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Hydrogen Storage in Offshore Salt Caverns for Reducing Ships Carbon Dioxide Footprint

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Abstract. Global shipping activity emits significant amounts of GHG (Greenhouse Gas) emissions, estimated to be around 2-3% of total global GHG emissions. Studies have been made for hydrogen refuelling hubs in the Pacific area, for container ships, that are the worst polluting sources in the oceans. The present paper will show an idea for creating such refuelling hubs using salt cavern for hydrogen storage in Black Sea, and also in other offshore places where the geological formations allow it. The study will allow also the using of hydrogen in military purposes for refuelling the coastal patrol ships or tactical warships like Romanian frigates.

Keywords. CO_2 emissions, hydrogen refuelling, salt caverns, hydrogen storage, global shipping emissions, maritime transport.

1. INTRODUCTION

The carbon dioxide emissions from maritime transport have entered under the position of the European Parliament since 2020, when the European Commission proposed the revision of the European Union's system for monitoring CO_2 emissions, along with other greenhouse gases emissions resulted from maritime transport, and the inclusion of maritime transport in the Emissions Trading Scheme (ETS) from 2022 [1].

Research studies at Jülich Institute for Energy and Climate Research (IEK-3) conclude that salt caverns are a feasible, flexible and efficient solution for hydrogen storage. Salt caverns are artificial cavities which are created in geological salt deposits (halite). To date, salt cavern storage facilities only exist in a very limited number in the United States and the United Kingdom. The research studies estimated a technical potential of hydrogen storage in bedded salt deposits and salt domes in Europe at about 84.8 PWh. Most of these salt caverns are concentrated in northern Europe at offshore and onshore locations. Germany accounts for the largest share, followed by the Netherlands, the United Kingdom, Norway, Denmark and Poland. Other potential sites are in Romania, France, Spain and Portugal [2].

Based on EN 1918-3 [3], caverns shall be designed to ensure long term integrity and containment, under a predefined operating envelope. In the figure 1 below it is shown a salt cavern made by dissolution.

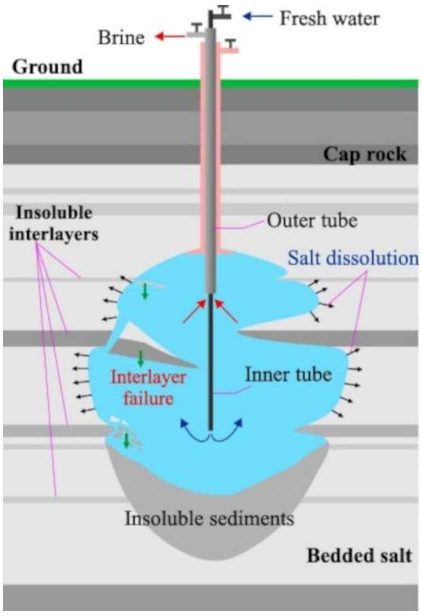

Fig. 1. Cavern geometry made by water dissolution [4]

The principle of salt cavern formation by water dissolution is to dissolve the salt in fresh water and evacuate the salt water through a single outlet, which then serves to inject the gas and withdraw it. These caverns are used to store relatively small amounts of gas compared to those that can be stored in depleted aquifers. The storage capacity for a cavity with a given volume is about of 50,000 ÷ 1,000,000 m^3, and, is proportional to the maximum operating pressure, which depends on the depth and the sedimentary cap rock over the halite. The underground cavities have the advantage of allowing storage at higher pressures (and hence higher temperatures) than surface installations. Although the thermal conductivity of salt is somewhat higher than frozen earths, 0.007113 kW/(m°C) for salt at 0°C vs 0.0021 kW/(m°C) for ice at this temperature, this disadvantage is offset by the higher storage temperature in underground cavities [5].

In Romania, there are some salines where the technology is implemented, like Ocnele Mari (Vâlcea), Ocna Mureş (Alba), Târgu Ocna (Bacău) and Cacica (Suceava). The advantages of using relatively small cavern are: fast delivery, high degree of availability, short filling period, low gas cushion percentage, total gas cushion gas recovery.

For the proposed study, the Black Sea coast contains salt deposits, such as the Vadu structure, located at 10 km from the Midia Navodari refinery. The structure was geologically studied due to the history of at least 40 years since the first seismic sections and from digging the first borehole to find oil and natural gas deposits [6, 7].

