

Recent Advances in White Hydrogen Exploration and Production: A Mini Review

ABSTRACT

The quest for natural or white hydrogen exploration and production emanates from the growing interest in clean, carbon-free hydrogen energy. Countries all over the world are beginning to formulate legislation to promote hydrogen production as a way of combating global warming occasioned by climate change. Currently, all avenues for producing hydrogen are either very expensive or environmentally unsustainable. White hydrogen in commercial accumulations might produce cheaper and more environmentally sustainable hydrogen energy, thus providing a viable alternative to other forms of renewable energy. Despite its potential to become the cheapest hydrogen source, published literature on its occurrence, sources, accumulation, generation processes, and recovery methods are scarce. Consequently, little is known regarding white hydrogen sources, accumulation, and extraction. This study reviewed the various sources and forms in which white hydrogen can exist in nature. The various processes by which white hydrogen is generated and extracted have also been presented. This work aimed to offer new perspectives and direction for future research on white hydrogen exploration and production. Furthermore, the current challenges of white hydrogen exploration and production, and its future outlook, were also presented.

Keywords: *Natural hydrogen; white hydrogen; hydrogen fuel; hydrogen production and extraction*

1. INTRODUCTION

The Climate change has necessitated an urgent need for managing and reducing GHGs in the environment in response to the extreme weather events that have occurred frequently in recent times at different locations worldwide. In this regard, energy transition – a concept that describes the transformation of energy systems from biomass to clean energy sources such as wind and solar [1] – has grown to become a popular term used by stakeholders in the environmental sustainability sector as it presents a solution to the dire problem posed by climate change. The underlining process of the global energy transition has an ultimate goal of ensuring that clean energy sources such as hydro (6.4%), nuclear (4.3%), and other renewables (wind, solar and hydrogen, etc.) (5%) dominate the world's energy mix which is currently being dominated by crude oil (33.1%), natural gas (24.2%), and coal (27%) [2 – 5].

Amongst the renewable energy sources that can ensure effective energy transition, hydrogen – a zero-carbon fuel – presents the cleanest option. Its direct combustion in internal combustion engines produces only heat and water as by-products. As a result, its energy conversion ratio remains the highest among all chemical fuels [6]. The equation of direct combustion of hydrogen is shown below;



The urgency with which several nations of the world are addressing the issue of climate change has created an enabling environment for the development of hydrogen as a potential energy source that would drive the global economy. Its non-polluting nature facilitates this as an energy carrier. Despite the potential of hydrogen as the world's cleanest energy source, its deployment in industrial systems and use in different national economies is still impeded, especially with the current market dynamics favoring hydrocarbon and other primary energy sources. This has necessitated the critical role of the public and private sectors in developing the future hydrogen global economy for sustainable development. This trend has recorded rapid growth through support from funds, direct government

support, and other mandatory targets. The private sector is estimated to have committed USD 124 billion to develop the global hydrogen economy [7].

An assessment of the hydrogen economy reveals that hydrogen demand has created a dominant business segment in the global economy. The hydrogen economy's market value is estimated at USD 135.5 billion [8]. This demand, according to the IEA, (2019), is facilitated by sectors such as oil refining (33%), the production of ammonia (27%), the production of methanol (11%), and the production of steel (3%) via direct reduction of iron ore which consequently consumes 3% of global demand. Figure 1 shows the demand trend. Fortunately, the over 300% increase in demand for hydrogen from 1975 is expected to increase to a market value of USD ~199.9 billion by 2023 [8]. It is essential to highlight that 60% of this demand is for pure hydrogen (an example is molecular hydrogen, the case study of the work), and 40% is for hydrogen-based fuels. This growing demand highlights the prevalent market for hydrogen as an energy source.

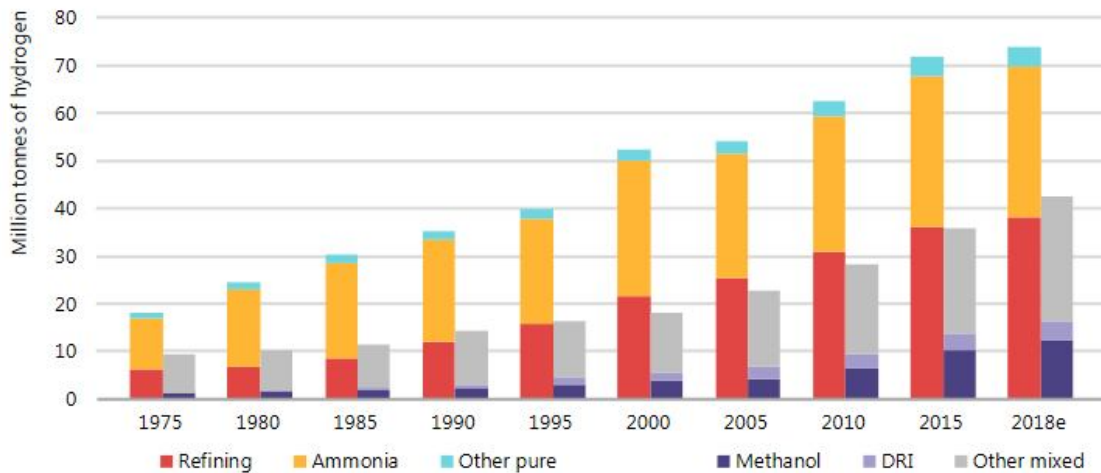


Fig. 1. Global Hydrogen demand from 1975 till 2018, reproduced from [7]

