Transactions on the Built Environment vol 24, © 1997 WIT Press, www.witpress.com, ISSN 1743-3509

Preparation of the compressed gas mixtures

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Abstract

The paper discusses preparation of breathing mixtures used in deep diving operations. The mathematical models describing of preparation compressed gas mixtures by the pressure transfer are reported on. A special computational protocol for preparation of helium - oxygen (HELIOX) mixture under isothermal conditons is presented. Problems of diving gas analysis and contaminant contents are reported.

1 Introduction

The deep diving operations require selection of an optimal breathing mixture for each of the actual operational situations. Oxygen is the major gas because is necessary for maintaining the diver's metabolism. Oxygen partial pressure is maintained at the proper level with the depth of diving by increasing the amount of the diluent gases: helium, nitrogen, neon ,argon or hydrogen.The factors relating to the choice of the breathing gas are: metabolic needs and toxicity of oxygen,inert gas narcosis,high pressure nervous syndrome and hyperbaric athralgia, density, viscosity, voice distortion, thermal properties,decompression, costs and availability,fire safety.

Much of mixed-gas diving is done with the use of the gas mixtures prepared on shore and shipped to the dive sites.To prepare a gas mixture one of the following methods can be used.

The gravimetric method [ISO-6142-1981]. The method relies on successive addition of the components gas to the tank.The mass of each gas components is determined by weighing the gasholder before and after filling it.Despite of high accuracy the method is not in common use in diving due to the small yield of the gas mixture.

The static volumetric method [ISO-6144-1981]. The gasholder of known volume is filled up with the gas components at atmospheric pressure and ambient temperature.Determination of the mixture composition is based on knowing the volume of each gas component.

The dynamic method . The method was described by Bøe [1]. It relies on simultaneous mixing of two or more streams of gases.The procedure is used to prepare the mixtures for the immediate use or when the mixture prepared is to be compressed into the gasholder.

The pressure transfer method [ISO-6146-1979]. The method involves mixing of the component gases under pressure in the cylinders.The possibility of preparing large amounts of the mixture with simple equipment makes the method useful in the field.

Tab.1 Analytical expressions of the equation of state

Clapeyron	$pV = nRT$
van der Waals	$\left(p+\frac{a}{V^2}\right)(V-b) = nRT$
Beattie-Bridgemann	$pV^2 = nRT\left[V = B_o\left(1-\frac{b}{V}\right)\right]\left(1-\frac{c}{VT^3}\right) - A_o\left(1-\frac{a}{V}\right)$
The virial equation	$pV = nRT[1 + b(T)p + C(T)p^2 + \ldots]$
R=8314.7 J/mol K a,b,c,the constants	B(T),C(T), the virial coefficients T, the absolute temperature ,K V, the gas volume

Despite of the procedure`s simplicity,there are some technical difficulties that make the method very laborious. After mixing the gas must be carefully analyzed and the percentage adjustment of the component gases is essential. The adjustment has to be preceded by calculating the magnitude of the pressure increase with pure component gases.To determine of that pressure, the equation of state is applied. Based on the assumptions and simplifications, we can use the different analytical expressions of the equation of state.The different analitycal forms of the equation are presented in Table1.

2 Computation of the gas mixture composition and partial pressures of component gases contained in the gasholder

The principle of the pressure transfer used for gas mixing is shown in Fig.1 The calculations are based on the equation of state for the ideal gas.More accurate computations are not necessary due to difficulties with keeping the constant temperature at mixing.

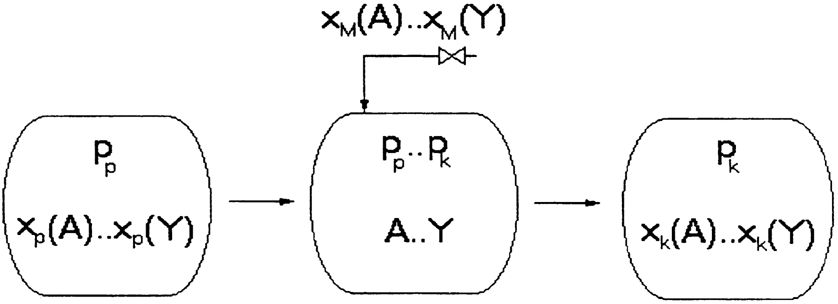

Fig.1 Preparation of the breathing mixture in the gasholder at constant temperature.

