

DIVING USING HYDROGEN-BASED RESPIRATORY GAS MIXTURES

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Rezumat. În cazul scufundărilor la adâncimi de peste 200 m, există doi factori care limitează eficacitatea scafandrilor utilizând amestecuri pe bază de heliu și anume: Sindromul Nervos al Înaltelor Presiuni (SNIP) datorat efectelor neurologice ale presiunii și limitările ventilatorii datorate densității unor astfel de amestecuri (pierderi de energie crescute prin sistemul respirator). Pentru a contracara în mod eficace efectele celor doi factori limitatori, specialiștii în hiperbar au considerat ca necesară utilizarea hidrogenului ca o componentă a amestecurilor pe bază de hidrogen, așa cum sunt amestecurile binare HIDROX (hidrogen - oxigen) și ternare hidreliox (hidrogen – heliu – oxigen).

Abstract. When diving to depths of over 200 m, there are two factors that limit the effectiveness of divers using helium-based mixtures, namely: High Pressure Nervous Syndrome (HPNS) due to the neurological effects of pressure and ventilatory limitations due to the density of such mixtures (increased energy loss through the respiratory system). To effectively counteract the effects of these two limiting factors, hyperbaric specialists considered necessary to use hydrogen as a component of hydrogen-based mixtures, such as the binary HYDROX (hydrogen-oxygen) and ternary HYDRELIOX (hydrogen-helium-oxygen) mixtures.

Keywords: commercial diving, saturation diving, breathing mixture, hydrogen

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1. BRIEF HISTORY AND GENERAL INFORMATION

The idea initiated by Lavoisier to use hydrogen as a low-density breathing gas dates back to the 18th century. After the well-known tests carried out by engineer Arne Zetterström between 1943 and 1945 as part of a Swedish Royal Navy program, with the exception of some animal experiments in the laboratory, no substantial program was undertaken until 1967. In 1968, as part of the HYDRA I

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program, COMEX attempted to dive one of its elite divers, René Veyrunes, to a depth of 250 m using hydrogen. However, the diving equipment was insufficient to protect him from the cold, and he had to return to the bell. It was not until 1982 that the research program on the use of hydrogen in deep-sea diving was relaunched, taking advantage of the evolution of materials and technologies for deep-sea diving developed on oil rigs.

The aim of the studies is to define the industrial methods necessary for the practical use of hydrogen-based mixtures and to study the limits of their use in humans.

The use of hydrogen in diving has been approached with diver safety as the main technical objective. The definition of the means, methods, and procedures must be based on precise knowledge of the following elements:

- the flammability limits of hydrox (hydrogen-oxygen) and hydreliox (hydrogen-helium-oxygen) mixtures under hyperbaric conditions;
- the compatibility of hydrogen with equipment materials and the breathability of hydrogen (research into pollutants);
- adaptation and compliance of all gas circuits, oxygen regeneration and automatic refill systems;
- development of a system to remove hydrogen during decompression by catalytic dehydrogenation.

In practice, with a significant safety margin, a maximum oxygen concentration of 3% has been set for all hydrogen-based mixtures. With this safety limit, all cases of hydrogen use in normoxic gas mixtures become impossible in the 0-60 m depth range. During the compression phase of a saturation dive, hydrogen is not injected into the hyperbaric chamber until 200 m and is then progressively eliminated during the decompression phase to reach a concentration of 3% at a depth of 300 m. This removal of hydrogen at the chosen decompression rate is achieved by catalytic dehydrogenation in a temperature-controlled reactor, combining hydrogen with oxygen to produce water.

These technological advances have enabled COMEX to successfully complete its HYDRA research program.

2. HYDRA-COMEX SYSTEM DIVING PROGRAM

In 1983, as part of the Hydra 3 program, sixteen divers, led by Henri Delauze, President of COMEX, carried out a series of dives between 70 and 91 m in the sea off Marseille. In the same year, as part of the HYDRA IV program, six divers breathed hydrogen for the first time in a hyperbaric chamber at a pressure of 31 bar (absolute), equivalent to a depth of 300 m. Two years later, in 1985, six divers achieved the first saturation with hydreliox (hydrogen-helium-oxygen) mixture at a depth of 450 m (HYDRA V). Thus, the first saturation dive, with

humans in a hyperbaric environment and using the hydrox (hydrogen-oxygen) breathing mixture, was carried out in 1985 through the HYDRA V experiment at a depth of 450 m. The experiments continued in 1986 with the HYDRA VI dive to a depth of 520 m, in 1987 with the HYDRA VII dive to a depth of 260 m, and in 1988 with the HYDRA VIII dive with 6 people for 6 days at a depth of 530 m, a dive carried out in real conditions at sea. These experiments carried out by COMEX in France paved the way for a new method of working underwater on subsea construction sites.

