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ARTICLE

AN ANALYSIS OF HYDROGEN GAS SATURATION IN THE SEDIMENTARY SEQUENCES OF VOLYN-PODILLYA (UKRAINE)

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Abstract: With the aim of Ukrainian industry using hydrogen energy, the paper considers the general patterns of hydrogen distribution in the sedimentary sequences of Volyn-Podillya. The general features of the distribution of water-dissolved and sorbed gases in rocks within productive and water-saturated complexes are analyzed. The genetic relationships between individual components of natural gases have been established, which allows us to identify depth intervals where hydrogen predominates in the well section. The latter, when used for regional forecasting, makes it possible to establish zones, and thus directions for the search for hydrogen accumulations in the sedimentary cover in Volyn-Podillya.

Keywords: hydrogen, gases, forecast, core, fluid, well

1. Introduction

The interest in hydrogen energy is primarily driven by the fact that hydrogen is the most abundant element on the Earth's surface and in space, it holds the highest energy content, and its combustion produces only water and not carbon dioxide emissions. Industries are therefore investing heavily in hydrogen as a key component of the fight against climate change, as natural hydrogen, or "white hydrogen", is considered to be one of the cleanest fuels.

In the Lorraine region, near the French-German border, a group of scientists has recently made a revolutionary discovery in the earth's interior. Jacques Pironon, a professor at the University of Lorraine, believes that they have discovered one of the world's largest deposits of natural hydrogen. They were amazed with their find: *large bubbles of hydrogen gas in the water column* indicating a potentially huge natural hydrogen deposit [1].

Currently, Canada is the leader in the pure hydrogen production. At the same time, Japan is actively implementing and developing hydrogen technologies, and has even created a hydrogen "ministry" to completely switch from nuclear to hydrogen energy by 2050 [2].

Ukraine also has plans to use hydrogen. Currently, the lifetime of some Ukrainian nuclear power plants has been extended for the second time, and it is physically dangerous to do so for a third. The country is facing the issue of how to replace the generating capacities lost with these power plants being decommissioned, as NPPs account for 35% of Ukraine's energy balance [3].

2. Gas-geochemical properties of sedimentary sequences

In order for the industry to switch to hydrogen energy, it is necessary to study the patterns of hydrogen distribution in the sedimentary stratum. To this end, the paper analyzes the patterns of distribution of water-dissolved and rock-sorbed gases within productive and water-saturated bodies. The genetic relationships between individual components of natural gases have been established, which make it possible to distinguish depth ranges in the well section with a predominance of a certain type of gases, namely syn- or epigenetic hydrocarbon components, nitrogen, hydrogen and unsaturated hydrocarbons.

The specifics of hydrogeochemical criteria related to oil and gas content are based on the study of the patterns of distribution and migration of water-dissolved gases in sedimentary strata.

It should be noted that against the general regional background of nitrogen gases, there are areas with increased concentrations of hydrocarbon components and gas saturation of formation waters, which are confined to the contour zones of oil and gas deposits.

With the distance from the contour, the gas saturation of water and the hydrocarbon content in gases decrease, which is confirmed by actual data from many oil and gas regions. For example, in the Volga-Ural oil and gas region, according to L. Zorkin [4], clearing off the oil and gas contour, the gas saturation of water and the concentration of hydrocarbons in water-dissolved gases decrease while the nitrogen content increases (Fig. 1).

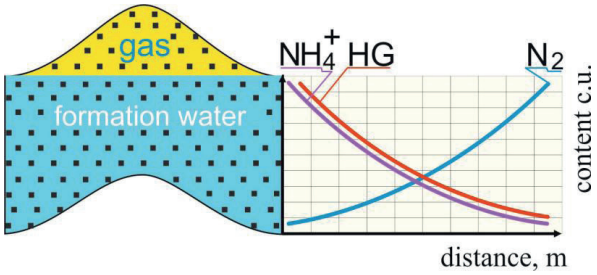

Fig. 1. Diagram of changes in hydrochemical parameters of formation water clear off the hydrocarbon reservoir contour
HG – hydrocarbon gases C_1-C_6 [%]; N_2 – nitrogen [%];
NH_4^+ – ammonium [mg/l];
content c.u. – conventional units

A similar pattern was detected by M. Gatalsky [5] in the Pripyat Basin, and by L. Shvay [6] in different stratigraphic horizons of the Dnipro-Donetsk Basin. The above shows that the main component of water-dissolved gases in different regions is nitrogen, and the presence of hydrocarbon gases is caused by the dispersion of hydrocarbons from deposits due to their diffusion in reservoir fluids.