Initially the gasholder is filled with the gas mixture containing pure gases A...Y, the molar fraction of each component at pressure p_p being $x_p(A)...x_p(Y)$.The filling procedure involves introduction of mixture of gasesA...Y to the gasholder, the mixture causing the pressure to increase up to p_k.

The composition of the complementary gas mixture is given as $x_m(A),..,x_m(Y)$. Finally, the gas pressure is p_k and molar fractions of gases are $x_k(A)...x_k(Y)$.The amount of the gas at the initial and the final state is calculated from the ideal gas equation and is given as :

$$\sum_{i=A}^{Y} n_p(i) = S_p = \frac{p_p V_z}{RT} \tag{1}$$

$$\sum_{i=A}^{Y} n_k(i) = S_k = \frac{p_k V_z}{RT} \tag{2}$$

where: p_p, p_k, initial, final pressure, Pa

R , universal gas constant, J/mol K
S_p, S_k, initial , final amount of gas, moles
T , absolute temperature,K,
V , volume of the gasholder, m^3

The amount Δn of the gas supplied to the gasholder is calculated from equations(1),(2) and is given as:

$$\Delta n = S_k - S_p = \frac{(p_k - p_p)V_z}{RT} \tag{3}$$

The amount of the j-th gas component at the final state, after the container has been filled with the gas mixture of composition x_M (A)...x_M(Y) is given as:

$$n_k(j) = x_p(j)\left[\sum_{i=A}^{Y} n_p(i)\right] + x_M(j)\ \Delta n = x_p(j)\frac{p_p V_z}{RT} + x_M(j)\frac{(p_k - p_p)V_z}{RT} \tag{4}$$

The molar fraction of the j-th gas in the mixture at the final state is given as:

$$x_k(j) = \frac{x_p(j) p_p V_z RT}{RT p_k V_z} + \frac{x_M(j)(p_k - p_p)V_z RT}{RT p_k V_z} \tag{5}$$

$$x_k(j) = \frac{p_p\left[x_p(j) - x_M(j)\right]}{p_k} + x_M(j) \qquad \text{for} \qquad T = \text{const} \tag{6}$$

Equation (6) makes it possible to calculate the partial pressure of the j-th gas in the gasholder at the final state:

$$p_k(j) = p_k x_k(j) \tag{7}$$

$$p_k(j) = p_p\left[x_p(j) - x_M(j)\right] + p_k x_k(j) \tag{8}$$

Equations (6),(8) are the basic equations describing the process of obtaining the arbitrary gas mixtures from the pure gases and other mixtures, Przylipiak[6].

3 Preparation of the gas mixtures of intended composition from the pure gas components by pressure transfer

The amount of the pure gas component j-th at the initial and final state is given as:

$$n_p(j) = x_p(j)\frac{p_p V_z}{RT} \tag{9}$$

$$n_k(j) = x_k(j)\frac{p_k V_z}{RT} \tag{10}$$

The amount of the supplied pure gas component j-th is given as:

$$\Delta n(j) = n_k(j) - n_p(j) = \frac{V_z}{RT}\left[p_k x_k(j) - p_p x_p(j)\right] \qquad (11)$$

To obtain the intended contents of the j-th gas in the prepared mixture at T=const, it is necessary to increase the pressure with the pure j-th gas:

$$\Delta p V_z = \Delta n(j) RT \qquad (12)$$

From equations (11) and (12) it follows that the pressure difference:

$$\Delta p = p_k x_k(j) - p_p x_p(j) = p_k(j) - p_p(j) \qquad (13)$$

Equation (13) is the basic equation for calculating of the parameters at preparation of the gas mixtures from the pure gas components. .Most of deep diving operations involve helium-oxygen (HELIOX) in which the contribution of oxygen is less than 20% by volume.With regard to fire safety Glenn [2], it is necessary to keep the percentage of oxygen less than 25% by volume throughout during mixture preparation.To make the preparation procedure more efficient, the special calculation blank was prepared.The blank presented as Table 2 allows to prepare the gas mixtures involving oxygen and helium, if the oxygen percentage is less than 20% by volume. When the percentage of oxygen exceeds 20% by volume, the blank should be modified. A part of the blank concerns the verifying calculations.Mistakes at the mixing are very expensive because preparation of the mixtures is very laborious and the high purity gas components are very costly.The quality assurance of the breathing gas is essential for the diver. The gaseous mixtures contain oxygen as the main biological component and inert gases.There are different breathing mixtures: NITROX (oxygen content less than 20% by volume-nitrogen), HELIOX (oxygen-helium), NEOX (oxygen-neon), ARGONIT (oxygen-argon), TRIMIX (oxygen-helium-nitrogen), HYDRELIOX (oxygen-hydrogen or oxygen-hydrogen and small percentage of nitrogen). Binary mixtures are the diving gases used most often. During preparation of the mixtures,the gas is not analyzed in the chemical laboratory immediately, only the oxygen content is analyzed with a high accuracy portable oxygen meter .As opposed to oxygen, the analysis of the inert gases is very difficult and sometimes not possible in the field ; therefore the multicomponent mixtures should be prepared with the special methods. TRIMIX is often used in diving operations.Oxygen and nitrogen are the gases that mix well (as opposed to mixing of those gases with helium) and there is no stratification of gases, Kłos [5]. The first stage at TRIMIX preparation is to prepare the basic NITROX of the same oxygen and nitrogen proportions as in TRIMIX that is to be prepared.

Tab. 2 The calculation blank for preparation of the breathing mixture

Pt 1. The calculation data

Pressure of Heliox remaining in the gasholder p_1=..... MPa
Molar fraction of oxygen in remaining Heliox x_1=..... mol mol^{-1}
Required final pressure of oxygen p_2=..... MPa
Required final molar fraction of oxygen in Heliox x_2=..... mol mol^{-1}

Pt 2. The introductory calculations

$$\Delta p = p_2 * x_2 - p_1 * x_1 = \ldots\ldots * \ldots\ldots - \ldots\ldots * \ldots\ldots = \ldots\text{ MPa}$$

$$p_x = 5 * x_2 * p_2 - \Delta p = 5 * \ldots\ldots * \ldots\ldots - \ldots\ldots = \ldots\ldots \text{ MPa}$$

if $p_x > p_1$ then go to **pt 3**, if $p_x = p_1$ then go to **pt 4**, if $p_x < p_1$ then go to **pt 4**

Note if $\Delta p < 0$,it is necessary to increase the final pressure as in this case preparation of the breathing mixture is not possible

Pt 3. Calculation continued

$$p_y = p_x + \Delta p = \ldots\ldots + \ldots\ldots = \ldots\ldots\text{MPa}$$

Process of obtaining Heliox.

1 Increase the pressure with He from p_1 =...MPa to p_x =.MPa
2. Increase the pressure with O$_2$ from p_x up to the pressure p_y =...MPa
3 Fill the gasholder with He up to p_2 =...MPa

Pt 4. Calculation continued

$$p_z = p_1 + \Delta p = \ldots\ldots + \ldots\ldots = \ldots\ldots \text{ MPa}$$

1. Increase the pressure with O$_2$ from p_1 =...MPa to p_z =...MPa
2 Fill the gasholder with He up to p_2 =.. MPa

The verifying calculations

If S calculated from the equation below is equal to zero to 0.01, the calculations are correct.

for pt 3
$$S = \frac{p_y - p_x + (p_1 \cdot x_1)}{p_y} - 0{,}2 = \frac{\ldots\ldots-\ldots\ldots+(\ldots\ldots\cdot\ldots\ldots)}{\ldots\ldots} - 0{,}2 = \ldots\ldots$$

for pt 4
$$S = p_2 \cdot x_2 + p_1 \cdot (1 - x_1) - p_z = \ldots\ldots\cdot\ldots\ldots+\ldots\ldots\cdot(1-\ldots\ldots)-\ldots\ldots=\ldots\ldots$$