The volume of such salt caverns made by dissolution is in the range of 50,000÷500,000 m^3, with an average of 200,000m^3, for Romanian salt beds. The best solution would be the storage of LH_2 (liquid hydrogen), but for relatively low deep caverns in Romania, the solution is not available. The hydrogen will be stored in the range of 7÷25Mpa for the safety of the stability of the caverns. Also, it is considered that in the cavern will remain a trapped volume at a minimum pressure for the stability of the cavern, for example 2 MPa (not to succumb).

2. Hydrogen amount energy stored in salt cavern for decarbonising the maritime transport

As explained above, for low deep cavern, the storage of LH_2 (liquid hydrogen) is difficult, and for short and mid measures regarding the CO_2 footprint, the solutions are about gaseous hydrogen pressurized at up to 25 MPa, stored in offshore salt caverns of medium sizes of ~200,000 m^3. Also, from thermodynamic point of view, the liquefication of hydrogen and ortho to para conversion is a very high energy consumer. The average operation temperature of hydrogen within the salt cavern is assumed to match the temperature of the surrounding salt rock. However, temperature in a sedimentary basin varies with respect to its depth; therefore, a gradient of 25°C/1000 m is assumed up to approximately 5000 m depth. Due to heights, the temperature variation results in a difference of 3°C between the top and bottom of a small caverns, and 7.5°C for a large salt cavern. Therefore, the average temperature of the gas is calculated using equation 1 [8] assuming a surface temperature of 288 K (15 °C).

$$T_{av} = 288 + 0.025 \cdot (D - H/2) \tag{1}$$

where: T_{av} – average gas temperature in K (T °C + 273.15), D = depth in m and H = cavern hight of the cavern in m, which are 120m and 300m for bedded and domal-salt caverns, respectively.

The density of the gas (ρ) in kg/m^3 is calculated using the real gas law, in which compressibility factor Z, pressure P in Pa, molar mass of the species M in kg/mol, universal gas constant R=8,314 J K/mol and temperature T in K are used. The compressibility factor is given by tables, function of pressure and temperature, see the equation 2 [8].

$$\rho_{H_2} = \frac{p \cdot M}{Z \cdot R \cdot T} \tag{2}$$

In figure 2 it is shown a cavern and the graph of pressure vs. depth [7].

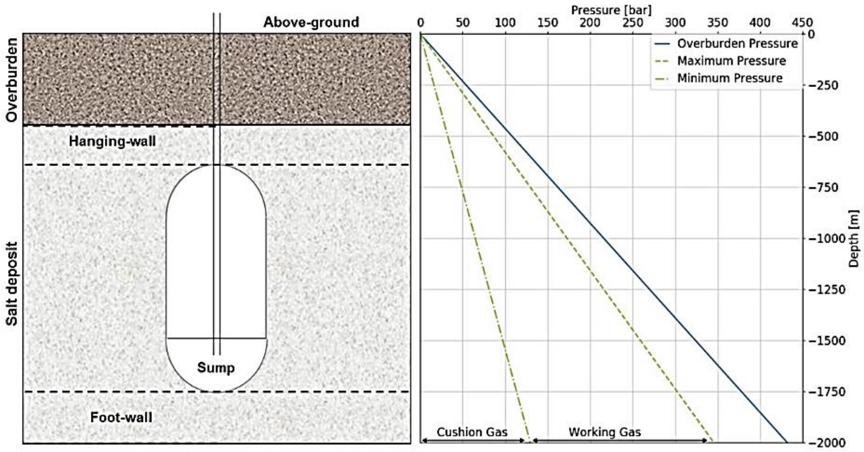

Fig. 2. A simplified representation of an exemplary cavern and estimated pressure limits as a function of depth

The minimum and maximum limits for density are used in the calculation of the mass of working gas, shown in equation 3 [8].

$$m_{wG} = \left(\rho_{H_2,max.} - \rho_{H_2,min.}\right) \cdot V_{cavern} \cdot \theta_{safety} \tag{3}$$

where: m_{wG} = the mass of working gas in kg, V_{cavern} = cavern volume in m^3, and θ_{safety} =70% the safety factor.

The storage capacity of a salt cavern in GWh is determined by using the lower heating value and mass of working gas calculated through specifications of the cavern and location, which is shown in the equation 4 [8].

$$Cavern_{capacity} = m_{wG} \cdot LHV_G \tag{4}$$

where: the lower heating value of the gas LHV is defined in GWh/kg.