If nitrogen is the main component of water-dissolved gases away from the hydrocarbon accumulation, the question arises regarding the reason why its content in formation water decreases as it approaches the reservoir contour. This is probably due to the transition of free nitrogen to the bound state in the form of ammonium (NH_4^+), the content of which is much higher in productive areas compared to water-saturated sections.

In the formation waters of prospective sites, ammonium and nitrogen demonstrate an inverse distribution, i.e. clear off the near-contour zone the ammonium concentration decreases while the nitrogen concentration increases (Fig. 1). For example, in the Crimean oil and gas region, the ratio of ammonium

to nitrogen (NH_4^+/N_2) in the near-contour waters of deposits is greater than 1, while it always decreases off the deposits [7].

The relationship between the forms of nitrogen NH_4^+ and N_2 is given in the work of J. Hunt [8], where it is expressed by the following equation (1):

$$N_2 + 3H_2 \leftrightarrow 2\,NH_3 + \Delta T \quad (1)$$

This process is in equilibrium and occurs in the gas phase with heat generation (ΔT); with a decrease in the temperature of the medium, the equilibrium shifts towards the evolution of ammonia, but the reaction rate slows down. Clay minerals containing aluminium oxide (Al_2O_3) can serve as a catalyst in formation conditions. The dissolution of ammonia in formation water and its removal as a reaction product facilitate the reaction.

Hydrogen is an important participant in the hydrochemical processes under consideration. There is no consensus on the sources of its origin and role in oil and gas origination. However, hydrogen is not only found in volcanic and metamorphic rocks, but also in sedimentary cover deposits; the latter, according to many researchers, is due to the catabolism of organic matter (OM).

3. Analysis of hydrogen distribution in geological sequences

Hydrogen is hardly ever found in the gases of oil and gas fields although there are a few exceptions. For example, one well is known in the Chechen Republic (Grozny district) and one in Uzbekistan, where the hydrogen content is 8.3 and 12.7%, respectively.

Hydrogen is also present in associated gases in a number of wells in Pennsylvania and Pittsburgh (USA), where its content reaches 7–35%. However, it should be noted that hydrogen is much more commonly present in a water-dissolved form in the formation waters of sedimentary basins [7].

V. Havrysh [9] believes that prolonged migration of hydrogen through the pore space leads to the origination of its own hydrodynamic systems, in which its oxidation processes occur in parallel with water exceedance, which causes leaching of rocks and brittle deformation development. This suggests that if the hydrogen content in the section is high, the latter will be water- or gas-saturated. For instance, in the Lokachynska-3 well, where the Middle Devonian rocks demonstrate high hydrogen content, a gas-water mixture was obtained during testing (Fig. 2).

