTERISTICS OF HIGH** PERFORMANCE SODASORB

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JUL 1 3 1982 . **B** 

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### ADMINISTRATIVE INFORMATION

The investigation described in this report was performed during fiscal year 1981 as part of the Advanced Surface Supported Diving System (ASSDS) project sponsored by NAVSEA 05R2. This phase of the ASSDS project is intended to develop a design handbook for use in designing  $CO_2$  scrubber systems for diving equipment.

Released by J. W. Grimes, Head Life Support Systems Division June 1982 Under authority of W. T. Odum, Head Diving and Salvage Department

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REPORT DOCUMENTA	TION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
NCSC TM 349-82	AD-A11690	<u> 8</u>
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
The Effects of Pressure and P Absorption Characteristics of Sodasorb	Particle Size on CO <sub>2</sub> High-Performance	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(a)		8. CONTRACT OR GRANT NUMBER(*)
A. Purer, G. A. Deason, B. H. M. L. Nuckols	Hammonds, and	
9. PERFORMING ORGANIZATION NAME AND AL	DDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Naval Coastal Systems Center Panama City, FL 32407		
11. CONTROLLING OFFICE NAME AND ADDRES	55	12. REPORT DATE June 1982
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS	different from Controlling Office)	15. SECURITY CLASS. (of this report)
		UNCLASSIFIED
I OLETHOUTION FTATEVENT (of this Danad)		N/A
17. DISTRIBUTION STATEMENT (of the abetract	entered in Block 20, il different fr	om Report)
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse eide II nece	eeery and identify by block number	)
Sodasorb; Carbon Dioxide; Abs Systems; Temperature; 1 Atmos	sorption; Pressure; M sphere Pressure; High	oisture Content; Diving Performance
20. ABSTRACT (Continue on reverse eide if nece The effects of $CO_2$ absorbent effect of pressure for a sing dardized methods for $CO_2$ absor between 4 and 60 mesh size. in gas linear velocity and mo 1 and 32 atmospheres. There at low linear velocities and	particle size at 1 a gle particle size at 1 a gle particle size wer option efficiency. T Testing for pressure pisture content at si was a tendency for p decrease efficiency	tmosphere pressure and the e investigated using stan- he study covered particles effects included variations mulated pressures between ressure to increase efficienc at high linear velocities for
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20. ABSTRACT (continued):

a saturated carrier gas. For a dry carrier gas, increased pressure decreased efficiency for all linear velocities. Decreasing particle size increased absorbent efficiency at the cost of increasing pressure differential across the canister.

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#### INTRODUCTION

The  $CO_2$  absorption characteristics of the absorbent material must be known over a wide range of conditions in order to design high-efficiency closed or semiclosed life support systems for diving applications. Parameters that may influence the efficiency of such systems include (a) absorbent mesh size; (b) type of absorbent; (c) water content of  $CO_2$  containing gas; (d) water content of the absorbent; (e) temperature; (f) gas density; (g) thermal properties; (h) linear velocity of gas stream, intermittent or continuous flow; (i)  $CO_2$  injection level; (j) canister packing density; and (k) conceivably other parameters not yet known.

This report presents the results of the second of a series of  $CO_2$ absorbent studies. The effects of increased pressure and absorbent particle size on  $CO_2$  absorbent efficiency are investigated. An earlier report<sup>1</sup> outlined the effects of moisture, absorbent cell dimensions, linear velocity, and temperature on  $CO_2$  absorption. This series of studies is intended to ultimately provide improved techniques for  $CO_2$  absorption from diver breathing systems and to establish guidelines for  $CO_2$  absorbent canister design.

As in the previous investigation, all evaluations in this study were conducted on a high-performance (HP) Sodasorb manufactured by W. R. Grace and Company. This high-moisture type absorbent has a reported water content of 14 to 19 percent, a calcium hydroxide content of about 80 percent, and about 5 percent activators which consist mostly of sodium and potassium hydroxide. A pH-type indicator, ethyl violet, is also incorporated into the mixture.

