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Geological Hydrogen: An Analysis of the Phenomena Occurring in Its Reservoirs

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The transition of the global energy matrix, driven by the climate emergency and decarbonization targets such as those set forth in the Paris Agreement, has highlighted hydrogen as a promising and versatile energy vector for achieving carbon neutrality. Despite its high calorific value and clean combustion, which yields only water, the production of green hydrogen (via water electrolysis powered by renewable energy) still faces significant economic barriers, such as the high cost of electrolyzers and the demand for extensive power generation infrastructure. In this context, geological, or natural, hydrogen emerges as an attractive and disruptive alternative, with renewable potential and the possibility of extraction through methods analogous to those used for natural gas, enabling the use of established technology, infrastructure, and expertise from the oil and gas industry. This article presents a critical review of the main processes governing the formation, migration, and accumulation of hydrogen in subsurface reservoirs, focusing on assessing the feasibility of its large-scale exploitation. Initially, the role of natural hydrogen is discussed in the face of global decarbonization challenges and the urgent need for sustainable, low-cost energy solutions. Subsequently, the unique dynamics of hydrogen in geological settings are examined, considering its low density, high mobility, and reactivity, which differentiate it from conventional hydrocarbons. Factors such as pressure and temperature—which control its solubility and reaction rates—salinity, which influences microbial activity, and rock mineralogy, which may act as a catalyst or reactant, are detailed. Fundamental aspects such as gas migration in porous media, including potential diffusive losses through cap rocks due to its small molecular size, and the associated physicochemical processes are addressed. Interactions with subsurface microbiota are also a central point, as microorganisms consume H₂ through pathways such as methanogenesis, sulfate reduction, and acetogenesis. This biological activity not only directly affects the volume of recoverable gas but can also generate byproducts such as H₂S and cause bioclogging of reservoir pores due to biofilm accumulation, compromising permeability. Finally, the study emphasizes the importance of an integrated approach encompassing physical, geochemical, and microbiological aspects to enable the utilization of geological hydrogen, as well as the ongoing need for research to develop exploratory models, sector-specific regulations, and more efficient extraction and monitoring technologies.

Keywords: Natural hydrogen; Underground hydrogen storage; Renewable energy; Bio-geo-reactive transport

1. Introduction

The global industry is currently undergoing a significant transition in its energy matrices, driven by international commitments to reduce greenhouse gas emissions, such as the Paris Agreement and the "Net Zero 2050" target [1]. In this context, several companies have been progressively seeking to replace fossil fuels with low-carbon energy sources.

Among the prominent alternatives, hydrogen stands out as a promising energy vector, exhibiting a calorific value three times higher than that of conventional fuels such as gasoline, diesel, and coal [2]. Moreover, its combustion results exclusively in the formation of water vapor, making it an environmentally clean solution.

However, the methods currently employed for hydrogen production—such as green hydrogen, generated through water electrolysis powered by renewable energy sources—still face technical and economic challenges for large-scale implementation, primarily due to high production costs [3].

ISSN: 2357-7592





In contrast, in recent decades, natural hydrogen emissions originating from the Earth's subsurface have been identified in several regions worldwide [4]. This discovery has attracted the interest of both the scientific community and industry, as so-called geological hydrogen exhibits extraction characteristics similar to those of natural gas, with the added advantage of being potentially renewable, given its continuous generation through natural processes [5].

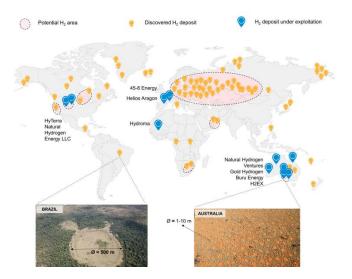
Accordingly, this study, through a literature review, seeks to identify the main phenomena influencing the behavior of hydrogen in natural reservoirs, contributing to the feasibility of its large-scale exploitation.

2. Theoretical Framework

Although hydrogen is the most abundant molecule in the universe, it is rarely found freely on planet Earth, primarily due to its high reactivity in the environment—a factor that, for a long time, led the scientific community to doubt the possibility of the gas existing in an isolated form in nature [6]. Several occurrences of geological hydrogen (H₂G) have already been documented globally, often manifesting at the surface as gas flows with H₂ concentrations exceeding 10% [7].

A remarkable characteristic of areas with potential for natural hydrogen is their strong association with geological anomalies of circular or elliptical morphology, also known as "fairy circles." Figure 1 illustrates the increasing identification of these structures around the world, highlighting not only promising locations, such as in Brazil and Australia, but also the exploratory interest of various companies in the sector (e.g., HyTerra, GoldHydrogen, H2EX).

Figure 1. Locations of natural hydrogen sources.



Source: Blay-Roger (2024).