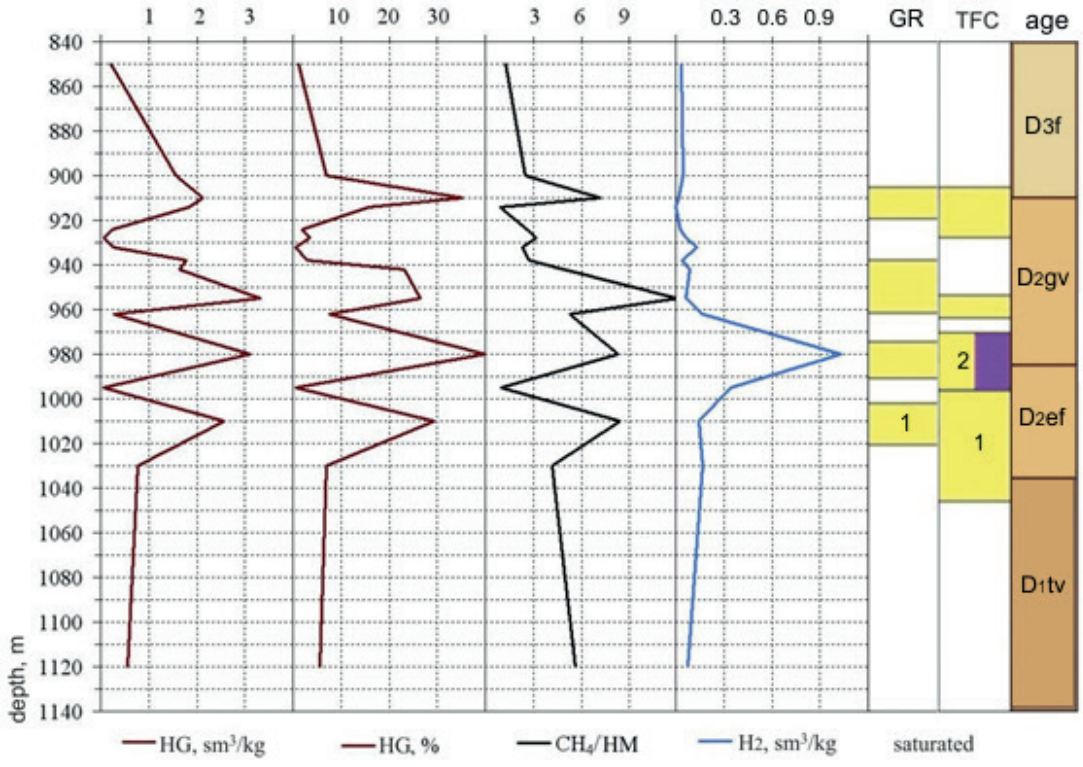

Fig. 2. Distribution of gas metering parameters in Lokachynska-3 well. HG – hydrocarbon gases C_1-C_6; H_2 – hydrogen; CH_4/HM – methane to homologues; GR – geochemical research, TFC – testing of formations in the column. Saturation: 1 – gas-saturated, 2 – water and gas saturated D_3fr – Frasnian; D_2gv – Givetian; D_2ef – Eifelian; D_1tv – Tiverska Series

It is also worth noting that unsaturated hydrocarbons (UH), such as ethylene (C_2H_4) and propylene (C_3H_6), as well as hydrogen (H_2) are also present in the thickness of sedimentary rocks, the distributions of which are similar in the studied sections (Fig. 3).

Timofeev G. and Umnova N. [10] point to a low concentration of hydrocarbon gases in intervals with high hydrogen and unsaturated hydrocarbons and express the opinion that such distribution of gases is specific to the syngenet ic processes of the lithification of organic matter during gas generation.

They are also supported by F.A. Alekseev and others [11], who believe that the confinement of increased concentrations of unsaturated hydrocarbons to sandy clay bodies and the correlation of their sectional distribution in terms of hydrogen are indicators of the transformation of organic matter (OM).

In the component composition of hydrocarbon gas deposits, unsaturated hydrocarbons (UH) are virtually absent, so the ratio of their content to the concentration of hydrocarbon gases (UH/H) allows us to assume the predominance of syn- or epigenetic hydrocarbon fluids in the studied section.

The decreased content of hydrogen and unsaturated hydrocarbons is observed only at depth intervals where the gas saturation of rocks increases, which is associated with the flow of methane gas into their section, as evidenced by a significant increase in the CH_4/C_2-C_6 ratio (Fig. 3). It can be assumed that the decrease in the amount of hydrogen and unsaturated methane homologues is caused only by geochemical processes in which they are directly involved.

These processes are likely to be the interaction of hydrogen and unsaturated methane homologues to form ethane and propane and the interaction of hydrogen and nitrogen to form ammonium. They occur only in the gas phase and do not take place in the aqueous medium (Fig. 4a).

In the gas phase, molecules are in constant chaotic motion, colliding with each other. These collisions release energy, which causes molecules to interact with each other (Fig. 4b).