To prepare TRIMIX, the basic NITROX of known composition is used and the parameters of mixing are determined from the equations (6), (7). During preparation of TRIMIX, only the measurement of oxygen content is needed because the ratio of oxygen and nitrogen has already been estabilished in the basic NITROX; helium is the complementary gas. Contents of oxygen, component gases and contaminants in TRIMIX must be determined prior to use;some of the contaminants are listed in Table 3 ,US Navy [9],Shilling [7]. The problems of gas analysis are presented in the papers of Kłos [3,4,5]

The breathing mixtures composition is usually determined with gas chromatography.The gas chromatograph should be able to determine Freon 113 to 0.5 ppm in the gas sample.The accuracy must be better than 5% (i.e. for the next injection the standard deviation should be less than 5%of the mean value obtained during calibration of the gas chromatograph with the standard gas).The mixture containing 5-10 ppm Freon 113 or toluene is used as the standard gas.The two standard gases should have the certificate stating that the relative error of their manufacture is less than 2%.Usually the contaminant content is related to the standard gas that contains Freon 113. All chromatograph peaks for which the relative contaminant content (in relation to Freon 113) exceeds 1ppm should be identified. Testing of the breathing mixtures involves the determination of content of the permanent gases: oxygen, argon, nitrogen, helium, carbon dioxide, carbon monoxide.To overcome the difficulties related to the carbon monoxide analysis , the content of carbon monoxide (after methanation) can be measured together with carbon dioxide with FID- detector.The measurement system should be able to determine 5 ppm of carbon monoxide. The relative error of mixing for the standard gas used in the gas analysis of the permanent gases should not exceed 1%. The required accuracy of the permanent gas is :

- oxygen, nitrogen, helium - the relative error not exceeding 0.1%,
- carbon dioxide - the absolute error less than 1ppm,
- if the contents of the carbon monoxide in the mixture exceeds 5ppm, the absolute error should not exceed 1%.

The results of the gas analysis are useful for determination of the maximum permissible depth of diving with regard to SEV(surface equivalent value) of the toxicological contaminant.The surface equivalent value of contaminant is defined as:

$$C_{SEV} = C \cdot \frac{p^H}{p_o} \tag{14}$$

C_{sev}, C, the surface equivalent value of the contaminant,the content of the contaminant in the gas sample, ppm,

p^H , p_o , the total pressure at the maximum diving depth, atmospheric pressure , ata,

Tab.3 Contaminants in the hyperbaric environment

Chemical compound	Suspected source	Maximum limits for exposures C_{sev}		
acetylene C_2H_2	cooking	6000ppm	6000 ppm	6000 ppm
acroleinCH_2CHCHO	cooking	-	0,1 ppm	-
antimony hydrideSbH_3	battery	-	0,05 ppm	0,01 ppm
ammonia NH_3	metabolic	400 ppm	50 ppm	25 ppm
benzene C_6H_6	solvents	-	100 ppm	1,0 ppm
chloroform $CHCL_3$	solvents	-	-	1,0 ppm
hydrogen chloride HCl	freons	10 ppm	4,0 ppm	1,0 ppm
nitrogen dioxide NO_2	compressors	10 ppm	1,0 ppm	0,5 ppm
sulphur dioxide SO_2	sanitary	10 ppm	5,0 ppm	1,0 ppm
carbon dioxide CO_2	metabolic	2,5 kPa	1,0 kPa	0,5 kPa
ethanol C_2H_5OH	solvents	-	-	100 ppm
hydrogen H_2	battery	1000 ppm	1000ppm	1000ppm
hydrogen fluoride HF	freons	8 ppm	1,0 ppm	0,1 ppm
formaldehyde HCOH	cooking	5,0 ppm	5,0 ppm	5 ,0ppm
freons 113, 11, 12,114	conditioning	-	-	100 ppm
ozone O_3	motors	1,0 ppm	0,1 ppm	0,02 ppm
nitric oxide NO	compressors	10 ppm	1,0 ppm	0,5 ppm
carbon monoxide CO	smoking	200 ppm	200 ppm	0,1 ppm
aliphatic hydrocarbons other than CH_4	solvents	-	-	10 mg m^{-3}
aromatic hydrocarbons other than benzene	solvents	-	-	10 mg m^{-3}