#### APPARATUS AND PROCEDURE

The laboratory apparatus displayed in Figure 1 is similar to that previously reported<sup>1</sup> with suitable modifications to facilitate the required high pressures. The only change made for the particle size investigation

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<sup>&</sup>lt;sup>1</sup>NCSC Technical Memorandum TM 327-81, "Carbon Dioxide Absorption Characteristics of High Performance Sodasorb at 1 Atmosphere Pressure," by A. Purer, G. A. Deason, M. L. Nuckols, and J. F. Wattenbarger, October 1981, UNCLASSIFIED.

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was to add a magnehelic differential pressure gauge directly across the cell. Helium was used as the major component because its high thermal conductivity, 5.8 times that of air,<sup>2</sup> would dissipate the heat of absorption faster than air and thus assure a more uniform temperature across the absorption cell.

Inlet gas flow was controlled with a needle valve. Inlet gas flowed through this valve to the 8 feet (2.4 metres) of 1/8-inch copper tubing of the temperature equilibrating coil submerged in the constant temperature bath. If a dry run was desired, the gas went directly to the CO<sub>2</sub> absorption cell assembly; for a saturated run, the gas would first pass through a bubble tower. The CO<sub>2</sub> containing gas then passed through a second temperature equilibrating coil, 6 feet (1.8 metres) of 1/8-inch copper tubing, before entering the absorption cell. The absorption cell had an internal diameter of 0.978 centimetre and a length of 12.50 centimetres. A maximum distance of 0.489 centimetre that a gas molecule could be from the constant temperature-maintained copper walls assured rapid dissipation of the heat of reaction. This small cell diameter ensured the near isothermal conditions desired for this parametric study.

The absorption cell was equipped with CPV O-ring type connectors. These connectors allowed easy access to the cell while ensuring a gas-tight seal during testing. Additionally, the flat ends of the CPV connectors facilitated volume calculations. A 5-gram charge of an absorbent of known absolute density was nominally used. Absolute density of the absorption material was obtained by expanding a known volume of dry helium gas into a container of known empty volume as described in References 1 and 3.

The constant temperature bath was capable of maintaining the required temperature within  $\pm 0.1^{\circ}$ C. Temperatures below ambient were obtained using an external cooling system.

The gas stream passed from the absorption cell into the  $CO_2$  analyzer, a Beckman Model 865 Infrared Analyzer. Instrument calibrations were made both prior to and after each run. If a calibration changed during the run, the calibration obtained immediately after breakthrough was used in the final calculations. Each run was terminated when the  $CO_2$  level reached 0.5 percent surface equivalent in the outlet gas. Total flow was recorded with a Precision Instruments wet test meter.

<sup>1</sup>ibid.

<sup>2</sup>Dal Nogare, S. and Jubet, R. S., <u>Gas-Liquid Chromatography</u>, Interscience Publishers, New York, pp. 132, 135; 1962.

<sup>3</sup>Purer, A., Hoffman, C. A., and Smith, D. R., "Chromatographic Determinations of Column Dead Volume and Absolute DEnsity of Absorbents of Cryogenic Temperatures," J. Gas Chromatography, Vol. 6, March 1968.

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#### CALCULATIONS

The weight of the absorbent used in each run was divided by the absolute density<sup>1 3</sup> to obtain the volume of the solid absorbent. This volume, subtracted from the canister volume occupied by the Sodasorb, represented the dead volume of the cell. This is the volume available for gas flow. Dividing this volume by flow yields the mean time individual gas molecules would spend in the cell. Dividing cell length by this time yields an average linear velocity of the gas stream within the canister. The absorption capability of each test canister is indicated by plotting linear velocity against the number of litres of 1 percent  $CO_2$  gas purified per gram of absorbent. Equations to carry out the above calculations follow:

$$V_{s} = \frac{W_{a}}{d_{a}}$$
(1)

where

 $V_s$  = volume of absorbent  $W_a$  = weight of absorbent  $d_a$  = absorbent density of absorbent.

$$V_{d} = V_{T} - V_{s}$$
(2)

where

 $V_d$  = dead volume of cell  $V_T$  = total volume of cell occupied by absorbent.

$$t = \frac{V_d}{F}$$
(3)

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where

t = time on individual gas molecule speeds in the filled portion of the canister

f = flow rate through cell.