Therefore, in order to demonstrate the industrial feasibility of hydrogen diving, the continuation of the research program for humans (divers) required the demonstration, in real conditions at sea, of the human capacity to work at a depth never before reached: over 500 m. To achieve this ambitious project, two training and selection dives were designed and carried out in the COMEX hyperbaric chambers in Marseille: HYDRA VI (1986) at 520 m with hydreliox (hydrogen-helium-oxygen) and HYDRA VII (1987) at 260 m with hydrox (hydrogen-oxygen). Confirmation under real conditions (HYDRA VIII) was carried out in the Mediterranean in February-March 1988, departing from the ship *Orelia*. This experiment demonstrated the remarkable effectiveness of the divers at depths of 520 and 534 m, similar to that commonly observed on a construction site at a depth of 200-250 m with HELIOX (helium-oxygen) mixture.

This was followed by the HYDRA IX experiment in 1989, which clarified the range of using hydrox (hydrogen-oxygen) mixture and its effects on humans during long-term exposure.

Ten years after the launch of the HYDRA program, the results were compiled and used to push the boundaries of human intervention. This was achieved through test dives as part of the HYDRA X program, which took place at the end of 1992 in the hyperbaric chambers of the COMEX Hyperbaric Testing Center in Marseille (fig. 1). The team consisted of three professional divers: Serge Icart, Théo Mavrostomos, and Régis Peilho. After thirteen days of compression, one of them, Théo Mavrostomos, reached a record depth of 701 m (71,1 bar (abs.), or 7,11 MPa (abs.)) (fig. 2) and performed a three-hour working demonstration in the water hyperbaric chamber (fig. 3).



Fig. 1. Hyperbaric chambers belonging to the system for simulation diving with hydrogen-based mixtures at C.E.H. COMEX in Marseille.



Fig. 2. Diver Theo Mavrostomos at a record depth of 701 m as part of the HYDRA X program



Fig. 3. Demonstration by Theo Mavrostomos in the water pressure chamber (HYDRA X experiment – 701 m)

Recently, a new method of using hydrogen has been developed in order to limit the cost of adapting systems. This method, called "Helium IN / Hydrogen OUT", consists of saturating divers with the classic HELIOX (helium-oxygen) mixture in the living hyperbaric chamber and in the diving bell, and supplying the diver, who is in the water, with hydreliox (hydrogen-helium-oxygen) through a specially adapted circuit. Two test dives, HYDRA XI and HYDRA XII (1994 and 1996), were carried out using this technique at depths of 350 m and 210 m respectively. HYDRA XI enabled procedures to be established and HYDRA XII demonstrated the advantages of this method at sea: greater ease of breathing for divers during strenuous efforts and greater efficiency at work.

Therefore, in 1998 and 1999, through the research program "HYDRA LUDION" (I and II) research program, COMEX studied the possibility of using hydrogen to achieve rapid pressure variations between the saturation depth of the diver (living level) and that of the underwater site (working level). Compared to the helium ludions currently in use, hydrogen has been shown to allow for twice as large pressure variations.

Hydrogen-based breathing mixtures can be used successfully at depths of 150 to 650 m.

Through the HYDRA program (Table 1), 17 years of intensive research on the use of hydrogen in deep diving has shown that psycho-sensory and behavioral manifestations, namely *hydrogen narcosis*, only occur at a partial pressure of hydrogen of 2 MPa (abs.) or 20 bar (abs.). Below this limit, the hydreliox

(hydrogen-helium-oxygen) breathing mixture, by limiting the effects of SNIP and increasing breathing comfort, significantly improves the effectiveness and working capacity of divers.