In order to meet this increasing demand, different routes exist for the production of hydrogen. These routes include:

- I. Production from steam reforming of methane obtained from natural gas without using Carbon Capture, Utilization, and Storage (CCUS) (*grey hydrogen* – the most popular route for hydrogen production).
- II. Hydrogen production through steam reforming of methane is also obtained from natural gas or biomass with the application of CCUS (*blue hydrogen*).
- III. Hydrogen production through water electrolysis using renewable energy like solar and wind energy (*green hydrogen*).
- IV. Hydrogen production through electrolysis of electrical grid (*yellow hydrogen*).
- V. Hydrogen production from the pyrolysis of methane (*turquoise hydrogen*).
- VI. Hydrogen production through electrolysis using nuclear energy (*pink hydrogen*).
- VII. Hydrogen production via gasification of brown and black coal (*brown and black hydrogen*).
- VIII. Hydrogen production by pumping CO₂-enriched water solution into reactive iron-rich rock formations (*orange hydrogen*).

- IX. Hydrogen production by drilling into naturally occurring sub-surface hydrogen reservoir deposits (*white or gold hydrogen*).

Only pink and green hydrogen is renewable among the various forms of hydrogen production. However, they comprise less than 1% of global hydrogen production [9]. Natural hydrogen is the white and orange hydrogen. Due to the prevalence of grey hydrogen in the global hydrogen economy, the need to decarbonize the production route arises. In line with the need to decarbonize the sector, the production route of blue hydrogen has been identified as the key to achieving decarbonization of the sector through disruption of the sector's supply chain and increasing the system's cost efficiency. However, if the hydrogen production chains need to be decarbonized, natural molecular hydrogen must be integrated into global hydrogen production. Unlike the other forms of hydrogen, natural or white hydrogen offers the following advantages:

- a. Cheaper production and low fixed energy costs.
- b. Sustainable source of unlimited hydrogen energy supply
- c. A negative to zero carbon emission footprint
- d. No energy input for its synthesis

Unfortunately, the exploitation and production of white hydrogen have not been achieved at the needed rate. The only location where natural hydrogen is presently used as an energy source worldwide is in a village near Bourakebougou, Mali, to produce electricity using an internal combustion engine. This occurrence has lasted for a few years. In other words, natural hydrogen plays a limited role in the present global hydrogen economy, a trend facilitated by little knowledge of the mechanisms of its occurrence and technologies for its exploration and production.

2. WHITE HYDROGEN: FORMS OF EXISTENCE

Molecular hydrogen, whose structure is shown in Figure 2, is one of the earliest elements discovered in science, dating as far back as 1766 [10]. It is the most abundant chemical substance in nature. Hydrogen is a colorless gas with an atomic weight of 1.008 under standard temperature and pressure. It remains the smallest atom in modern science, exhibiting a low boiling point of -253°C , hence its existence as a gas.

Although the chemistry, production, and technological application of hydrogen are well-researched areas of science, an in-depth understanding of its free existence in geological systems and nature, in general, remains limited. Smith et al. [11] put this in clear terms in their report, stating that "from a geological perspective, hydrogen has been neglected." Due to the limited knowledge in this field, which can be attributed to the fact that the natural occurrence of hydrogen is perceived as a rare occurrence, efforts have been underway to ensure that vast knowledge is built and mechanisms of occurrence of natural hydrogen are understood.

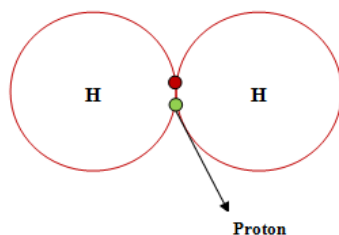


Fig. 2. Structure of molecular hydrogen

However, it is essential first to highlight the states in which naturally occurring hydrogen exists in nature in line with reported discoveries within different geological formations to understand its prevalence in natural systems. Naturally occurring hydrogen exists in different states based on subjective categorization depending on the surface conditions or subsurface systems in which it is found. It is important to highlight that the formation's geology influences these categorizations. In this regard, hydrogen exists as (i) a free gas, (ii) an inclusion of rock formations, and (iii) a dissolved gas

in water. Therefore, these three states of natural (white) hydrogen will be discussed in this section to create a broad perspective of its presence in nature.

The discovery of free hydrogen dates back to ancient times, resulting in naturally burning flames that have lasted for thousands of years. For example, the gas seeps at Chimaera, Turkey, and Los Fuegos Eternos, also known as eternal flames, located in the Philippines where the concentration of free hydrogen in these locations is as high as 41.4 – 44.5%, a concentration influenced by the nature of the vents [12]. Free hydrogen is primarily found in areas where tectonic forces have facilitated an upward movement of the crust of oceans into continental margins, highlighting a source of hydrogen in ophiolites. Hydrogen that exists as an inclusion entails rock samples that contain hydrogen as an occluded gas due to the formations in which these rock samples exist; in this case, the gas is trapped inside the rock pores or adsorbed state [13]. Cases of hydrogen found in inclusions in rock have been reported in Zambales, Philippines, where olivine samples show the presence of hydrogen gas [14]. Finally, natural hydrogen also exists in dissolved groundwater, mostly within formations recently exposed to tectonic activities. Examples are the rift areas and deep faults where background hydrogen levels in groundwater have been as high as 1500 mL/L [13].