The movement of molecules in a liquid differs from that in gases: water molecules form an ordered structure due to hydrogen bonds (Fig. 4c), which makes it impossible for gas molecules to move chaotically, which excludes the interaction between hydrogen and unsaturated hydrocarbons, as well as between hydrogen and nitrogen.

Therefore, the flow of free methane gas into reservoir deposits results in gaseous fluid accumulation, which in turn creates the prerequisites for the interaction between hydrogen and unsaturated hydrocarbons or nitrogen. The absence of hydrogen in the context of productive oil and gas bearing structures is confirmed by the materials presented in works of G. Lebed' and others [12].

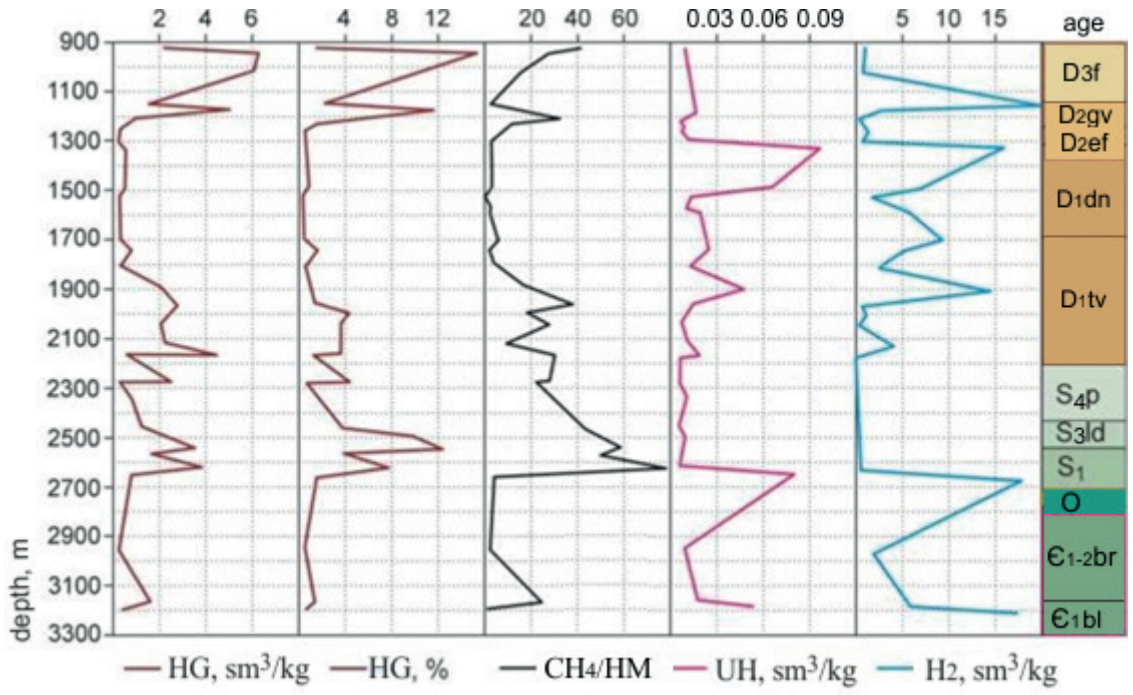

Fig. 3. Distribution of gas parameters in the Volyn-Podillya well based on the results of geochemical studies.
HG – hydrocarbon gases C_1-C_6; CH_4/HM – methane to homologues ratio; UH – unsaturated hydrocarbons; H_2 – hydrogen
D_3fr – Frasnian; D_2gv – Givetian; D_2ef – Eifelian; D_1dn – Dnisterska Series; D_1tv – Tiverska Series ; S_4p – Pridoli; S_3ld – Ludlow;
$Є_{1\text{-}2}$br – Berezskivska Series; $Є_1$bl – Baltic Series