Table 1

Experimental saturation dives with hydrogen-based breathing mixtures based on hydrogen, carried out by C.E.H. COMEX

Experimental dive	Diving depth [m]	Type of breathing mixture used	Breathing mixture pressure p_{am} [bar (abs.)]	Partial pressure of hydrogen	Exposure time to hydrogen mixture [days]	Nr. of divers
				bar (abs.)		
HYDRA V (1985)	450	hydreliox (H ₂ -He-O ₂)	46	25	4	3
	450		46	25	18	3
HYDRA VI (1986)	520	hydreliox (H ₂ -He-O ₂)	53	24	15	8
HYDRA VII (1987)	260	hydrox (H ₂ -O ₂)	2	25	5	4
HYDRA VIII (1988)	520/534	hydreliox (H ₂ -He-O ₂)	53/54.4	2	18	6
HYDRA IX (1989)	300	hydrox (H ₂ -O ₂)	31	30	19	4
	225/200		23.5/21	19	30	3
HYDRA X (1992)	675/701	hydreliox (H ₂ -He-O ₂)	68.5/71.1	2	29	3
HYDRA XI (1994)	350/335/365	HELIOX (He-O ₂)	36/34.5/37.5	-	-	4
		hydreliox (H ₂ -He-O ₂)				
HYDRA XII (1996)	200/210	HELIOX (He-O ₂)	21/22	-	-	4
		hydreliox (H ₂ -He-O ₂)				
HYDRA LUDION I (1998)	200/260/300	HELIOX (He-O ₂)	21/27/31	-	-	2
		hydreliox (H ₂ -He-O ₂)				
HYDRA LUDION II (1999)	200/290/100/160/	HELIOX (He-O ₂) HYDROGEN-HELIUM MIXTURE (H ₂ -He-O ₂)	21/30/11/17	-	-	5

3. PRESENTATION OF THE HYDRA VII PROGRAM

For example, Figure 4 shows the saturation dive profile, with hydrox (hydrogen-oxygen) breathing mixture, at a depth of 260 m, of the HYDRA VII experiment. Figure 5 shows a general diagram of the diving assembly used for this experiment.

In the HYDRA VII experiment, the divers were compressed in 4 hours with HELIOX mixture at a depth of 180 m, after which the HELIOX (helium-oxygen) mixture was replaced with the hydrox (hydrogen-oxygen) mixture until the hydrogen concentration in the new mixture in the diving assembly reached 90%. During this period, the divers experienced a slight euphoria for 15 to 30 minutes, comparable to the narcosis experienced in compressed air dives at a depth of 40 to 50 m. This slight narcosis disappeared fairly quickly, allowing pressurization to continue at the pressure corresponding to a depth of 260 m. Before decompression, dehydrogenation was performed for 40 hours at 260 m, at a rate of 0.6 bar (absolute) of hydrogen per hour. The final decompression was performed with a HELIOX (helium-oxygen) mixture.

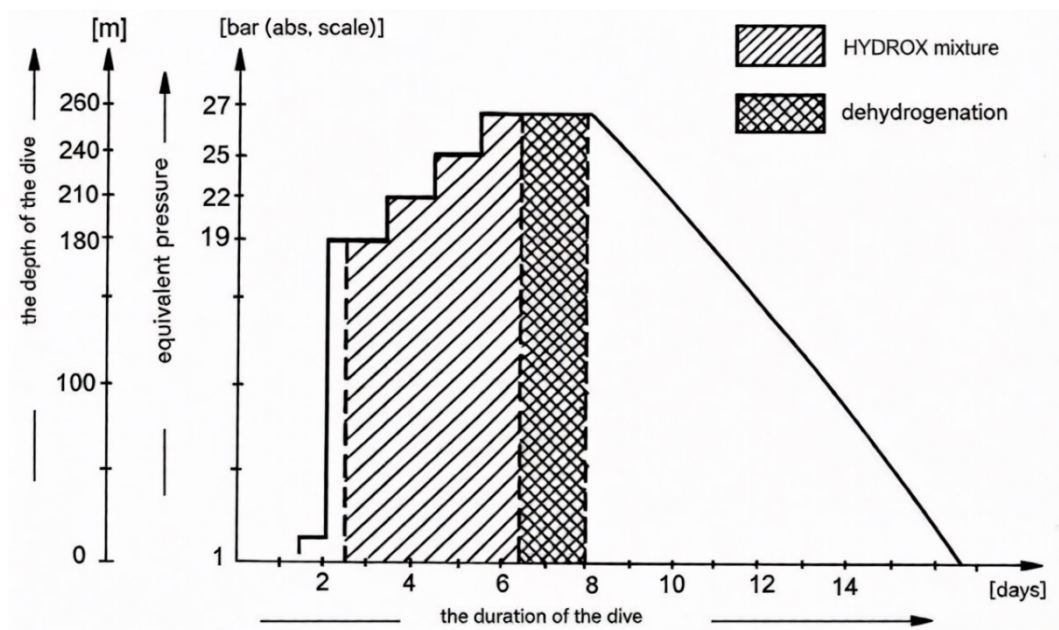


Fig. 4. Profile of the saturation dive with hydrox breathing mixture performed as part of HYDRA VII (COMEX) experiment.

