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Up-to-Date Status of Geoscience in the Field of Natural Hydrogen with Consideration of Petroleum Issues

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Abstract: The perspective of natural hydrogen as a clear, carbon-free, and renewable energy source appears very promising. There have been many studies reporting significant concentrations of natural hydrogen in different countries. However, natural hydrogen is being extracted to generate electricity only in Mali. This issue originates from the fact that global attention has not been dedicated yet to the progression and promotion of the natural hydrogen field. Therefore, being in the beginning stage, natural hydrogen science needs further investigation, especially in exploration techniques and exploitation technologies. The main incentive of this work is to analyze the latest advances and challenges pertinent to the natural hydrogen industry. The focus is on elaborating geological origins, ground exposure types, extraction techniques, previous detections of natural hydrogen, exploration methods, and underground hydrogen storage (UHS). Thus, the research strives to shed light on the current status of the natural hydrogen field, chiefly from the geoscience perspective. The data collated in this review can be used as a useful reference for the scientists, engineers, and policymakers involved in this emerging renewable energy source.

Keywords: renewable energy; hydrogen detection; hydrogen production; energy; climate change; H_2

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1. Introduction

From the early exploration of oil in Pennsylvania in 1859 [1], fossil fuels have been the dominant source of energy in the world. However, at the beginning of the new millennium, humans encountered a pressing problem derived from the usage of fossil fuels: global warming. The threat of global warming, together with other environmental impacts arising from the consumption of fossil fuels, triggered the notion of the search for likely renewable energy sources. To achieve this goal, solar, wind, and geothermal energy systems have been profoundly studied in recent decades. Nevertheless, the share of such renewable energy sources is still inadequate. Figure 1 shows the current percentage of each energy source in the world energy market [2]. As it is evident, nearly 81% of the total global energy supply comes from fossil fuels, while the rest is generated from renewable energy sources.

In 2012, in parallel with the human search for renewable energy sources, an accidental discovery of natural hydrogen occurred. Originally, the initial discovery dated back to 1987 in the village of Bourakebougou in Mali when some local drillers were drilling a water well [3]. As the drill bit penetrated into the depth of 108 m, a driller threw away his cigarette towards the well collar; abruptly, a giant flame of fire rose from the well, thereby shocking the drilling crew. The fire continued to burn for several weeks without generating any black products, such as carbon dioxide. Finally, the drillers managed to cap the well, and they abandoned the well, searching for water in other spots of the area. The abandonment of the well continued until 2012, when a new investor gained the state's permission to explore the region. The exploratory team sampled the gas coming from the dry well. They reported that the gas contained nearly 98% molecular hydrogen (H_2) [3]. Subsequently, an engine was installed on the well to convert the gas to electricity for the village's residents. From that time to the current date, the electricity for Bourakebougou village is supplied by the uninterrupted natural hydrogen from the subsurface formations.

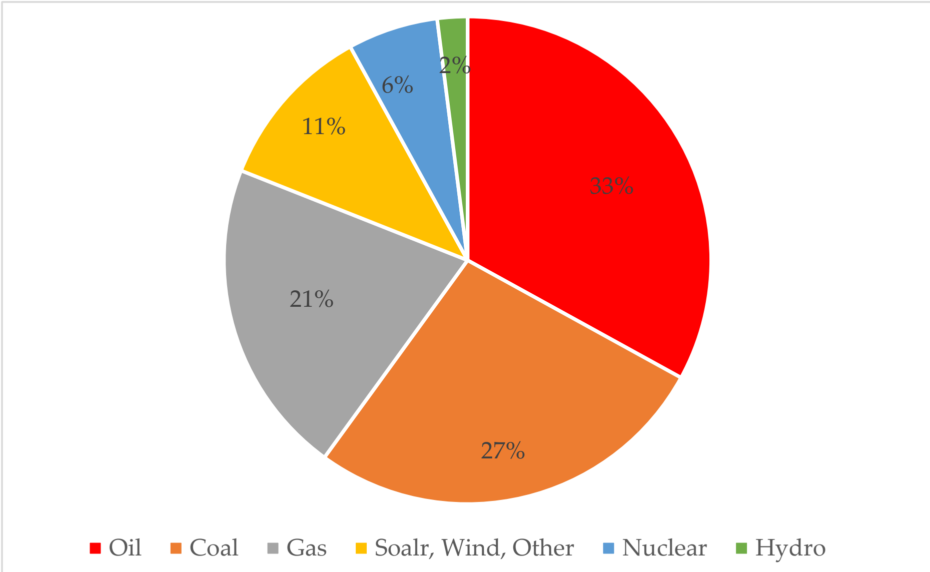

Figure 1. Current energy sources consumed in the world.