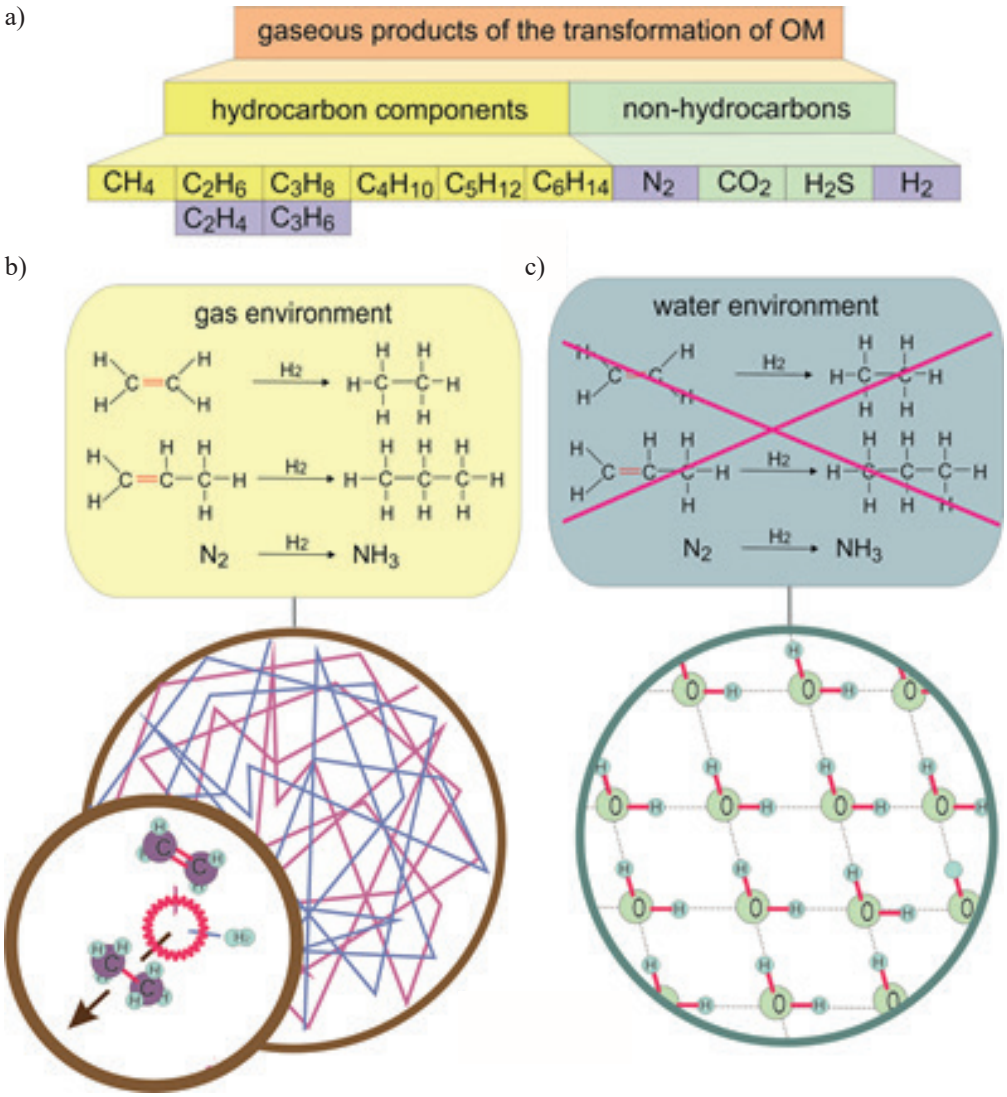

Fig. 4. Interaction of gaseous products of OM transformation depending on the nature of fluid saturation of the section (a); chaotic movement of molecules in the gas phase, interaction between them (b); hydrogen bonds between water molecules (c)

Based on the above materials, conclusions can be drawn about the distribution of gases, including hydrogen, in the sedimentary complex:

- Nitrogen is the main component of water-dissolved gases in formation waters of the sedimentary complex; towards the gas reservoir, the concentration of nitrogen decreases, but the concentration of ammonium increases.
- There is a similarity in the distribution of hydrogen and unsaturated hydrocarbons in well sections, the maximum content of the latter is confined to intervals with background hydrocarbon gases; in gas-saturated formations, the concentration of hydrogen and unsaturated methane homologues decreases significantly.
- The processes of the interaction of gaseous substances only occur in the gas phase and do not take place in the aqueous medium. Methane gas entering the sediments triggers the origination of a gas phase, i.e. an environment in which hydrogen interacts with both nitrogen and unsaturated hydrocarbons. The result of these processes is that the nitrogen content in formation water in the gas deposit zone is significantly reduced, and unsaturated hydrocarbons and hydrogen are absent in the component composition of the hydrocarbon accumulation.
- There is a similarity in the distribution of hydrogen and unsaturated hydrocarbons in well sections, the maximum content of the latter is confined to intervals with background hydrocarbon gases; in gas-saturated formations the concentration of hydrogen and unsaturated methane homologues is significantly reduced.