For a salt cavern like the Vadu one, see the figure 3 [6, 7], have been made geological prospection, that opened oligoacene deposits, in the almost all area of the Romanian offshore, up to 2,500m in the Hristia Basin. The Oligocene deposits reach a maximum thickness along the axis of the Histria Depression, increasing from 1,100 m in the Portita area to 4,900 m in the Ovidiu area. The aquatic areas of Central and Southern Dobrogea are characterized by lower thicknesses of Oligocene deposits [6, 7].

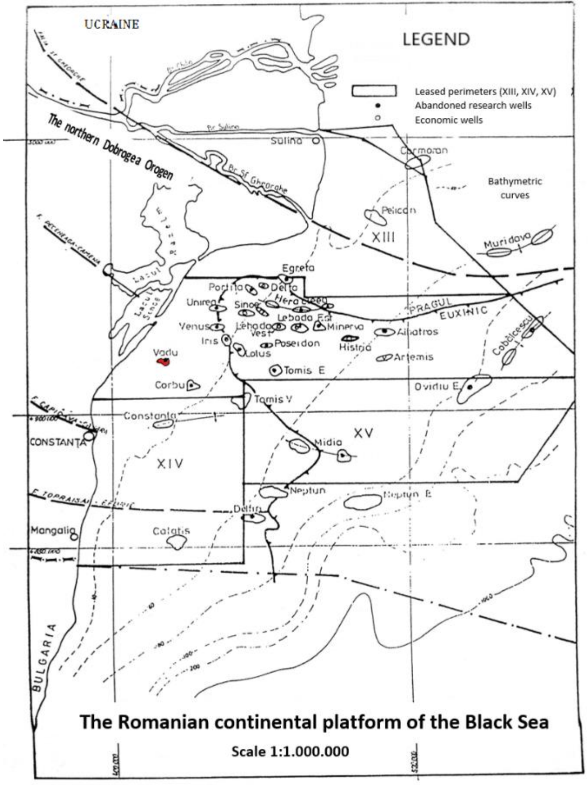

Fig. 3. Potential gas structures identified in the Romanian part of Black Sea continental platform

The basin extension limit is very close to the current shoreline and the Eocene basin extension limit. It is a period strongly affected by the relative level oscillations of the sea, the Miocene, represented by the Sarmatian-Bardenian, being discordant over the Oligocene and the Pliocene-Quaternary being placed in turn over the Miocene sequence. It is presented as a well-defined sequence of two strong discrepancies, with relatively small thicknesses, up to 200m in the inner area of the continental shelf, but which thickens significantly to the sea. In the thickening areas from the sea, on quite large areas, the Miocene is affected, with numerous systems with growth faults, oriented North-East/South-West, perpendicular to the traditional structural directions of the basin. There are also identified the presence of Bardenian and Sarmatian, which were most often dated together, without any separation between them. Vadu formation, attributed to a lagoon environment, and dating since the Jurassic-Cretaceous era, following the Casimcea formation, has been found to contain calcareous deposits. The deposits and the very thick layers seem to indicate a sedimentary environment with active subsidence, most probably algae [6, 7].

Figure 4 [9] shows the necessary infrastructure for LH_2 (liquid hydrogen) supply adopted by The International Maritime Organization (IMO), with points for refuelling along the transpacific corridor, between China and United States.

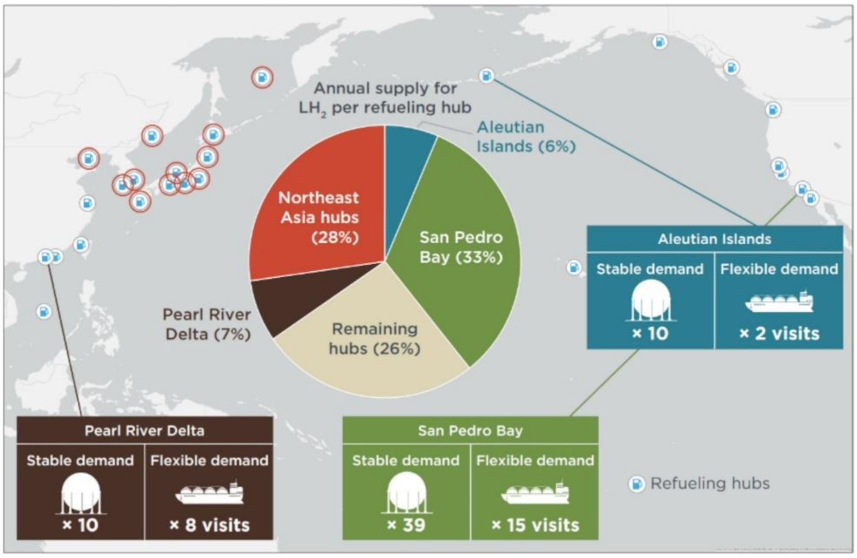

Fig. 4. Hydrogen demand and refuelling infrastructure required for transpacific container ships