Prior to the Mali case, the flow of hydrogen gas from different mines, faults, seeps, and hydrocarbon wells was frequently reported throughout the world; however, the idea of natural hydrogen as a renewable energy source was overlooked or underestimated for three main reasons: the first reason is that most deep wells were drilled for the purpose of oil and gas exploration in sedimentary rocks. In such rocks, the presence of free hydrogen is less possible as it rapidly converts to hydrocarbons [4,5]. The second reason is that the hydrogen is highly light and diffusive, thereby escaping from the rock pores (or potential underground traps) into the ground surface [6]. The third reason originates from the widespread notion that free hydrogen sources are rare. In fact, because of this misconception, no one has sampled the natural hydrogen concentration in the gases released from underground during geoscience studies. Even if someone aimed to do this, the lack of the appropriate equipment would prevent the measurement of the hydrogen content of the gases released from underground geological structures [4]. However, at the present time, the majority of gas detectors in the field of geoscience lack the H_2 detection sensor.

The commercialization of natural hydrogen in Mali persuaded many researchers and companies to explore the subsurface resources of natural hydrogen throughout the globe. In addition, the Russian invasion of Ukraine in February 2022 forced the European Union (EU) to replace Russian gas with renewable energy sources such as natural hydrogen. This is why the EU, in May 2022, announced a demand for 20 billion kg of natural hydrogen by 2030. In addition, the US drilled the first hydrogen borehole in 2019 [7]. In September 2022, the US government announced an investment of about USD 700 million for natural hydrogen discovery.

Moreover, in 2021, the Australian government issued permission for investors to discover potential sources of natural hydrogen in Australia [7]. It appears that Australia possesses remarkable hydrogen-bearing formations, such as iron-containing and uranium-containing rocks. As will be discussed in the subsequent sections, the iron-containing rocks react with hot groundwater and release hydrogen (serpentinization process). Moreover, the uranium-containing rocks propagate radioactive rays, leading to splitting the groundwater and generating natural hydrogen (Electrolysis process). It is noteworthy that the Australian continent is surrounded by water, thereby, the crustal rocks are partially or completely saturated.

In this research, the status of natural hydrogen as a renewable energy source is reviewed. The concentration is on the main origins, visible outcrops, and extraction technologies related to natural hydrogen. Moreover, some of the major detections of natural hydrogen in the world are presented. Those detections are dominantly associated with ophiolites, Precambrian rocks, oil and gas reservoirs, coal basins, and salt formations. The main incentive of this review is to present the newest advancements and discoveries in the natural hydrogen field. Moreover, it strives to recount the available limitations related to the characterization of natural hydrogen reserves. With the recent boom in natural hydrogen investigations, this review can be referred to as a useful reference for the scientists and researchers who aim to conduct research on this hot topic.

2. Natural and Manufactured Hydrogen

2.1. Different Types of Hydrogen

In general, hydrogen can be found anywhere, including the atmosphere, hydrosphere, and lithosphere. However, only hydrogen concentrations in the lithosphere have been significant in some regions of the world. Note that groundwater resources can also contain noticeable concentrations of dissolved hydrogen. Moreover, it should be noted that the natural (geologic) hydrogen industry is still in the beginning stage, and hence, the exact volume of molecular hydrogen is undiscovered. In this article, by "natural hydrogen", only the hydrogen extracted from the geological structures, such as boreholes, faults, seeps, mines, etc., are targeted. Thus, the description of the atmospheric hydrogen is neglected as it is not adequately H_2-rich to extract the hydrogen economically and sustainably from it.