2.1 Hydrogen as a free gas

Hydrogen, in its free state, has been encountered in nature since millennia ago. For example, gas seepages found in Antalya, Turkey, shown in Figure 3, fuelled by free hydrogen with a concentration of 7.5 -11.3% from active hydrogen gas vents, indicate hydrogen gas is a free gas in nature. These gas seepages, whose origin is attributed to a mixture of organic thermogenic and abiogenic gas, are reportedly referred to as the first source of the Olympic flames continuously burning for over 2500 years, whose flame intensity is influenced by seasonal variations. Another example of hydrogen occurring as a free gas is found in the Philippines in "*Los Fuegos Eternos*," also known as eternal flames. These flames of burning gas have been active for over two centuries and are reportedly fuelled by hydrogen of concentration of 41.4 – 44.5% formed through serpentinization. The hydrogen concentration from these vents has been stable for the last 25 years [15]. Other places where hydrogen as a free gas has been found include the USA, New Caledonia, Bosnia and Herzegovina, and Oman. In some of these places, such as Nizwa in Oman, concentrations of hydrogen are as high as 99%.



Fig. 3. Gas seepages in Antalya, Turkey, reproduced from [15]

In terms of geology, hydrogen as free gas is mostly found in regions of the world where tectonic forces have uplifted the ocean crust to the surface of the continental margin. These regions are referred to as ophiolites. Due to the prolific nature of ophiolites for natural hydrogen production, a lot of attention has been geared toward studying these formations for hydrogen presence, with results showing that the process of hydrogen production is mainly serpentinization. However, other

geological features have been identified as hydrogen deposits existing as free gas. These include rift zones, mid-ocean rift zones, and formations containing Precambrian ancient rocks (these have been reported to contain the hydrogen concentration of the highest concentration ranging up to 80%) [16]. Also, other features include geysers and hydrothermal systems, kimberlitic pipes, coal basins, and igneous rocks. These geological features reside in super-deep wells as deep as 8.5 km [17].

Furthermore, other features containing hydrogen as a free gas include volcanic gases (mining sites exploring gold, uranium, iron, mercury, nickel, copper, and other polymetallic ores), oil and gas exploration sites, and sedimentary rocks and salt deposits. Amongst these features, sedimentary rocks remained the most studied due to the presence of hydrocarbon within its ranks; hence different locations of natural hydrogen in these formations have been identified. However, it is essential to highlight that hydrogen as a free gas has been discovered among these formations, and most deposits have been found in ophiolites [13]. Some sites of natural hydrogen accumulation that have been identified in literature at different spatial locations all over the world are shown in Figure 4.



Fig. 4. Sites of natural hydrogen accumulation as a free gas, reproduced from [13].

2.2. Hydrogen as an inclusion

In most natural systems, hydrogen does not exist as a free gas, as earlier highlighted; instead, it exists as an inclusion due to its high diffusivity through geological formations, which makes it embedded in rocks over different geological ages [18]. This corroborates the studies that reveal that hydrogen seeps through the earth's crust to its surface. In this case, soil sample analysis showed that hydrogen concentration at values as high as 0.6% has been recorded from soils in Kansas [19]. As an inclusion in geological formations, hydrogen is regarded as an occluded gas in different rock formations that produce gas of variant compositions [20]. Unlike hydrogen existing as a free gas, hydrogen as an inclusion is a less common discovery, an event attributed to limited exploration and research in this area.

Examples of some of the geologic formations and features in which hydrogen in its inclusion state has been found include ophiolites, ultrabasic rocks, and minerals extracted from rift zones such as ocean rift zones (hydrogen concentration of as high as 45%). Also, other deposits where hydrogen as an occluded gas has been found include geologic rocks from the Precambrian age, igneous rocks (hydrogen concentration of as high as 99% in granite), and volcanic rocks (in this case, the hydrogen concentration of ~45% from degassed rock samples). Furthermore, occluded hydrogen has been found in kimberlitic rocks, minerals extracted from the mine, and other ore bodies such as gold, nickel, chrome, iron, and other polymetallic ores.

2.3. Hydrogen as a dissolved component in groundwater

In nature, the presence of hydrogen in groundwater has been reported in some locations where recent tectonic activities have occurred [21]. One such occurrence was reported in a Soviet camp where over 2000 water samples were analyzed. In other instances, results of 2215 groundwater analyses showed that the concentration of hydrogen in groundwater could range from 50 mL/L to as high as 1500 mL/L, especially in geological formations exhibiting deep faults and rift areas. Groundwater samples from Western Siberia showed an increase in hydrogen concentration as the depth of the aquifer increased (15% of all samples analyzed showed the presence of hydrogen). In comparison, similar trends as regards the increase in hydrogen concentration as the depth of the aquifer increased were also recorded in Crimea in Ukraine (hydrogen concentration ranged from 0.2 – 53.6%) – in this case, an increase in hydrogen concentration as dissolved iron content increased was also recorded [13].