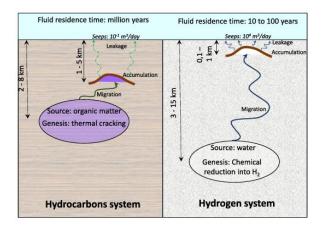
However, despite the existence of multiple documented sites with potential for geological hydrogen extraction, understanding the behavior of this gas in the subsurface remains essential. This encompasses elucidating its generation processes—whether abiotic or biotic—and the relative influence of each on system productivity, well characterizing migration as its mechanisms, its interactions with rocks, fluids, and resident microbiota, and the processes governing its accumulation in geological traps. Such knowledge is crucial for the development of commercially viable exploitation models [8]. Despite these particularities, from a structural





standpoint, hydrogen (H₂) systems display notable similarities to natural gas systems, as illustrated in Figure 2.

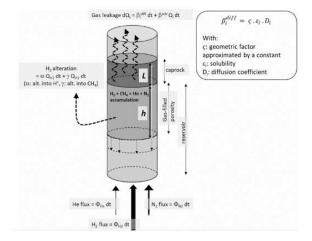
Figure 2. Comparison between hydrocarbon and hydrogen reservoirs.



Source: Prinzhofer (2023)

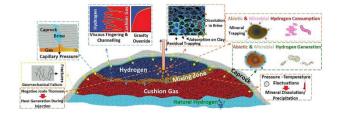
Nevertheless, when the subsurface dynamics of hydrogen are examined in greater detail, specific phenomena become apparent, such as formation of methane (CH₄) through the methanation process occurring within the reservoir storage zone, as represented in Figure 3, and its metabolic consumption by microorganisms—including bacteria and archaea—present in the subsurface, as depicted in Figure 4.

Figure 3. Dynamics of natural H₂ reservoirs.



Source: Prinzhofer (2023).

Figure 4. Phenomena occurring during underground hydrogen storage.



Source: Kumar (2023).

The ability of these phenomena to continuously alter the volume of accumulated hydrogen substantially differentiates H₂ systems from those of natural gas. It is precisely the in-depth investigation of the processes governing migration and reserve formation that constitutes the central focus of this work, with a detailed analysis presented in the following section.

3. Results and discussion

A review of the literature on natural hydrogen reservoirs reveals that their formation is governed



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by two critical stages: migration and storage. It is during these stages that the main physicochemical and mobility-related phenomena occur, defining the dynamics of H₂ in the subsurface.

Regarding geochemical processes, this study will focus on rock-fluid interactions in sandstone reservoirs. This choice is justified by the predominance of this lithology in the case studies reported in the reviewed literature.

3.1 Migration phenomens

Geological migration is the process by which fluids move through preferential pathways in a porous medium within the subsurface. This movement continues until the fluid encounters a low-permeability rock (seal), which traps it and forms an accumulation zone [9].

Similarly, hydrogen is also subject to this dynamic. However, its behavior is substantially more complex due to a set of unique properties, such as its small molecular size, low viscosity, high diffusivity, and high chemical reactivity. These factors intensify both fluid—rock and fluid—fluid interactions, potentially altering migration pathways and significantly impacting the final volume of hydrogen accumulated in the reservoir [10].

Although hydrogen exhibits solubility in water, fluid-fluid interactions between hydrogen and water become more relevant under high-pressure conditions, which promote increased dissolution of the gas in the liquid phase [11]. However, the presence of dissolved salts—such as sodium chloride (NaCl)—reduces hydrogen solubility in water. This effect results from the preference of water molecules for interactions with the ions present in the saline solution, thereby decreasing the number of molecules available to interact with the gas. Such behavior characterizes the phenomenon known as *salting-out*, in which the presence of ionic solutes promotes the exclusion of dissolved gases from the aqueous phase [12].

In spite of that numerous studies have investigated the solubility of H₂ in water under reservoir pressure and temperature conditions, there is still no consensus on whether dissolution in formation waters constitutes a favorable or unfavorable mechanism for the formation of a geological reserve of natural hydrogen during the migration and storage process [13–14].

Regarding the geochemical interactions between hydrogen and the rock matrix, these exert a fundamental control over its migration in the subsurface. Due to its high chemical reactivity, H₂ is susceptible to reacting with various minerals present in the porous medium. Such reactions can lead either to hydrogen consumption (loss) or to of formation the secondary compounds, significantly altering the volume and composition of the gas during its migratory path. Among the main minerals involved in sandstone reservoirs commonly studied, carbonates such as calcite,





dolomite, and siderite stand out, as they can promote methane-generating reactions (1) [15]. Sulfates, such as anhydrite and gypsum, as well as sulfides—particularly pyrite (FeS₂)—can dissolve within the sandstone reservoir environment, releasing ions that participate in geochemical reactions (2) leading to the formation of hydrogen sulfide (3) [15].