From another perspective, hydrogen can also be manufactured through industrial mechanisms; however, manufactured hydrogen is accompanied by pollutants such as CO_2, which are not climate-friendly. Furthermore, most methods of hydrogen production through human-made techniques are costly. On the contrary, natural (geologic) hydrogen is carbon-free and also economical. As a matter of fact, natural hydrogen extraction from the subsurface rocks does not require the large drilling structures commonly used in the oil and gas industry.

In the following sections, firstly, the different techniques for the production of "manufactured" hydrogen are recounted. Then, the focus shifts to the geologically natural hydrogen, especially the origins and the exploitation methods.

2.1.1. Manufactured Hydrogen

Manufactured hydrogen has a variety of colors. The color of hydrogen represents the manufacturing technique and the extent of the carbon impact [8]. Table 1 shows the manufactured hydrogen rainbow. As can be seen, different primary substances such as water, methane (or natural gas), and coal can be utilized in the manufacturing of molecular hydrogen. Production of the molecular hydrogen from the water, methane, and coal is conducted through the electrolysis, steam reforming, and gasification process, respectively. As it is evident, the most sustainable, carbon-free type of manufactured hydrogen is green hydrogen, which is obtained from water electrolysis by the electricity generated from renewable energy sources. The second appropriate type of manufactured hydrogen is called blue hydrogen. This type is manufactured through the steam reforming technique in which the produced CO_2 is captured and sequestrated. Currently, the green and blue types of manufactured hydrogen are in demand by governments and authorities. By contrast, the most environmentally unfriendly types of manufactured hydrogen are the black and grey hydrogen obtained from gasification and steam reforming (without capturing and sequestering CO_2), respectively [8].

Grey hydrogen is presently produced as the most widespread type of hydrogen. However, it annually emits a huge amount (nearly 900 billion kg) of CO_2 into the atmosphere [7]. Hence, due to this impact on global warming, natural hydrogen must be made a priority for countries and governments.

Table 1. The rainbow of manufactured hydrogen.

H_2 Color	Primary Substance	Manufacturing Technique
Green	Water	Water electrolysis using the electricity produced from renewable energy sources such as wind, solar, and geothermal.
Blue	Methane	Steam reforming (methane or natural gas reacts with water vapor) along with capturing and sequestering CO_2.
Yellow	Water	Water electrolysis using the electricity produced from the combination of renewable energy sources, e.g., solar and non-renewable energy sources.
Turquoise	Methane	Methane pyrolysis (methane is decomposed to gaseous H_2 and solid carbon). Afterward, the solid carbon is sequestered underground.
Pink	Water	Water electrolysis using the electricity produced from nuclear sources.
Grey	Methane	Steam reforming without carbon capturing.
Black	Coal	Gasification process (adding water vapor or oxygen to the highly heated coal).

2.1.2. Naturally Occurring Hydrogen

As mentioned earlier, natural hydrogen can be extracted from the subsurface rocks. Since this review is on natural hydrogen, its main characteristics, including the origins, visible exposures, extraction methods, up-to-date detections throughout the world, exploration methods, and the Underground Hydrogen Storage (UHS) application, will be presented in the following subsection.

2.2. Natural Hydrogen

2.2.1. Origins

Different researchers have attributed several origins to natural hydrogen [9,10]. The discrepancy between such hypotheses may come from the fact that the discovery equipment and knowledge for the characterization of natural hydrogen has remained insufficient. In the literature, four main origins have been proposed for natural hydrogen. Those origins include:

- Natural radiolysis of deep groundwater by the radioactive elements available in the high-radioactivity rocks.
- The serpentinization process in which hot groundwater reacts with the iron-rich formations, e.g., ophiolites, and natural hydrogen is released.
- The deep-seated origin in which natural hydrogen comes out from the Earth's core, or mantle.
- The change in the in situ stress regime may lead to fault reactivation, earthquakes, and activity of the regional tectonics.

Those four origins have been depicted in Figure 2. In the following paragraphs, those four origins are discussed.