Similar trends were noticed in hydrogen found in 24 South African wells in deep, saline, and non-meteoric fractured aquifers. In this case, increased depth increased hydrogen concentration [22]. Similarly, the presence of hydrogen in dissolved water was recorded in samples collected from Idaho wells present in geological formations of Pliocene age caldera. Despite these discoveries of hydrogen in groundwater, there have been reports of non-discovery of hydrogen in water samples in recent times. For example, Ostojic [23] reported no evidence of hydrogen in natural spring water. However, it must be highlighted that such recent discoveries do not negate the narrative of the presence of hydrogen in its dissolved state in groundwater; instead, it can be attributed to the fact that attention has not been directed toward sampling hydrogen in these groundwater systems.

3. NATURAL ACCUMULATIONS OF WHITE HYDROGEN

3.1. Geologic accumulations of white hydrogen

Natural hydrogen accumulation occurs in specific types of geological formations, which are influenced by different factors such as the type of rock sediment, types of reactions within rock sediments, and surrounding conditions of geological formations. This section discusses and evaluates the selected natural accumulations of natural hydrogen.

3.1.1 Basins bearing hydrocarbons

There have been reports of the presence of hydrogen in petroliferous and gas-prone basins of sedimentary nature. A phenomenon that can be attributed to the reaction of biogenic sediments with different components. The presence of hydrogen in such basins has been detected in mixtures wherein the composition of hydrogen is >10%. For example, a hydrogen gas composition of 20.8% has been recorded in a field in a hydrocarbon-bearing basin in Estonia at a depth of 27m. However, lower compositions of hydrogen have also been found in some cases. A composition of 4.9 % of hydrogen in the Cambrian reservoirs on the island of Oland has been reported in the literature. A hydrogen concentration of 0.1% has also been identified in extreme cases [11].

3.1.2 Young-rich organic sediments

Biogenic activities have been identified in organic-rich sediments to produce hydrogen [24]. Generally, such biogenic activity occurs on the surface of the sediments, which subsequently permeates into the source rock, a thermogenic field at a depth of ~600m. This has reportedly led to the discovery of hydrogen in the Caspian Sea and some freshwater lakes at concentrations of 7.3 cm^3/l and 8 cm^3/l respectively. In another instance, a concentration of hydrogen at 0.6 cm^3/kg at a depth of 3 – 8m was discovered in the Baltic Sea. On the other hand, the presence of hydrogen has been recorded in landfill sites where their source consists of biogenic and abiogenic sources. In this process, the hydrogen content is usually lost to the environment. This is shown in Figure 5, highlighting how hydrogen concentration drops in the conversion process of wood to graphite.

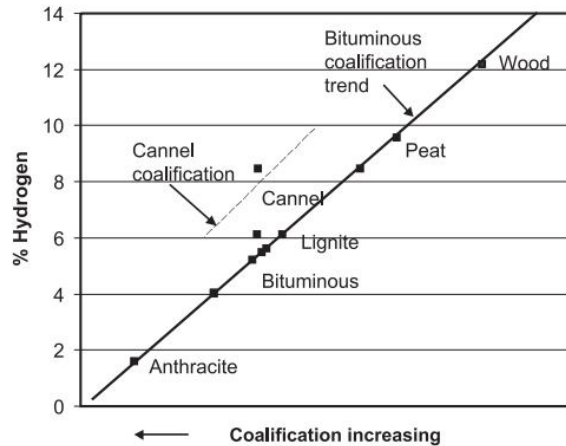


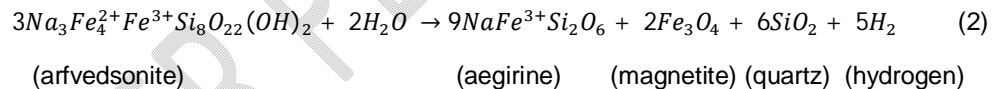
Fig. 5. Change in hydrogen concentration during the coalification process, reproduced from [11].

3.1.3 Non-ultramafic igneous rocks

The reaction between dissolved gases in the C-H-O-S system in basaltic magmas has produced hydrogen [24]. This reaction has been attributed to the presence of hydrogen in calc-alkaline volcanoes. Such volcanoes have been identified to contain steam, carbon (IV) oxide, nitrogen, hydrogen sulfide, hydrogen chloride, hydrogen fluoride, and hydrogen gas. In some cases, hydrogen concentration within the 0.5 – 4 % range has been recorded in places such as Surtsey, Iceland [25].

3.1.4 Igneous complexes of alkaline nature

Alkaline igneous rocks comprise failed arm volcanic lineaments and aulacogens extending from continental and ocean areas. Such alkaline intrusions comprised of olivine-rich rocks generated from the mantle have been reported to contain hydrogen [26]. On the other hand, mafic intrusive rocks have been shown to contain little hydrogen content. The hydrogen generation in alkaline igneous rocks is reaction-based and shown in equation 2.



3.1.5 Ultramafic igneous rocks

Among the different compositions of igneous rocks, ultramafic rocks have been identified to contain hydrogen gas [11]. Figure 6 shows the hydrogen content of other igneous complexes. These ultramafic rocks are composed of the earth's core and are produced from melts from the mantle, which are intruded into the crust and high-level volcanic complexes in large and small volumes, respectively. They are found near the earth's surface, usually in large volumes and or in the continental crust, which also occurs close to the earth's surface as tectonically emplaced ophiolites. In addition, ultramafic rocks contain olivine (70 – 80%) and dunite, whose exposure to water facilitates serpentinization, a process of hydrolyzing ferromagnetic materials to produce hydrogen.