From the lithologic column from figure 5 [6, 7] below, can be seen the salt deposits and the depth. The most important zones for the study are between 705 ÷ 905 m and 1,542 ÷ 1,728 m with differences of about 200 m. The first layer of salt is covered with anhydrite and gypsum, a very soft rock, and the supposed storage pressure is that it is not very high one. The second area of interest is covered with limestone and dolomitic schists, that is supposed to store a higher hydrogen pressure.

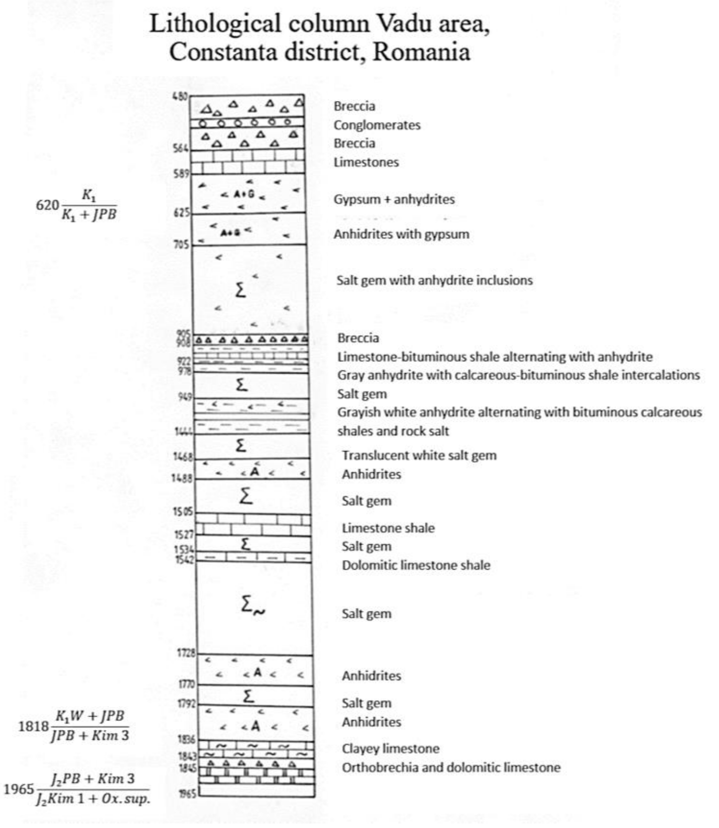

Fig. 5. Lithological column Vadu area, Constanța county, Romania

From figure 2 above, it can be deducted that the possible pressures that can be stored are between 10 MPa and 25 MPa, even up to 30 MPa at 1700m.

The thickness of the salt layer thickness of the salt is around 180 m. If we suppose a 200,000 m^3 salt cavern, with a high of 100 m, results a diameter of 50m. It will remain about 40 m from the upper to bottom sides. The total depth will be about 1682 m. The temperature, according to equation (1), will be T_{av} = 55.65°C. From the linear interpolations from the excel table [10], the Z factor at 2 MPa for hydrogen at 55.65°C, will be Z = 1.0111. The value was taken for minimum hydrogen pressure for cavern functioning, of 2 MPa. The Z factor at 25 MPa for hydrogen at 55.65°C, will be Z = 1.09515. The densities of hydrogen will be in conformity with equation (2): $\rho_{(H2,min.)} = 0.145$ kg/m^3, and $\rho_{(H2,max.)} = 1.67$ kg/m^3.