Radiolysis of groundwater by the energy released from the radioactive decay was initially proposed by Vernadsky [11]. The energy of radioactive decay can easily split the groundwater molecules to generate oxygen and hydrogen. Such a mechanism has been referred to as the most likely process for a large generation of natural hydrogen [12]. A very minor proportion (nearly 1%) of the total energy released from the radioactive decay is spent on the decomposition of groundwater molecules. The remaining 99% of the energy is converted to heat in the solid skeleton of the rocks. Hence, it can be expressed that as the rock porosity is higher, the generated volume of natural gas is higher [13].

The second origin of natural hydrogen is the serpentinization process. In this process, ultramafic formations are subjected to intensely high-temperature groundwater, thereby leading to the oxidization reaction and releasing natural hydrogen [10,14,15]. The Earth's mantle is dominantly composed of ultramafic stones such as perdiorite. The primary mineral of perdiorite is olivine with the chemical formulae of $(Mg,Fe)_2\ SiO_4$. When olivine reacts with hot groundwater, three new compounds are generated: hematite, silica, and molecular hydrogen. In addition to the ultramafic rocks in the mantle, the crustal basaltic formations may also react with hot groundwater to produce natural hydrogen [16]. Some investigations on the specimens captured from the crustal basaltic rocks have confirmed the high concentration of hydrogen [17,18].

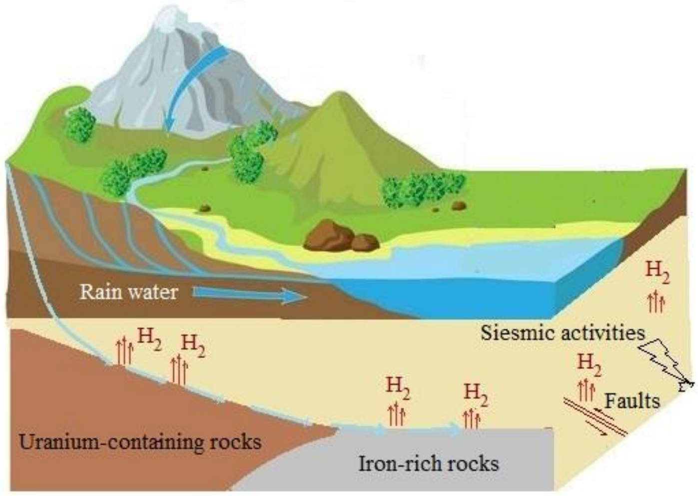

Figure 2. Four main origins of natural hydrogen.

The third origin of natural hydrogen is the deep-seated source. Such resources have been attributed to the deep rocks in the Earth's core and mantle. A number of investigators have reported that the hydrogen concentration in subsurface rocks increases with depth [6,19–22]. This is why this specific type of natural hydrogen is known as the deep-seated source. Since the drilling industry is not currently capable of reaching the Earth's core or mantle, the characterization of deep-seated sources seems to be a tough and complicated task. Due to this limitation, some researchers have linked the deep-seated sources to the mantle rocks [23–25], while others have attributed them to the core rocks. For instance, the natural hydrogen detected in the Kansas region was attributed to mantle rocks [26]. On the other side, some investigators have expressed that the core may contain several tens of natural hydrogen more than the oceanic hydrogen [27].

The fourth origin of natural hydrogen is the change in the in situ stress regime in the tectonic-active areas. A number of experimental tests have reported that on the surface of active faults, the hydrogen concentration is very high [28–30]. Based on those tests, it was concluded that the reaction between groundwater and the Fe-rich fresh rock surfaces of faults generates hydrogen [31]. However, the amount of natural hydrogen generated by this process is far less than that from other origins, such as serpentinization [32,33]. Earthquakes can activate the crustal faults, thereby leading to generating natural hydrogen in the subsurface fractures and faults [34]. Moreover, long-term research monitoring some aquifers revealed that the hydrogen concentration in the water-bearing rocks has a direct relation with the last tectonic activity of the area [19]. Furthermore, other studies reported that the newly propagated earthquake-induced fractures have a larger volume of H_2 content in comparison to the old, non-activated fractures [35,36]. Due to this matter, some researchers have proposed hydrogen concentration as an indicator of predicting occurrences of earthquakes.