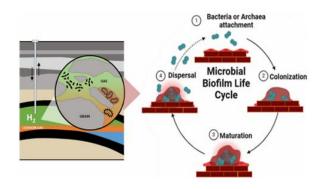
$$CO_3^{2-} + 4H_2 + 2H^+ \rightarrow CH_4 + 3H_2O$$
 (1)

$$MSO_4 \rightarrow M^{2+} + SO_4^{2-} (2)$$

$$SO_4^{2-} + 4H_2 + 2H^+ \rightarrow H_2S + 4H_2O$$
 (3)

In addition to the formation of new compounds, subsurface microorganisms can directly influence the physical properties of the reservoir, particularly rock porosity. The adhesion of these organisms to mineral surfaces can result in bioclogging processes, which affect gas sealing, alter medium permeability, and interfere with fluidrock interactions, thereby impacting the storage and migration dynamics of hydrogen, as illustrated in Figure 5 [16].

Figure 5: Bio-clogging in H₂ reservoirs.



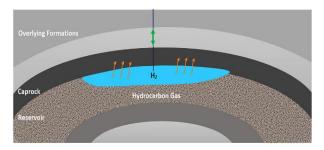
Source: Gomez (2024).

ISSN: 2357-7592

3.2. Storage phenomena

In subsurface hydrogen accumulation zones, multiple physicochemical and biological interactions directly influence the formation, preservation, and viability of natural reservoirs of this gas [17]. The viability of a geological hydrogen accumulation system is conditioned by the presence of a trap, composed of the juxtaposition of a reservoir rock and a sealing rock. The effectiveness of the seal lies in its extremely low matrix permeability—an essential property to ensure the retention of the gas column and to prevent its vertical escape. The absence or impairment of this flow barrier results in dissipation of the accumulation the atmosphere, as represented in Figure 5 [18].

Figure 6: Storage structure with sealing rock.



Source: Ghaedi et.al (2023)

Hydrogen reservoirs, however, exhibit specific features that distinguish them from conventional systems. Subsurface prokaryotic microorganisms (bacteria and archaea) can consume hydrogen as a metabolic energy source, producing various compounds through reactions such as methanation (1),methanogenesis (2),acetogenesis (3), sulfate reduction (4), iron reduction (5), denitrification (6), sulfur reduction (7), and aerobic oxidation of H₂ (8) [18–20].







These biologically driven processes, which generate secondary compounds, significantly affect both the volume of hydrogen effectively available in the reservoir and its purity, making them critical factors in estimating the potential for exploitation and utilization of this energy resource.

The extent of microbial colonization in geological reservoirs remains the subject of ongoing study. The survival and metabolic activity of microorganisms, particularly from the domains Bacteria and Archaea, are determined by a set of environmental factors. These include typically neutral pH ranges (6-7) and low salinity, as well as specific thermal limits for each which can widely—from group, vary psychrophilic conditions °C) hyperthermophilic conditions (121 °C) [20].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
 (1)

$$^{1}\!\!/_{4}$$
 HCO₃⁻ + H₂ + $^{1}\!\!/_{4}$ H⁺ \rightarrow $^{1}\!\!/_{4}$ CH₄ + $^{3}\!\!/_{4}$ H₂OCO₂ + 4H₂ \rightarrow CH₄ + 2H₂O (2)

$$^{1}/_{2} SO_{4}^{2-} + H_{2} + ^{1}/_{4} H^{+} \rightarrow ^{1}/_{4} HS^{-} + H_{2}O (3)$$

$$2 \text{ FeOOH} + \text{H}_2 + 4 \text{ H}^+ \rightarrow 2 \text{ Fe}^{2+} + 4 \text{ H}_2\text{O} (4)$$

$$2/5 \text{ NO}_{3}^{-} + \text{H}_{2} + 2/5 \text{ H}^{+} \rightarrow 1/5 \text{ N}_{2} + 1/5 \text{ H}_{2}\text{O} (5)$$

$$H_2 + S \rightarrow H_2S$$
 (6)

$$\mathrm{H_2} + {}^{1}\!\!/_{\!2} \mathrm{O_2} \rightarrow \mathrm{H_2O} \ (7)$$

ISSN: 2357-7592

 $H_2OCO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (8)

4. Conclusion

Thus, it is evident that the dynamics of natural hydrogen reservoirs require a multidisciplinary approach for a comprehensive understanding of the phenomena occurring in the subsurface. with conventional Compared hydrocarbon hydrogen exhibits unique systems, characteristics—such as its small molecular size, high reactivity, and relevance to the metabolic processes of subsurface microorganisms—which confer upon the reservoir system a distinct and challenging behavior. Therefore, integrated studies that address physical, chemical, biological, and geological aspects are essential to advance the characterization and utilization of these natural resources.

Acknowledgement

We would like to express our deep gratitude for the financial support from the Human Resources Program of the National Agency of Petroleum, Natural Gas and Biofuels (PRH/ANP – PRH27.1/SENAI CIMATEC), supported by resources from the investment of qualified oil companies in the R&D Clause of ANP Resolution No. 50/2015 and from the São Paulo Research Foundation (FAPESP), process No. 2024/10433-6.

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ISSN: 2357-7592