The mass of working gas from (3) will be:

$$m_{wG} = 213.500 \text{ kg} = 213.5 \text{ T} \tag{5}$$

From equation (4), the energy stored, knowing the LHV = 119.96 MJ/kg, will be about:

$$Cavern_{capacity} = 25610.4 \text{ GJ} = 7.114 \text{ GWh} \tag{6}$$

3. CO₂ emissions from fuel combustion

The IEA (International Energy Agency) uses the simplest Tier 1 methodology to estimate CO_2 emissions from fuel combustion based on the 2006 GLs. The computation follows the concept of conservation of carbon, from the fuel combusted into CO_2 [11, 12]. From 2006 IPCC Guidelines for National Greenhouse Gas Inventories, chapter 3, Mobile Combustion, can be taken the CO_2 emissions for all water-borne transport from recreational craft to large ocean-going cargo ships that are driven primarily by large, slow and medium speed diesel engines and occasionally by steam or gas turbines [13, 14].

Water-borne navigation causes emissions of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), as well as carbon monoxide (CO), non-methane volatile organic compounds (NMVOCs), sulphur dioxide (SO_2), particulate matter (PM) and oxides of nitrogen (NO_x), that contribute to the greenhouse effect. The fuel consumption data and emission factors in the Tier 1 method are fuel-type-specific and should be applied to the corresponding activity data (e.g. gas/diesel oil used for navigation). The calculation is based on the amount of fuel combusted and on emission factors for CO_2, CH_4, and N_2O [15]. The calculation is shown in (7) [15] below:

$$Emissions = \sum Fuel_{a,b} \cdot EF_{a,b} \tag{7}$$

where:
Fuel = fuel consumed (TJ)
EF = emission factor (kg/TJ)
a = fuel type (diesel, gasoline, LPG, bunker, etc.)
b = water-borne navigation type (i.e., ship or boat, and possibly engine type. Only at Tier 2 is the fuel used differentiated by type of vessel, so b can be ignored at Tier 1)

Default carbon dioxide emission factors (table 1) are based on the fuel type and carbon content and take account of the fraction of carbon oxidised (100 percent) [16].

Table 1. CO_2 emissions factor (kg/TJ)

[1] **Fuel**	[2] **EF**
[3] Gasoline	[4] 69,300
[5] Kerosene	[6] 71,900
[7] Gas/Diesel Oil	[8] 74,100
[9] Residual Fuel Oil	[10] 77,400
[11] Liquefied Petroleum Gases	[12] 63,100
[13] Natural Gas	[14] 56,100
[15] Other Petroleum Products	[16] 73,300

There are given the average consumptions (tonne/day) for commercial ships. The 2006 IPCC Guidelines do not provide a distinct method for calculating military water-borne emissions. Emissions from military water-borne fuel use can be estimated using the equation 6 and the same calculation approach is recommended for non-military shipping. Due to confidentiality issues, many inventory compilers may have difficulty obtaining data for the quantity of military fuel use. Military activity is defined here as those activities using fuel purchased by or supplied to military authorities in the country. It is good practice to apply the rules defining civilian domestic and international operations in water-borne navigation to military operations when the data necessary to apply those rules are comparable and available.

For the frigate UK Broadsword class (Type 21 - 5300 tons), “Regele Ferdinand”, with 18 years in the service of the Romanian Naval Forces, see the figure 6 below [17, 18], the power is ensured by 2 gas turbines Rolls-Royce Marine Olympus TMB3 with a power output of max. 21 MW. and 2 gas engines Pratt&Whitney ST40M with a power of max. 4.04 MW, in a CoGoG configuration [19, 20].

The specific fuel consumption of an Olympus TMB3 engine is about 0.478 lb/bhph [21] or 0.291 kg/kWh and of ST40M engine is about 0.379 lb/bhph [22 - 24] or 0.231 kg/kWh.

The range of the frigate is about 4,500 nautical miles (8,300 km), with a cruise speed of 21 mph or 33 km/h. That means a total hours/cruise of 251.5.

The quantity of fuel consumed for a cruise regime with just 2 engines, without Olympus engines, that are used just in special missions, the fuel consumed for a 6,640km cruise (0.80% from the total range = approx. 200 hours), and taking about 0.87% the power of the engine, is about:

$$Fuel\ cons = 324767.5\ kg \sim 325\ tonnes \tag{8}$$

The energy of the fuel depending of the fuel used, and in this case is kerosene [22], is about:

$$LHV_{ker} = 12.22\ kW/kg\ or\ 46.2\ MJ/kg \tag{9}$$

Fig. 6. “Regele Ferdinand” frigate

The CO_2 emissions according to (6), with the transformations from MJ in TJ will be:

$$CO_{emiss} = Fuel_{cons} \cdot LHV_{ker} \cdot EF_{ker} \sim 1080\ tonnes \quad (10)$$

If the fuel of the frigate will be mixed with hydrogen, in the proportions of 5…40% energy, the amount of the emissions will be expected to decrease with the energy of hydrogen injected. Can be considered that the amount of the hydrogen injected will contribute with 13.6% to the CO_2 emissions according to a 86.4% efficiency of hydrogen production with CCS technology (carbon cavern storage) [8]. It was demonstrated that a percent of more than 40% of hydrogen injected in a conventional fuel it is not efficient due to other reaction involved, and because the apparition of water in the burned gases that can affect negatively the gas flow over the blades and the corrosion in the flow ducts.