2.2.2. Visible Exposures

Regardless of the origin, the subsurface's natural hydrogen is very light and diffusive. Thus, it simply travels towards the ground surface. Meanwhile, travelling natural hydrogen may react with the rock minerals, or is consumed by subsurface microbes, or be trapped by impermeable rocks such as salt layers. When natural hydrogen reaches the ground surface, it may create some circular outcrops called fairy circles. Researchers still have yet to understand the cause of this phenomenon. A variety of those fairy circles along the eastern seaboard of the United States, referred to as Carolina bays, has already been studied [7]. In the majority of them, a consistent release of hydrogen was observed. The researchers noticed that the hydrogen concentration increased as they delved deeper. The weak H_2 seepages might explain the formation of such fairy circles [7].

In Ref. [7], there is an illustration of a large fairy circle in Brazil as a consequence of hydrogen leakage from underground to the ground surface. In that fairy circle, the hydrogen has destroyed the local vegetation [7]. As well as Brazil such a phenomenon has been observed in Namibia and Australia [7]. To explain the vegetation degradation by the hydrogen seepage from the fairy circles, some researchers stated that there might be something to do with hydrogen-loving microbes consuming other nutrients [7]. Nevertheless, further investigations are required to discover the main cause of such a phenomenon.

Another exposure type of natural hydrogen is the seeps, which may appear in the form of continuous long-term fire burning on the ground's surface. In Ref. [37], there is an image of the hydrogen seep at the Chimarea region close to Antalya in Turkey. The hydrogen concentration of such seeps was reported to be more than 11%. The burning H_2 at the Chimaera region was ascribed to the presence of ophiolite rocks [7]. The local ophiolites contain iron-rich minerals such as olivine. Due to the continuous reaction of the subsurface ophiolites with the hot groundwater, natural hydrogen is constantly generated that travels through the crustal fractures and reaches the ground's surface [38,39].

2.2.3. Extraction Technologies

There are three available technologies for the extraction of natural hydrogen from underground resources [7]. Figure 3 shows those technologies in number order. They are described as:

1. If natural hydrogen is trapped in an underground space, it can be extracted by drilling a single wellbore. The impermeable formations, such as salt rocks, can act as cap rocks for trapping natural hydrogen underground [7].
2. If there are shallow iron-rich formations subjected continuously to the hot groundwater, the generated natural hydrogen can be collected and extracted by drilling a single wellbore from the ground surface to the iron-rich formation level.
3. When there is not enough groundwater to serpentinize the shallow iron-rich formations, an enhanced hydrogen recovery system can be utilized. To do this, water is injected from the injection well into the iron-rich formation to generate economically profitable concentrations of natural hydrogen. Then, the generated hydrogen is extracted from the production well. In this technique, carbon dioxide can also be pumped into the ground for sequestration purposes.

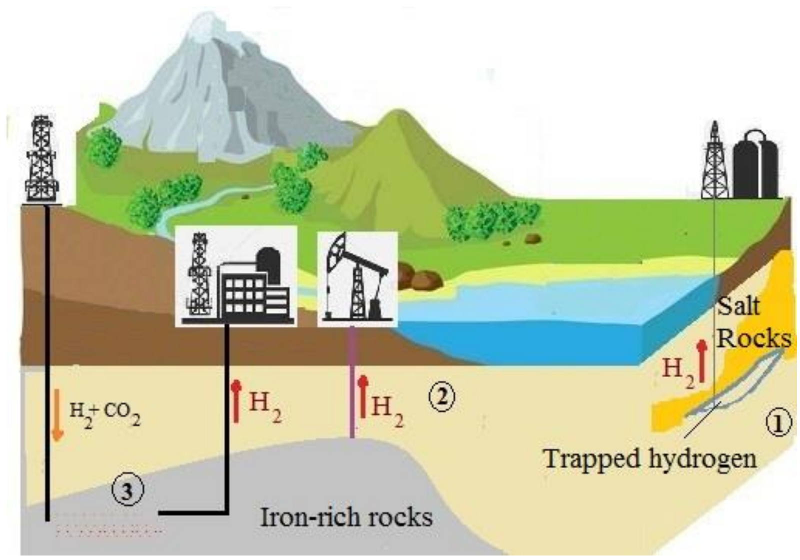

Figure 3. Three different extraction methods for natural hydrogen from underground reserves. The description of each method has been provided just before the figure.