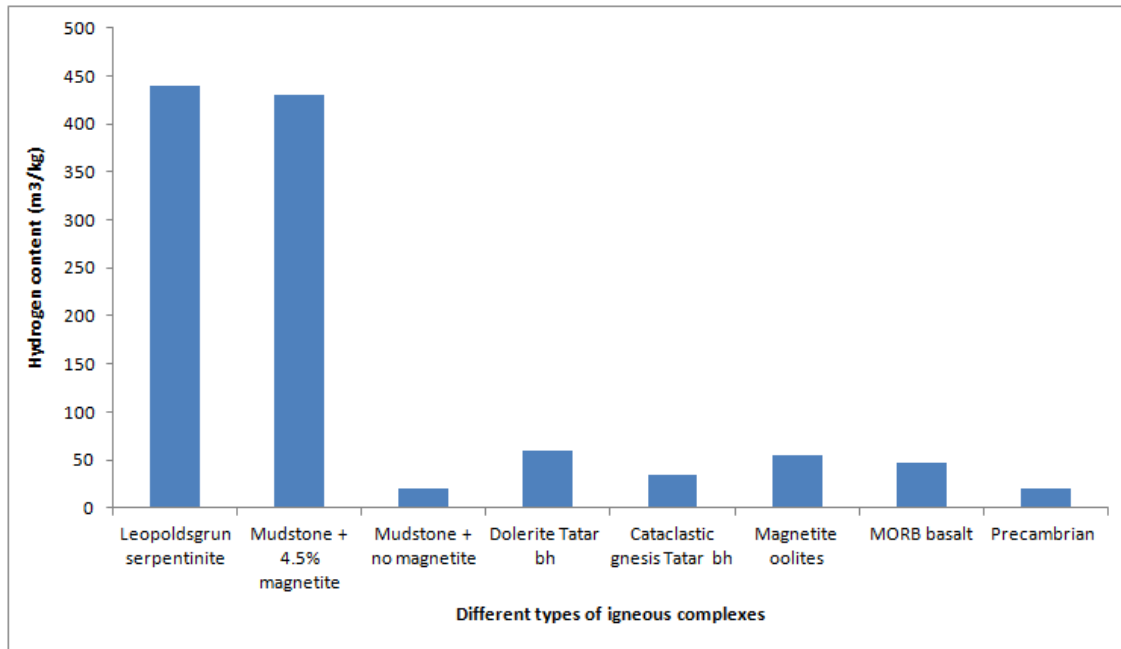


Fig. 6. Hydrogen content of different igneous rock complexes, reproduced from [11].

3.1.6. Mantle beneath Ocean Crust

Along the mid-ocean ridges and their transform faults, such as Mid-Atlantic Ridge, Reykjanes Ridge, Henghill, SouthWest Iceland, and Rainbow Field off the Azores, high hydrogen content coincides with values higher than the averages, indicating that the mantle as the source of hydrogen [27]. One fault-topped core complex is located in a peridotite seamount east of Bermuda that is serpentinized where gas venting occurs. In this system, the vents contain fluids that are alkaline (pH of 9 – 9.8), exist at temperatures of 45 – 75 °C, and exhibit high content of hydrogen (ranging from 249 – 428 mmol/kg) [28]. Within these formations, the influx of hydrogen into the ocean at a capacity of 125 MMcfd was observed. The contribution of hydrogen at 17000 mol/day by the basaltic layer to the ocean crust and the release of ~301 mol/m³ of hydrogen from the mid-Atlantic ridge have all been reported [29].

3.1.7 Surface Ophiolites

These geologic formations in Phanerozoic mountain belts and Precambrian greenstone belts comprise large blocks of oceanic crust and mantle facilitated by tectonic emplacement unto continental margins. The outcrop size of these geological features ranges from a few kilometers to thousands of kilometers; ultramafic rocks can go as wide as 5 km thick. In literature, surface ophiolites have been reported to show hydrogen gas presence. Selected examples include Semail Ophiolite of the Cretaceous age, Ural Mountains of the Variscan age located in Russia, Kempirsay, Poison Bay Fiordland, South Island, New Zealand of Palaeozoic period, and Zambales Ophiolite of Luzon Island, Philippines of Cretaceous age.

3.2. Atmospheric Hydrogen

In the atmosphere, the fraction by volume of hydrogen in dry air (which refers to the atmosphere) is estimated at 500 ppbv. In other words, the atmospheric hydrogen concentration is valued at 0.531 ppm [30], an estimated value that varies with the position of the equator and poles, as the case may be. For instance, the concentration at the equator is estimated at 545 ppb while that at the poles is valued at 535 ppb at 88°S and 490 ppb at 80°N, respectively. This variability in hydrogen concentration is attributed to intra- and inter-annual variability facilitated by different mixing hydrogen ratios [31]. Due to this variation, a cumulative volume of hydrogen in the atmosphere is estimated to range between 76 – 176 Tg, with specific values valued at 155 ± 10 Tg [32].

Due to the lightweight (lightest element) and high reactivity of hydrogen, it is challenging to have hydrogen resident in the atmosphere for a long time. Instead, the gas exhibits a short residence time. This is estimated at 3 – 2 years [30], 2 years [31], 1.9 years [32], 7 – 4 years [33], and 1.4 years [34]. This limited residence time raises severe concerns about a steady gas supply from natural processes that supplement its consumption process. Examples of such processes include the photolysis of water, biologically driven processes, other anthropogenic reaction pathways, and *in situ* hydrogen production through the photochemical reaction of water.