Table 2. CO_2 emissions factor (kg/TJ)

[17] **Hydrogen percent** [18] **(%)**	[19] **Hydrogen energy** [20] **(MJ)**	[21] **CO_2 emissions** [22] **(tons)**
[23] 5	[24] 2.31	[25] 1,026
[26] 10	[27] 4.62	[28] 972
[29] 15	[30] 6.93	[31] 918
[32] 20	[33] 9.24	[34] 864
[35] 25	[36] 11.55	[37] 810
[38] 30	[39] 13.86	[40] 756
[41] 35	[42] 16.17	[43] 702
[44] 40	[45] 18.48	[46] 648

For a percent of 40% hydrogen direct injected in the fuel, the amount of the CO_2 saved from the normal cruise is about: CO_2 emissions = 432 tons / 200 hours = 2.16 tons/hours. The hydrogen consumed from the cavern is about:

$$H_{cons} = 7 \cdot 10^{-5}\%/cruise\ or\ 3.5 \cdot 10^{-8}\%/hour \quad (11)$$

Extrapolating to other same ships, the number of hours covered by the amount of hydrogen stored in the cavern is about:

$$Hours_{available} = 285.7\ milion\ hours \tag{12}$$

The CO_2 emission saved are:

$$CO_{2\_emiss\_saved} = 0.5714\ Gtonnes \tag{13}$$

Considering a total lifetime of 140,000 hours for this type of frigate [24], and considering that Romania has 2 frigates of this type, it means about 604,800 tons CO_2 that can be saved. The consumptions can be extrapolated to other ships, but the emissions can be considered the same for a first approximation, for a same size of 5,000 tons, or more. From a simply calculation, it results an amount of ~945 same ships that can function using a single salt cavern of 200,000 m^3, at 25Mpa hydrogen stored.

4. Conclusions

The paper presented aims to show a valuable and feasible solution for decarbonising the atmosphere, in accordance with the current requirements for carbonization and reduction of the CO_2 footprints for naval transport and/or other types of water-borne navigation. We applied the study on the possibility of reducing the emissions of a military frigate, used by Romanian Navy, with more than 50% lifetime remained for military missions (around 70,000 hours). Hydrogen is recognized as the future fuel and the most promising alternative of fossil fuels or for using in combinations with them. Have been taken a mixing of kerosene with hydrogen in a roughly manner considering just the amount of the energy used. Has been not taken into consideration the real LHV value generated by hydrogen and kerosene mixture. The quantity of the specific fuel consumption has been considered constant for fuel energy/kWh generation point of view.

The offshore Vadu well was considered as studies have been done to store natural gas, LPG and more recently hydrogen. The lithography of the Romanian offshore is well defined and also methane and crude oil exploitation platforms are in use. The Offshore Safety Law established also a new regulatory authority – the Competent Regulatory Authority for Black Sea Offshore Petroleum Operations (CAROPO) overseeing the performance of offshore operations and exploitation of offshore installation from a safety perspective [25]. Also, the Ministry of Energy already started working on the national hydrogen strategy and planned to draft legislation for the use of this fuel by 2023.

The presented work will be a start-up for researching more opportunities in decarbonising of the atmosphere and for reducing the CO_2 footprints for shipping and not only.

Acknowledgement

The National Research and Development Institute for Gas Turbines COMOTI start the developing of storage projects in depleted gas deposits or in depleted or conserved coal or salt mines due to collaboration with the University of Petroșani - Faculty of Mines and the University of Bucharest - Faculty of Geology and Geophysics. The collaborations are aimed at developing topics with fundamental and applicative impact, in integrative, multidisciplinary and interdisciplinary approaches, in accordance with the priority issues at regional, national and international level, which will ensure the increase of visibility and competitiveness, regarding the new era of hydrogen storage, solving Romania's energy requirements, accentuated by the global changes regarding decarbonization through the use of green energy,

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