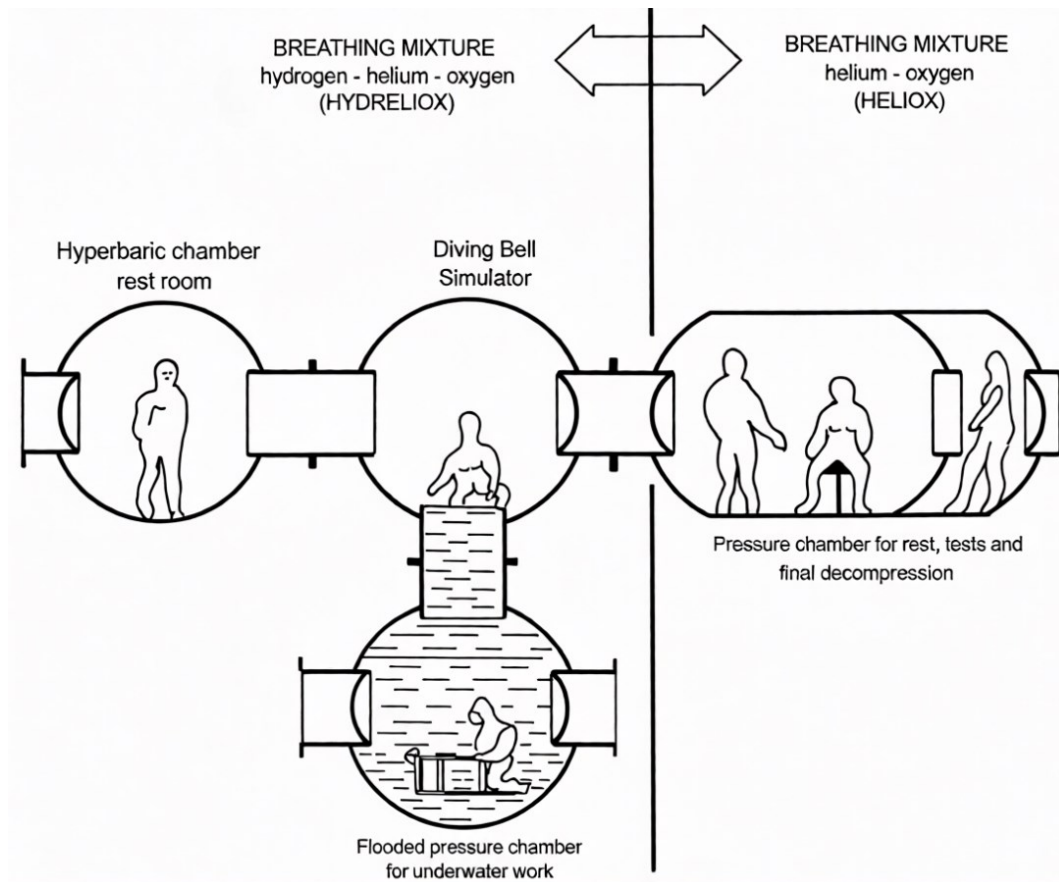


Fig. 5. General diagram of diving assembly used for the HYDRA VII experiment (COMEX).

The experimental dives using hydrogen carried out by COMEX at the Hyperbaric Testing Center in Marseille continued with the HYDRA IX experiment in 1989, which made it possible to specify the field of use of the hydrox (hydrogen-oxygen) mixture and its effects on humans during long-term exposure.

The results obtained in the use of hydrogen as an oxygen diluent for saturation diving at great depths were positive. Technical problems related to the injection of oxygen into hyperbaric chambers to replenish that consumed by divers, as well as problems related to sealing, were solved, and it was concluded that hydrogen could be a new solution as an oxygen diluent for life under pressure.