– The processes of interaction of gaseous substances occur only in the gas phase and do not take place in the aqueous medium. Methane gas entering the reservoirs leads to the formation of a gas phase in the reservoirs, an environment in which hydrogen interacts with both nitrogen and unsaturated hydrocarbons. As a result of these processes, the nitrogen content of produced water in the gas reservoir zone is significantly reduced, and unsaturated hydrocarbons and hydrogen are absent from the hydrocarbon accumulation.

4. Results of hydrogen research in Volyn-Podillya

There is no consensus on the sources of hydrogen. However, hydrogen is not only found in volcanic and metamorphic rocks, but also in sedimentary cover deposits; the latter, according to many researchers, is due to the catabolism of organic matter.

At present, there is only one known natural deposit of geological hydrogen (almost pure – 98% content) in the world – Burakebougou in Mali, which is unique in its nature and essence. The issue of the genesis of hydrogen in this field has not been fully clarified [13].

Taking into account the above patterns, we analyzed gas logging in the Lutsk-1 well, which was drilled to study the geological section of Palaeozoic-Proterozoic sediments and the prospects for their oil and gas content.

4.1. Geochemical studies of the Lutsk-1 well

The Lutsk-1 parametric well was drilled within the area of the same name on the northeastern side of the Lviv Palaeozoic trough to study the stratigraphy, oil and gas content and filtration capacity characteristics of Palaeozoic and Proterozoic sediments (Fig. 5a). During drilling, the Lutsk-1 well reached a depth of 2,442 m, having penetrated the crystalline basement rocks from the mark of 2,404 m (Fig. 5b).

According to the results of the core gas survey, the highest hydrocarbon saturation of rocks was determined in the Archean-Proterozoic sediments (int. 2,440.2–2,441.8 m) and at the boundary of the Middle and Lower Devonian (int. 309–318 m) (Fig. 6).

With regard to study findings, it should be noted that the hydrogen content in the studied gases, starting from the Cambrian sediments and down the section, significantly increases to 40% (Fig. 6), which exceeds the hydrocarbon concentration by 5–10 times.

It is observed that intervals with high hydrogen content are characterized as water-saturated and water-gas-saturated according to the data of reservoir testing (RST) and the results of geochemical studies (GC).