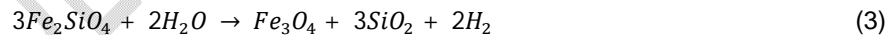
However, the production of atmospheric hydrogen through the process of photochemical reaction is limited in hydrogen production capacity because of the limited amount of water in the atmosphere. This is facilitated by the existence of water as ice at high altitudes and inhibiting property of oxygen to the photochemical reaction. A reduction of 0.001% in the amount of oxygen from its present value [35] would halt the photochemical reaction of water to produce atmospheric hydrogen.

4. WHITE HYDROGEN GENERATION PROCESSES

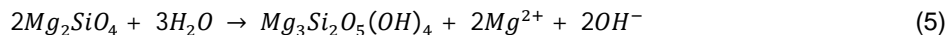
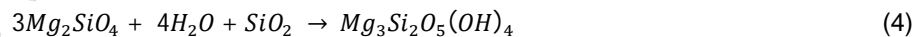
Different processes have been proposed to be responsible for producing natural hydrogen. Some authors proposed a single production route, while others postulated a combination of techniques, underscoring the uncertainty surrounding the production of natural hydrogen in different geologic formations [36]. The prevalence of these proposed generation pathways of hydrogen is due to the fact that hydrogen is a ubiquitous gas in nature; hence it is present in almost all systems – biotic and abiotic. Coupled with hydrogen gas's high reactivity and diffusivity, it exists as a component of different systems that release molecular oxygen under certain reactive conditions into the environment. These reactive conditions can be facilitated by living organisms, variations in temperature and pressure conditions, or redox reactions [13]. Hence, due to the abundance of hydrogen-bearing compounds in nature and the diversity of different mechanisms through which the gas can be released to the environment, a plethora of proposed pathways for generating natural hydrogen exists. These proposed pathways include:

4.1 Serpentinization

This metamorphic process is popular among earth scientists due to the prevalence of serpentinization as the main oxidation reaction pathway that facilitates the conversion of ultramafic rocks – the main component of the earth's crust – into serpentine-producing hydrogen in the presence of water [37]. In detail, a typical ultramafic rock is made up of olivine with a strong tendency to react with water. Also, the ultramafic rock contains peridotites whose variation to the serpentine content influences the permeability of the rock formation to water, consequently inhibiting the formation of more hydrogen. This mineral olivine is a series between forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4); herein, the iron content of fayalite's capacity to react with water to produce hydrogen using its Fe^{2+} atom. The reaction pathway is shown below;



However, forsterite does not undergo similar reactions to produce molecular hydrogen. Instead, it produces serpentine and magnesium, as shown in equations 4 and 5.



In the process of serpentinization, the role of temperature has been studied. The optimum temperature of hydrogen through the serpentinization process is within the range of 200- 310 °C [38]. At lower temperatures, the reaction is impeded. However, hydrogen production through contamination from container materials has been reported [39], while at higher temperatures, a significant decrease in reaction rate results due to constraints of thermodynamics.

The hydrogen production capacity of serpentinization in nature varies based on different studies due to the assumed amount of ultramafic rocks in specific systems where outcrops from the earth's mantle have been exposed to the surface. In some cases, the mantle is exposed on rift zones in the oceans or raised to the surface via the ophiolites belt. Considering these geologic formations, hydrogen flow from the ocean crust through serpentinization within the range of 0.16 – 0.26 Tg/year has been

reported [40]. The annual hydrogen flux from the ocean crust on the assumption that 10% of the ocean crust is made up of 10% serpentine is estimated at 0.76 Tg/year [41], hydrogen flux values of 0.89 ± 0.6 Tg/year were estimated using drilled samples of ocean crust [42], while hydrogen flow from Semail ophiolite in Oman was estimated at 0.18 – 0.36 Tg/year [17].

4.2 Water radiolysis

A school of thought argues that the vast amount of molecular hydrogen in nature can be facilitated by radiation energy [24]. Energy from the radioactive decay of materials such as uranium, thorium, and potassium provides energy for the breakage of water into oxygen and hydrogen molecules in a process known as the radiolysis of water [43]. In this process, ionizing radiation from radioactive elements facilitates the excitation and ionization of molecules of water molecules to produce molecular hydrogen and hydrogen peroxide (which decomposes to form oxygen and water). However, it is essential to highlight that water molecules do not solely absorb energy from ionizing radiation. The different components of the geologic formations also absorb it.

For example, it is reported that 1% of energy from radiogenic decay is absorbed by water in the pores of rock formations while the remaining is absorbed by the rock matrix and transformed into heat energy. Hence, it becomes evident that the amount of molecular hydrogen produced is proportional to the porosity of the rock matrix filled with water [22]. An even smaller percentage >1% of ionization energy consumption by water in rock pores is reported. For instance, 0.002 – 0.06% and 0.03 – 0.6% of radiation energy consumption by water molecules are recorded for igneous rock and clay, respectively [13]. In another study, it was shown that the effect of gamma radiation on bodies containing hydrogen produces molecular hydrogen with higher yields recorded from brine than pure water [44].