During dives conducted as part of the French HYDRA program, using hydrogen-based breathing mixtures at partial hydrogen pressures of 1.9...3 MPa (abs.) (Table 1), certain effects of the hydrogen-based mixture on human body were observed, effects that can be grouped under the name of *hydrogen narcosis*. These

effects could be studied in relation to clinical observations made during dives at equivalent depths using a HELIOX (helium-oxygen) mixture.

It was found that hydrogen acts on the human body as follows:

- causes controlled psycho-sensory and behavioral manifestations (perceptual disturbances, sleep changes, psychological and intellectual changes, for 2,4 MPa (abs.)) or uncontrolled manifestations (anxiety, depression, confusion and disorientation, for 2,4...3 MPa (absolute pressure)) in divers;

- mitigates the effects caused by high-pressure nervous syndrome (SNIP) (almost complete disappearance of tremors), high-pressure joint syndrome (SAIP) (significant reduction in joint pain and discomfort), and high-pressure respiratory syndrome (SRIP) (easier ventilation with less intense respiratory muscle effort).

Tests carried out by COMEX as part of the HYDRA diving program have shown that, for a hydrogen-based mixture with a partial hydrogen pressure in the range of 2 MPa (absolute), the disorders caused by "hydrogen narcosis" are well controlled and compensated for by divers. It can also be concluded that, through the use of hydrogen-based breathing mixtures, depths between 150 m and 650 m can be considered accessible to a wide range of divers. The hydreliox (hydrogen-helium-oxygen) breathing mixture, by limiting the effects of SNIP and increasing respiratory comfort, significantly improves the efficiency and working capacity of divers at underwater hydrocarbon production facilities. Thus, oil companies are now assured of human technical capacity in areas with depths exceeding the possibilities of conventional helium diving (depths of over 200 m).

The advantages of using hydrogen are also related to its abundance compared to helium. However, hydrogen cannot completely replace helium, especially during decompression, when the oxygen concentration increases as the pressure decreases, up to 24% in the last 10 m toward atmospheric pressure.

Hydrogen has the disadvantage of being an explosive gas when mixed with air in proportions that include the presence of 5,3% oxygen. When mixed with more than 4% oxygen, hydrogen spontaneously becomes explosive. To avoid the risk of chemical combination, the volume concentration of oxygen in the hydrox (hydrogen-oxygen) breathing mixture must be less than 4% ($< 0,04$). Between 2,5% and 0,6% ($= 0,025...0,006$), and therefore harmless in combination with hydrogen, this oxygen concentration allows the use of the hydrox (hydrogen-oxygen) mixture for diving at depths between 70 and 700 m.

4. ROMANIAN HYDROGEN DIVING PROGRAM HYDRODIVE

Hyperbaric engineering specialists from the Hyperbaric Laboratory at the Constanța Diving Center belonging to the Romanian Navy, in collaboration with specialists in the thermohydraulics of compressible fluids applied to human underwater penetration from the Department of Hydraulics and Environmental Protection at the Technical University of Civil Engineering Bucharest, will develop

a research program called HYDRODIVE on using hydrogen as a component of hydrogen-based mixtures, such as the binary hydrox (hydrogen-oxygen) and ternary hydreliox (hydrogen-helium-oxygen) mixtures.

The HYDRODIVE program will be designed to include the following main stages:

- The theoretical preparation phase of the program, tracking the physical characteristics of the components of hydrox binary mixtures (hydrogen-oxygen) and ternary hydreliox (hydrogen-helium-oxygen) mixtures and the limits of volume fractions and partial pressures of gaseous components to avoid ignition of the mixture and to reduce the narcotic effects of hydrogen-based mixtures.
- The phase of performing dives with a open (wet) diving bell or a open bell pressurized with HELIOX (helium-oxygen), divers breathing from the umbilical, for a short time, binary hydrox mixture (hydrogen - oxygen), at a depth where both the danger of ignition of the mixture and the occurrence of narcosis at an unbearable level will be avoided.
- Calculation and preparation phase for a diving technology using hydrogen-based mixtures, i.e., binary hydrox (hydrogen-oxygen) and ternary hydreliox (hydrogen-helium-oxygen) mixtures in a hyperbaric system, with the preparation of hyperbaric chambers and related installations.
- Phase of performing a system dive with professional divers from the Hyperbaric Laboratory, using hydrogen-based mixtures at depths of up to 300 m.

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