2.2.4. Natural Hydrogen Detection

Hydrogen accumulations occur in nature in various ways. Generally, the detected hydrogen is found in three forms: natural hydrogen as free gas, natural hydrogen dissolved in aquifers, and natural hydrogen within inclusions. Since these forms of hydrogen are out of the scope of this paper, only the detections related to natural gas as a free gas are elaborated. In what follows, such detections are presented:

(1) Ophiolites: As explained previously, ophiolites, e.g., peridotite, contain olivine mineral, which is Fe-rich. It reacts with hot groundwater, and natural hydrogen is released from it (serpentinization mechanism). Some significant detections of natural hydrogen in ophiolites have been shown in Table 2. A good example is the natural hydrogen seep in Chimarea in Turkey [40]. Moreover, in Los Fuegos Etornos in the Philippines, there has been an uninterrupted underground fire. In this place, the H_2 concentration was measured in the range of 41.4–44.5% [41]. The origin of that natural hydrogen was attributed to ophiolites.

Table 2. Hydrogen detection in ophiolites.

H_2 Concentration (%)	Location	Country	Reference
7.5–11.3	Chimaera	Turkey	[40,41]
15.7	Austin Greek	The US	[42]
35.1	Mangatarem	Philippines	[41]
26.8–36.1	Kaoris, Carenage	New Caledonia	[43]
34–39.2	Barnes Spring	The US	[42]
41.4–44.5	Los Fuegos Eternos	Philippines	[41,44]
41.4–45.6	Mt. Lanat	Philippines	[45,46]
48.3	Vaiceva voda	Bosnia and Herzegovina	[47]
50.9	Camp Spring	The US	[42]
58.5	Nagsasa	Philippines	[41,48]
37.1–60.5	Kurtbagi	Turkey	[49]
39–69	Howgain	Oman	[41,50,51]
81–97	Bahla	Oman	[41,50–52]
22–99	Nizwa	Oman	[51]

(2) Precambrian rocks: Some of the major hydrogen detections have been related to Precambrian formations. Table 3 summarizes those detections. As can be seen, in two countries, including the USA and Australia, high hydrogen concentrations have been detected in Precambrian rocks [41,53,54].

Table 3. Hydrogen detection in Precambrian rocks.

H_2 Concentration (%)	Location	Country	Reference
12.8	Juuka	Finland	[55,56]
17.2	Wilson well	The US	[57]
30.4	Pori	Finland	[55,56]
56, up to	Scott well	The US	[41,57–60]
68.6	Penneshaw	Australia	[54]
80, up to	Heins well	The US	[41,58,60]
84	Minlaton	Australia	[54,61]
91.8, up to	Sue Duroche2 well	The US	[59]

(3) Oil and gas reservoirs: During the drilling of hydrocarbon wellbores, different gases are released from underground. In many cases, those gases contain natural hydrogen. Table 4 summarizes some of those detections. As can be observed, the hydrogen concentrations in oil and gas reservoirs are mainly under 50%. The reason for

this is that hydrogen reacts rapidly with the in situ hydrocarbons, which are very reactive substances.

A number of researchers have stated that hydrogen is an essential element in the process of hydrocarbon formation [62]. During such processes, hydrogen reacts with carbon-containing substances, thereby leading to hydrocarbon formation. Due to this matter, usually, the hydrogen concentrations of gas-bearing formations are lower than those of remote formations [63]. In addition, a group of scientists have stated that natural hydrogen can be considered an indicator in the exploration of oil and gas reservoirs [64]. They reported that there is a close correlation between the hydrogen concentration and hydrocarbon presence in oil and gas fields.

Table 4. Hydrogen detection in oil and gas fields.