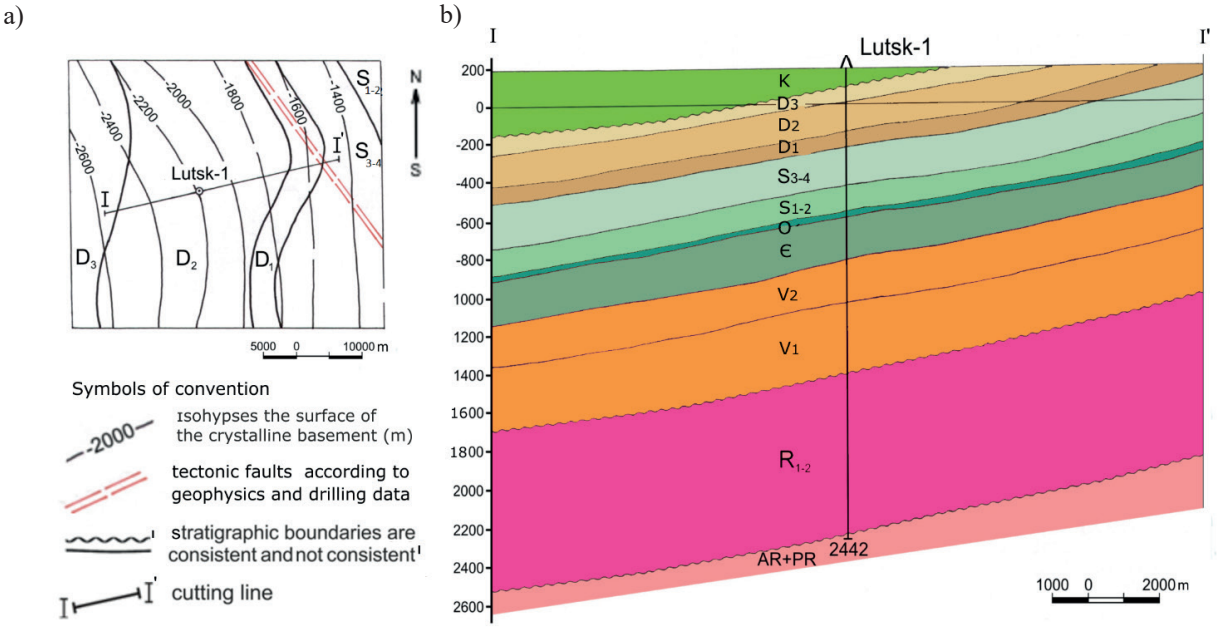

Fig. 5. Structural map of the crystalline basement roof (a) and geologic section along the I-I line (b) within the Lutsk area
D_3fr – Frasnian; D_2 (gv – Givetian, ef – Eifelian); D_1tv – Tiverska Series; S_{3-4} (p – Pridoli, ld – Ludlow);
Є ($Є_{1-2}$br – Berezskivska Series, $Є_1$bl – Baltic Series); V_2 (kn – Kaniliv Series, mp – Mogiliv-Podilska Series);
V_1 (brs – Berestovetska Suite, gr – Gorbaschivska Suite); R_{1-2} (pl – Polytska Suite, rm – Romeikivska Suite); AR-PR – metamorphic rocks