<sup>1</sup>ibid.

<sup>3</sup>ibid.

 $\mu = \frac{\ell}{t}$ 

where

 $\mu$  = linear velocity through cell

l = length of cell filled with absorbent.

The above equations are applicable only to cells with parallel walls.

#### RESULTS

#### THE EFFECTS OF INCREASED PRESSURE ON CO2 ABSORPTION

To evaluate the effects of increased pressure on the chemical absorption capability of Sodasorb, the cell's effective length and diameter were fixed at 6.5 centimetres and 0.978 centimetres, respectively, with a 5-gram charge. The cell temperature was held constant at  $21.1^{\circ}C$  (70°F); the inlet CO<sub>2</sub> partial pressure was maintained at 1.0 percent surface equivalent (0.01 ata); the inlet gas helium pressure was varied over a series of runs at 1, 2, 4, 8, 16, and 32 atmospheres. Canister breakthrough was defined as in the previous studies, as 0.5 percent  $CO_2$  surface equivalent measured at the cell exit. An absolute density for Sodasorb of 2.49 g/cc<sup>1</sup> was used to calculate canister dead volume, residence time, and the gas stream linear velocity. All runs used 4 to 8 mesh (Tyler) Sodasorb.

The following conditions were used for both the dry and water saturated runs to achieve the desired surface equivalent conditions:

Pressure			H <sub>2</sub> O Content
Equivalent	CO <sub>2</sub> Inlet	CO <sub>2</sub> Break-	for Saturated
Depth (FSW)	(%)	through (%)	Runs @ 21.1°C (ppm)
0	1.0	0.5	24,690
33	0.5	0.25	12,345
99	0.25	0.125	6,173
231	0.125	0.625	3,086
495	0.0625	0.03125	1,543
1023	0.03125	0.015625	772
2079	0.015625	0.0078125	386

The dry runs all had a moisture content of less than 100 ppm. As indicated above, the saturated runs represented a decreasing water content

<sup>1</sup>ibid.

(4)

as pressure was increased. This effect is created by the fact that the vapor pressure of water at a specified temperature is a fixed value; therefore, as the total pressure of the system increases, the ppm water concentration will decrease. This is illustrated in Figure 2. Thus, at 1 atmosphere of pressure and 21.1°C (70°F), a saturated system contains 24,690 ppm water. Increasing the total pressure to that obtained at 2000 feet of seawater (61.6 atm) reduces the saturated water content to 386 ppm. This reduction in moisture content could tend to affect canister performance at elevated pressures.

The effects of water content of the gas stream on the absorbent's efficiency have been well established.<sup>1</sup> It was previously found that the higher the absolute moisture content of the gas stream, the higher the efficiency. The saturated runs (Figure 3) offer some interesting comparisons. As the pressure increases, the ppm water decreases due to the increased total pressure. Thus, increasing pressure, resulting in reduced water content, should reduce the absorbent's efficiency. This was found to be true, with the exception of the 1-atmosphere runs at a linear velocity above 13 centimetres/second. However, at the lower velocities, below about 7 centimetres/second, increasing pressure from 1 to 4 atmospheres tended to increase efficiency. There was little change in efficiency from 4 to 32 atmospheres. It appears that the reduction of water content resulted in an increase in the reaction time; such time was not available at the higher velocities.

The efficiencies obtained with the dry carrier gas at elevated pressures (Figure 4) show that pressure has little effect at low velocities. However, as velocities increase, efficiencies quickly drop. Again, with the exception of the 1-atmosphere data, the increase in pressure results in decreased efficiency.