Based on the results of the gas analysis C and maximum permissible limits for different exposures C_{sev} presented in Table 3, the maximum permissible depth of diving H_{max} can be calculated with a gas mixture containing the contaminants of interest.The maximum pressure in the hyperbaric facility:

$$p^H \cong 0.1\, H_{max} + 1 \qquad (15)$$

Equations (14) and (15) allow to determine the maximum depth of diving.
The mixtures are manufactured in horizontal cylinders.The cylinders refilled with the gas mixture need some time for homogenization. Mixing through molecular migration may be accelerated by overturning the cylinder. A large amount of helium was observed to accumulate in the space below the cylinder valve,particularly when the cylinder was stored vertically. A significant amount of helium was accumulated after 0.5-1 month of storage.There are two trends in manufacturing of the breathing gases containing nitrogen.One recommends the use of pure component gases that have special purity certificate which eliminates pollution of the mixtures at preparation.The deficiency of the method

is the time necessary for the gases to homogenize; however,the stratification usually occurs.The control of the gas composition is essential.The second recommended method involves the use of natural NITROX.That method minimizes the risk of a gross error.For that procedure, the quality of the air filters and contents of the naural contaminants in the air are of the utmost importance, Klos [5], Glenn [2]. The gas must be analyzed at least two times prior to use.

The use of the ideal gas model in the pressure transfer is succesful within the pressure range of 10-12 MPa. Above that limit, errors resulting from the assumption of the ideal gas model are significant. The pressure effect of an isothermal mixing can be determined as the difference of the pressures calculated from the Clapeyron and Beattie-Bridgemann equations.That problem was analyzed by Sobański [8].The pressure effect of oxygen-helium mixing at the constant temperature is presented in Fig.2.

At the pressure range up to 10- 12 MPa and low oxygen content in helium or low content of helium in oxygen, the errors are comparable to these resulting from inevitable variability of temperature at mixing.To eliminate those errors ; a two stage mixing of the gases is recommended.The first stage involves preparation of the mixture of an approximate composition. The cylinders refilled with the gas should be analyzed after allowing them some time standing for homogenization of the mixture. Then, at the second stage of mixing, the adjustment of the component gases is carried out.

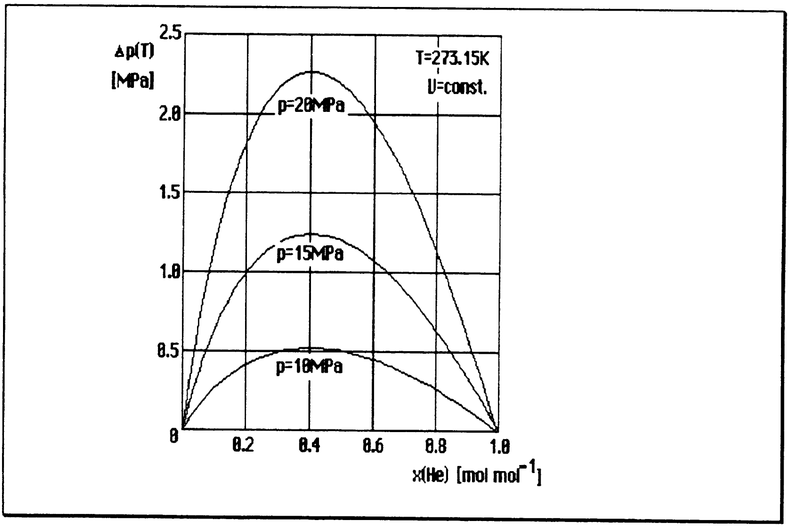

Fig.2 The pressure effect of an isothermal mixing of oxygen and helium, Sobański [8]

When the refill station is well equipped with the computers the calculations should be performed using the Beattie - Bridgemann equation of state. It is particularly recommended when the mixtures can be prepared very slowly or when the gasholder is equipped with a thermostat; that procedure eliminates the temperature variations at gas compression.

Summary

The methods presented were experimentally verified at preparation of the gas mixtures for operational diving down to 100 m in the sea.

Key words: breathing mixtures, diving,

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