The open literature has reported high amounts of molecular hydrogen produced through this radiolysis method. For instance, Lollar et al. [45] reported a hydrogen production capacity of 0.03 – 0.09 Tg/year ($0.16 - 0.47 \times 10^{11}$ mol/year). At this juncture, it is critical to state that hydrogen is not the only by-product of radiolysis. Hydrogen peroxide is produced alongside. This hydrogen peroxide decomposes to oxygen and water, indicating the presence of oxygen in a similar stoichiometric ratio to hydrogen in places where natural hydrogen exists. However, this is not the case, as most natural accumulations are devoid of oxygen presence, a phenomenon that remains to be explained. Such a phenomenon can be attributed to the high diffusivity of hydrogen, which facilitates its movement from its origin to a new location where oxygen cannot diffuse.

4.3 Biological Activity

Hydrogen gas has reportedly been produced from an organic substrate, especially natural gas, through biological activities. These production routes include fermentation, anaerobic decay of organic matter, and nitrogen-fixing bacteria activity [13]. In nature, it is challenging to find hydrogen-producing microorganisms existing alone; they co-exist with hydrogen-consuming microorganisms [46]. Hydrogen-producing organisms cannot exist without hydrogen-consuming microorganisms because hydrogen inhibits the latter's activity. In this regard, it is evident that the consumption process of molecular hydrogen is as crucial as the production route. Hence, the consumption pathways will be briefly discussed below.

In literature, two biologically driven hydrogen consumption pathways have been identified through the activities of microorganisms and soil. Amongst these routes, soil activity, a non-biological process, is highlighted to be more critical than microbial pathways in molecular hydrogen consumption, accounting for ~80% of the consumption of atmospheric hydrogen where most of these microorganisms are resident [47]. Due to this, the soil is perceived as a primary sink in atmospheric hydrogen. Humidity plays a significant role in influencing the reaction pathway of hydrogen consumption in the soil. In this case, wet soils show a higher capacity to consume hydrogen than less humid soils [48]. Although the narrative has favored soil as an efficient hydrogen consumer, it is essential to highlight that soil produces hydrogen in lesser quantities than its consumption rates.

As highlighted earlier, hydrogen production and consumption go in tandem. Produced hydrogen by wet soils (an intensive process compared to other soil types) is usually converted to methane by methanogens. For upland soils which are referred to as oxic soils, hydrogen is produced through the activity of nitrogen-fixing bacteria and consequently consumed by abiotic enzymes, while for anoxic

wetland soils, bacteria fermentation is responsible for hydrogen production, a phenomenon followed by consumption by sulfate bacteria, methanogens, denitrifiers, ferric iron reducers, and Knall gas bacteria. Furthermore, temperature and concentration play a vital role in the production and consumption of hydrogen. In this regard, the optimum temperature of hydrogen consumption is revealed to be 30 °C in humid soil, a condition in which hydrogenase (the microorganism responsible for decomposition) remains active even in below-freezing point temperatures [49] while an increase in the concentration of hydrogen in soil results in an increase in the consumption rate [50].

4.4 Volcanic reactions and hydrothermal processes

In volcanic systems, hydrogen is the third most prevalent gas emitted after H₂O and CO₂, a phenomenon that is influenced by the equilibrium state of the volcanic gas with the molten rock mixture [13]. For instance, at an equilibrium temperature of 500 °C of FMQ (Fayalite, Magnetite, Quartz) buffer, a hydrogen concentration of 1% is recorded, while in geothermal fluids, equilibrium temperatures of 200 °C result in a hydrogen concentration of <0.001 [51]. However, these recorded hydrogen concentrations must be lower when compared to that recorded in practical volcanic gases and hydrothermal systems, thereby highlighting the presence of hydrogen from other sources. Among these probable routes, the thermal decomposition of water is exempted because reaction conditions do not favor hydrogen generation because the reaction is not spontaneous. Even in temperatures as high as 1000 – 1500°C, production of thermally dissolved water is low; however, an increase is recorded at conditions of 2000 – 3000°C and 0.1 bar.

Based on the assumptions that hydrogen and CO₂ are in equilibrium amongst volcanic gases, estimated hydrogen of $4.8 \pm 3.6 \times 10^{12}$ (mol/year) or an equivalent of 9.6 ± 7.2 Tg/year was projected to be released from volcanoes [52]. This comprised different estimated values from various volcanic sites, as highlighted below;

- i. Hydrogen production from a volcano in Antarctica, Erebus, is estimated at 0.001 Tg/ year.
- ii. Hydrogen production from Mountain Etna is estimated at 0.00065 Tg/year.
- iii. An estimated value of $0.9 - 3.4 \times 10^{11}$ mol/year or an equivalent of 0.18 – 0.7 Tg/year is recorded in Subaerial volcanoes.
- iv. Hydrogen production from mid-ocean ridges is estimated at $0.07 - 0.2 \times 10^{11}$ mol/year or an equivalent of 0.02 – 0.05 Tg/year.

Furthermore, another route of hydrogen production in volcanoes and hydrothermal systems is the reaction of hydrogen sulfide with water or the decomposition of hydrogen sulfide. This former reaction route is proposed as the reason for the presence of hydrogen in Mount St. Helens volcano in the US, while the addition of oxygen to the former reaction is identified as a possible reaction route for hydrogen production. In addition, the reaction of hydrogen sulfide with copper produces by-products, including hydrogen, a phenomenon proposed to be responsible for the presence of hydrogen in a mill chamber. Through all these different proposed routes, it is evident that hydrogen sulfide enhances hydrogen production.