Figure 5 shows a comparison of data from both the wet and dry runs. To simplify the graph, only data for 2, 8, and 32 atmospheres pressure are displayed. Moisture content has a very prominent effect on the ability of the absorbent to remove  $CO_2$  at linear velocities up to about 10 centimetres/second. At higher linear velocities, especially at the higher pressures, the effect of moisture is not as significant.

#### THE EFFECTS OF PARTICLE SIZE ON PRESSURE DIFFERENTIAL

Decreasing particle size should create two effects. It should increase absorbent efficiency at the cost of greater pressure drop across the canister. This increased pressure drop increases the diver's breathing effort. This limits the application of small diameter particles.

<sup>1</sup>ibid.

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FIGURE 3. HP SODASORB EFFICIENCY AT VARIOUS PRESSURES WITH A SATURATED CARRIER GAS

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1% CO2 (SURFACE EQ.) PURIFIED TO 0.5% (SURFACE EQ.)/GRAM OF ABSORBENT (LITRES)

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Linear velocity of gas flowing through a canister should be similar to that of a chromatographic column and thus exhibit streamlined or laminar flow. Such pressure drop can be written as:<sup>2</sup>

$$A_p = (\frac{n}{K}) L\bar{u}$$

where

A<sub>p</sub> = pressure drop n = gas viscosity K = permeability of the canister to gas flow L = canister length u
= average linear velocity.

The permeability factor K is defined by the Kozeny-Corman equation (2, 3, 4) as

$$K = (\frac{\frac{d}{p}^{2}}{180})\epsilon^{3}/(1 - \epsilon)^{2} = (\frac{2n\epsilon Lp_{o}}{\frac{p_{i}^{2} - p_{o}^{2}}{p_{o}^{2}}})\mu_{o}$$

where

d = effective particle diameter
 ε = fraction of canister cross section available
 to the moving gas stream
P = inlet pressure
P = outlet pressure

 $\mu_{o}$  = outlet velocity.

Since permeability is proportional to  $d_p^2$ , decreasing particle size should rapidly increase the pressure drop across a canister. Another factor affecting  $\Delta p$  (pressure change) that is related to particle diameter is the distinction between interparticle porosity and total porosity of the Sodasorb particles. Moving gas is found only in the interparticle channels; thus, stagnant gas in the pores tend to restrict flow. The fractional gas cross section of the canister thus would decrease slightly with particle size due to the increased surface area. Pressure drop at a

<sup>2</sup>ibid.

given gas velocity increases in a rough proportion to  $1/d_p^2$  and directly proportional to canister length. The work of Bohemen and Purnell<sup>2 4 5</sup> on diffusion in packed columns indicates that about 80 percent of the column's volume is available to the gas. Irregular surfaces impede flow; thus, the smallest pressure drop would be obtained with solid spherical particles.

To evaluate the effects of particle size, a 4- to 8-mesh highperformance Sodasorb was ground to smaller sizes under a helium atmosphere. The material was then sieved to the desired particle size range and blown with helium to remove fines which would contribute to excessive pressure drop.

Table 1 shows the relationship between mesh size and maximum particle diameter. The uniformity of particle size is represented by the ratio of the maximum and minimum diameters. Average particle size listing was calculated on the assumption that the particle sizes were distributed equally throughout the mesh range.

#### TABLE 1

#### MESH RANGE AND DIMENSIONS

Tyler Mesh Range	Mesh Opening (d_)(mm)	Average d (mm) p	Max d Min d P	
4-8	4.75 - 2.36	3.56	2.0	
8-20	2.36 - 0.85	2.36	2.8	
10-20	1.70 - 0.85	1.28	2.0	
20-60	0.85 - 0.25	0.55.	3.4	
32-60	0.50 - 0.25	0.38	2.0	

Cell length 6.9 centimetres, cell diameter 0.978 centimetre, and temperature 21.1°C (70°F) were maintained constant, as previously stated, while varying the absorbent mesh size in a test series at 1 ata.