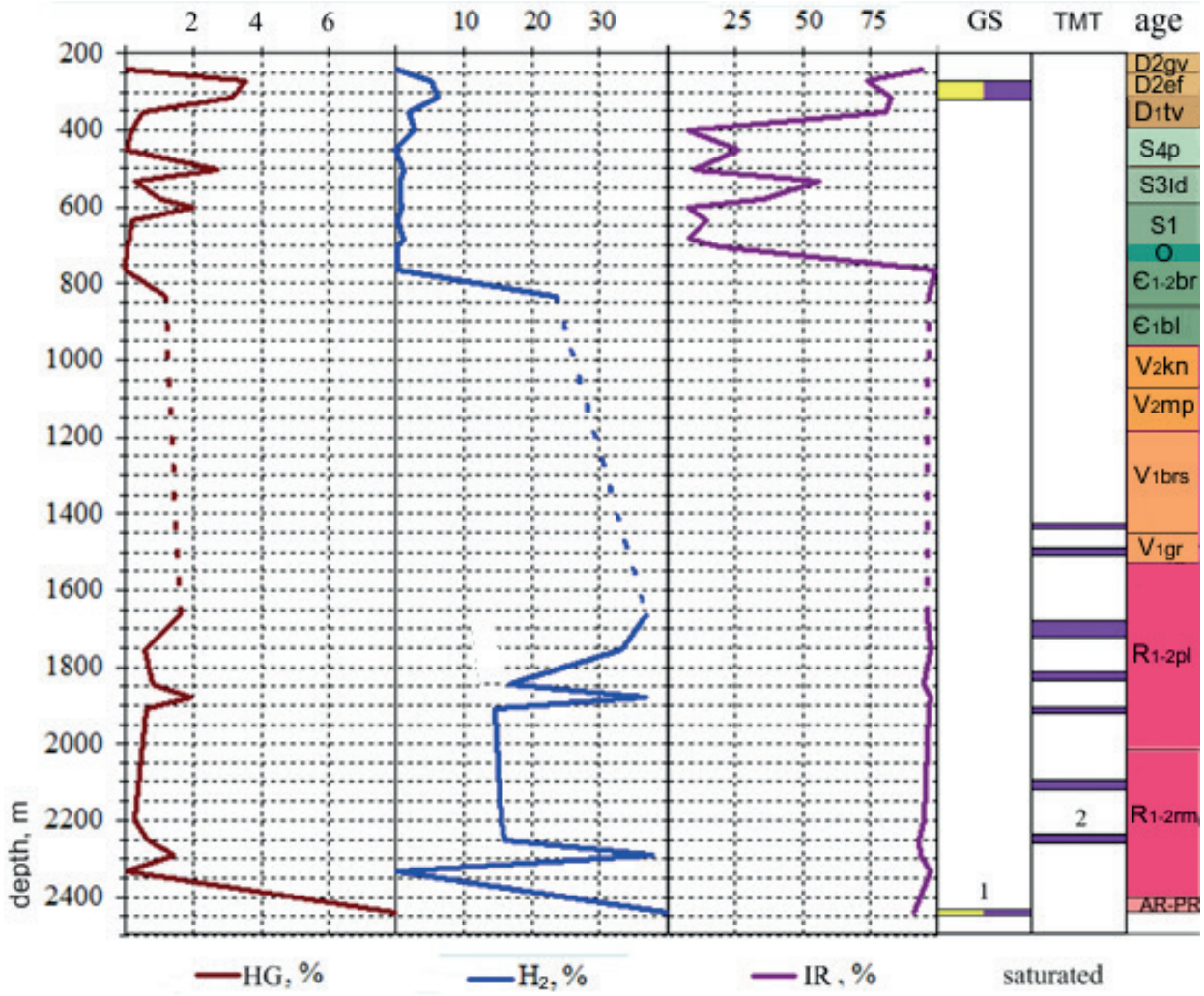

Fig. 6. Saturation pattern of the Lutsk-1 well section based on the results of geochemical studies (GS) and test materials (TMT). HG – hydrocarbon gases C_1-C_6, H_2 – hydrogen, IR – insoluble rock residue in HCl. Saturation: 1 – water and gas saturated, 2 – water-saturated D_2gv – Givetian; D_2ef – Eifelian; D_1tv – Tiverska Series; S_4p – Pridoli; S_3ld – Ludlow; $Є_{1-2}$br – Berezskivska Series; $Є_1$bl – Baltic Series; V_2kn – Kaniliv Series; V_2mp – Mogiliv-Podilska Series; V_1brs – Berestovetska Suite; V_1gr – Gorbaschivska Suite; R_{1-2}pl – Polytska Suite; R_{1-2}rm – Romeikivska Suite; AR-PR – metamorphic rocks

5. Conclusions

Based on the above materials, it is possible to draw conclusions about the need to study the distribution of gases, including hydrogen, in the sedimentary section of the studied areas.

Taking into account the above-mentioned regularities, we analyzed gas logging in the Lutsk-1 well, which was drilled to study the geological section of Palaeozoic--Proterozoic sediments and the prospects for their oil and gas content.

According to the results of geophysical surveys, all the selected layers in the well section are watered, and the best reservoir properties are in the Cambrian and Riphean sandstones.

The core gasometric studies indicate that the highest hydrocarbon saturation of rocks is found in the Archean-Proterozoic sample in the interval of 2,440–2,442 m.

However, it should be noted that in the context of Proterozoic and Cambrian rocks, the hydrogen content in the component composition of gases absorbed by rocks increases significantly, which significantly exceeds the hydrocarbon concentration (Fig. 6). Of note is that the intervals with high hydrogen content, according to the data of reservoir testing (RST) and the results of geochemical studies (GC), are estimated as water-saturated and water-gas-saturated. This correlates with the data of the University of Lorraine, which found hydrogen gas bubbles in a water-saturated section [1].

Hydrogen was detected in many wells in the Volyn-Podillya region of Ukraine based on the results of core sampling. Generalization of the results of hydrogen distribution in these wells will allow us to further identify zones characterized by high hydrogen content as well as to establish geological and structural elements to which the increased hydrogen content in the rock section is confined. The obtained materials will allow directions for the search for hydrogen in the sedimentary cover within the territory of Volyn-Podillya to be established.

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