4.5 Deep-seated hydrogen

The presence of hydrogen in deep seated formations has been recorded in published literature. An increase in depth translates to increased hydrogen concentration, especially in deep and super-deep wells. For instance, hydrogen detections were recorded at a depth of 500 – 600 m, while tens of hydrogen detection were recorded at a depth of 800 – 1000m [13]. Based on these findings, the narrative that natural hydrogen originates from the earth's core is strengthened. However, the processes are driven by crustal processes. Empirical evidence substantiates this claim as rich hydrogen presence is found within gas samples obtained from the super-deep well of the Kola super-deep drilling program. From these practical pieces of evidence, it is argued that hydrogen is generated from the layer below ophiolites and underlying peridotites.

In addition, the deep-seated origin of hydrogen is supported by its discovery in rift and fault zones [53]. This is corroborated by the high diffusivity rate of hydrogen in deep-seated zones in the order of thousands of kilometers due to the geodynamics of the earth. Furthermore, another school of thought argues that hydrogen is produced from the mantle of the earth's core, especially under reducing

conditions. In one such study, Yang et al. [54] observed the presence of hydrogen in minerals under reducing conditions. Also, the analysis of the earth minerals such as diamond existing at equivalent depths in which deep-seated hydrogen has been previously reported shows hydrogen presence [55]. Similarly, the upper mantle of the earth's core and a significant part of the asthenosphere is reportedly saturated with metal-containing hydrogen [56] due to its deep-seated nature in rock matrices. However, there are numerous controversies surrounding the deep-seated generation of white hydrogen.

5. RECOVERY METHODS OF NATURAL HYDROGEN

The industrial exploration and production (recovery) methods of natural hydrogen from sub-surface formations are synonymous with oil and gas exploration and production. Herein, the tripartite approach of a geologist – source rock, reservoir, and trap – forms the basis for exploration activities. For instance, prolific rock formations and origins of natural hydrogens, such as ultramafic rocks, hydrothermal fields, surface ophiolites, alkaline igneous complexes, etc., have been established as sources of natural hydrogen. In this regard, geochemical analysis can be deployed to determine the composition of hydrogen in the formation to ascertain the presence of a large sample (commercial quantity) of hydrogen reservoir in the subsurface. Thereafter, a successful hydrogen exploration would be commenced by identifying where these source rocks are located in line with oil and gas industry practices.

At this juncture, drilling wild cat wells to determine the presence of high-concentration hydrogen in the subsurface is carried out. This is similar to drilling the first hydrogen exploration and production wells in Bourakebougou, Mali. In the case of the Bourakebougou well, the wild cat is synonymous with the Bourakebougou water well, Bougou-1, which was drilled in Proterozoic sedimentary formations with the intention to produce water resulting in gas explosion, and the subsequent plugging of the well. However, identifying high concentrations of hydrogen of 98% of hydrogen, 1% of methane, and 1% nitrogen facilitated the drilling of 12 exploratory wells within the vicinity of the wild cat well to confirm the presence of vast reserves of natural hydrogen [57]. Also, wildcat wells for natural hydrogen exploration and extraction were drilled in Nebraska, USA, in 2018 and 2019. Hydrogen extracted from the well had a 96 % purity. Once the hydrogen “reservoir” is determined and the positions of stacked reservoir intervals separated by doleritic walls are ascertained, production from the reservoirs for onward utilization begins.

Other methods of extracting white hydrogen are directly tapping the resource from shallow and fractured iron-rich source rocks and through enhanced recovery by pumping CO₂- rich water into iron-rich rocks during CO₂ sequestration.

6. CONCLUSION AND FUTURE OUTLOOK

Natural or white hydrogen, if fully developed, has the potential to cause one of the most significant disruptions in the global energy mix in the near future. White hydrogen can be tapped and produced as a seep directly from shallow and fractured iron-rich rocks or as a resource that can be trapped in the sub-surface, like oil and gas accumulations. This study has reviewed the various sources and forms in which white hydrogen can exist in nature. The multiple processes by which white hydrogen is generated from natural processes have also been presented. However, there is insufficient knowledge of its origin of formation, source rock types and characteristics, type, and size of accumulation, and recovery methods of natural hydrogen. Questions such as “What are the volumes of H₂ in these reservoirs? What are the results of the production test of the wells? Is long term exploitation feasible? Is this resource renewable? Can we artificially enhance production? [58], how can it be transported and stored? To develop profitable field development plans for producing hydrogen reservoirs, these questions must be answered. Specifically, this would increase the marketability of such projects regarding investors' funding.

Finally, the detection methods applied in exploring the resource are critical to recovering natural hydrogen from deep formations and reservoirs. The most used method is the presence of hydrogen in soils or aquifers close to the earth's surface [58]. Unfortunately, these detection methods are limited as hydrogen is a highly diffusive gas that can diffuse into the atmosphere and environment. Also, the high reactivity of hydrogen with other oxidants such as nitrates, iron oxides, and manganese oxides makes it challenging to find molecular hydrogen in nature, especially in oxidized near-earth surface environments. In addition, the current exploration methods for natural hydrogen are limited as their

detection abilities are impeded due to abiotic reactions and the fact that microorganisms resident in geologic formations feed on hydrogen as an energy source, consequently depleting natural hydrogen accumulations [59].

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