The pressure drop across the test cell was measured with a 0- to 25-inch  $H_2O$  magnehelic. Background pressure drops obtained from an empty cell were subtracted from the differential pressures generated by the full cell. The pressure drop across the cell charged with 4 to 8, 8 to 20, 10

<sup>2</sup>ibid.

<sup>4</sup>Bohemen, J. and Purnell, H. H., Journal of Chemical Society, p. 360, 1961.

<sup>5</sup>Bohemen, J. and Purnell, J. H., <u>Gas Chromatography 1958</u>, E. H. Desty, Editor Academic Press, New York, p. 6, 1958.

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to 20, 20 to 60, and 32 to 60 mesh at various flow rates are displayed in Figure 6. These data indicate that 10 to 20 mesh and possibly 15 to 32 mesh, which was not tested, could represent a more optimum particle size for diver's breathing apparatus since the added flow resistance over 4 to 8 mesh is minimal for the anticipated advantage in absorbent efficiency.

The results of the effects of particle size on pressure drop across the 6.9-centimetre long cell for a dry gas are displayed in Figures 6 and 7. Figure 6 shows that pressure drop for a fixed mesh range is directly proportional to linear velocity. This figure also indicates that there is little difference in pressure drop of 4 to 8 mesh and 8 to 20 mesh material. Figure 7 shows that decreasing particle size has a very noticeable effect on pressure drop at 8 centimetres/second. It also indicates that if a canister system could be designed to operate at lower linear velocities, smaller particles could be used and thus higher anticipated efficiencies.

The effects of particle size on pressure differential with a gas saturated with water were also investigated. The wet runs started with the same pressure differential as the dry; however, as they progressed, the differential increased in a linear rate. At breakthrough, the increase equaled about 10 percent of the starting pressure for the 32 to 60 mesh size. The 10 to 20 mesh size did not exhibit as large an increas in  $\Delta p$ ; the average pressure increase for this range was normally less than 5 percent of the starting pressure. The dry gas runs tended to show a slight increase in  $\Delta p$  as they approached the end of a run. This effect may be due to slight changes in particle geometry or possible channeling.

#### THE EFFECTS OF PARTICLE SIZE ON CO2 ABSORPTION BY HIGH-PERFORMANCE SODASORB

Increased total absorbent surface area due to decreasing particle size should yield improved absorbent efficiency. The ratio of a particle's surface area to its volume increases rapidly with decreasing particle diameter. This added surface area should increase contact between the absorbent and the  $CO_2$  molecules. To evaluate these effects, the standard conditions<sup>1</sup> of cell length 6.5 centimetres, cell diameter 0.978 centimetre, cell temperature 21.1°C (70°F), 1 percent  $CO_2$  in dry helium, and an absorbent absolute density of 2.49 g/cc were maintained.

Figures 8 and 9 represent the relationship between particle size and efficiency for a dry, 1 percent  $CO_2$  in helium mix. The same information for a saturated, 1 percent  $CO_2$  in helium mix is displayed in Figures 10 and 11. For comparisons, selected data from the dry runs have been included in Figure 10.

<sup>1</sup>ibid.





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For both the dry and saturated gas streams, decreasing particle size increases efficiency. The effect is more pronounced with the dry carrier gas. The smaller particle size tended to hold the exit  $CO_2$  content to a very low value for the total run. As absorbent exhaustion was reached, the  $CO_2$  content would quickly increase. The exact time of breakthrough was well defined. The effect of linear velocity on absorbent efficiency at small particle size was greater for the dry  $CO_2/He$  mix. The saturated  $CO_2/He$  mix showed little change.

#### CONCLUSIONS

The effects of pressure and particle size on  $CO_2$  absorption characteristics of high-performance Sodasorb were investigated. For a saturated carrier gas, pressure tended to increase efficiency slightly for low linear velocities and decrease efficiency for high linear velocities. For a dry carrier gas, increased pressure decreased efficiency for all flow rates. Decreasing particle size increased absorbent efficiency at the cost of increasing pressure difference across the canister.

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