H_2 Concentration (%)	Location	Country	Reference
11.5	Navajo	The US	[65–67]
17.9	Jeffers	The US	[67]
19.5	Cascade	The US	[65,68]
20.4	Hortenstein	The US	[67]
20.8	Kokshер	Estonia	[69–71]
26.3	Horse point	The US	[67,68]
27.3	Stavropol	Russia	[9,71]

(4) Salt rocks: Salt rocks are well-known cap rocks of oil and gas reservoirs [72]. Such evaporative formations may trap the natural hydrogen [73]. In this way, an invaluable reserve of natural hydrogen is stored beneath the salty deposits [74]. As mentioned earlier, the trapped natural hydrogen can be simply extracted through a single borehole. Table 5 summarizes some of the natural hydrogen detection in salt rocks.

Table 5. Hydrogen detection in salt rocks.

H_2 Concentration (%)	Location	Country	Reference
8.4–13.3	Siegfried-Giesen	Germany	[73]
16	Tonder	Denmark	[4]
17.4	Chusovskie Gorodki	Russia	[71]
22.1	Eristgal	Germany	[73]
24.6	Burbach	Germany	[73]
32.9, up to	Solikamsk	Russia	[75]
61.5	Muhlhausen	Germany	[9]
82.3–93	Stassfurt	Germany	[76]

As well as the salt rocks, coal basins have been frequently reported as places in which the release of natural hydrogen is a common instance. For example, the coal mines located in the Central/Eastern European countries are good examples of such hydrogen detections [73]. In some of these countries, such as Poland, the natural gas extracted from the coal basins has been vastly studied [77,78].

In the previous sections, some of the major detection methods and areas of natural hydrogen have been recounted; however, this does not mean that only the above-mentioned countries possess natural hydrogen resources. There is no exact estimation method for natural hydrogen resources since they have not been systematically studied. In fact, the aforesaid detections were recorded during the projects in which the main purpose was searching for hydrocarbons, water, minerals, coal, etc. Therefore, to detect the potential natural hydrogen resources, a well-planned scheme must be adopted by different countries or global unions.

2.2.5. Exploration of Natural Hydrogen

The exploration of natural H_2 can be executed by two methods: direct and hybrid. In the direct method, natural H_2 is the primary subsurface target to be explored. Only a limited number of countries, e.g., Mali, are exploring natural H_2 using a direct method. In the hybrid method, natural H_2 is explored in association with the oil, gas, and geothermal wells. For instance, in Australia, the search for natural H_2 is currently being conducted parallel to the oil/gas explorations. In fact, in the hydrocarbon fields, the deep fluids play an integral role throughout the entirety of hydrocarbon creation and accumulation via interactions involving both organic and inorganic elements. The nutrients transported by those deep fluids stimulate the proliferation of organisms that generate hydrocarbons, leading to an additional infusion of carbon and hydrogen sources [79].

Furthermore, in Iceland and Djibouti, natural H_2 is explored where the geothermal wells are drilled. Such geothermal wells are commonly drilled in the crystalline formations where there are active tectonics regimes. As a result, the faults are activated, and the crustal natural H_2 flows toward the surface (and inside the geothermal wells). Elevated levels of hydrogen concentrations are also found within the volcanic rock layers in northern Oman and the geothermal springs of New Zealand [80]. Additionally, the geothermal spring gas located in the Tengchong area of Yunnan Province, China, revealed a hydrogen content ranging from 5% to 15% [80].

Whether a direct or hybrid method is selected for natural H_2 exploration, there is an imperative need for highly robust gas analyzers to quantify the H_2 concentrations reaching the surface. It is noteworthy that such reliable analyzers are applicable not only to H_2 exploration but also to the production and transportation processes. In this way, the H_2 concentration, or any potential H_2 leakage from the pipelines, can be precisely assessed. At present, there is still a lack of reliable analyzers to quantify the natural H_2 concentrations, even in the oil/gas exploratory wells, which are the deepest human-made boreholes. This issue is rooted in the challenges related to the logging of natural H_2 contained in the drilling fluid (mud). In general, there are four main challenges in logging the H_2 concentration in the mud. Those challenges are shown in Figure 4. In the following paragraphs, those challenges are described.

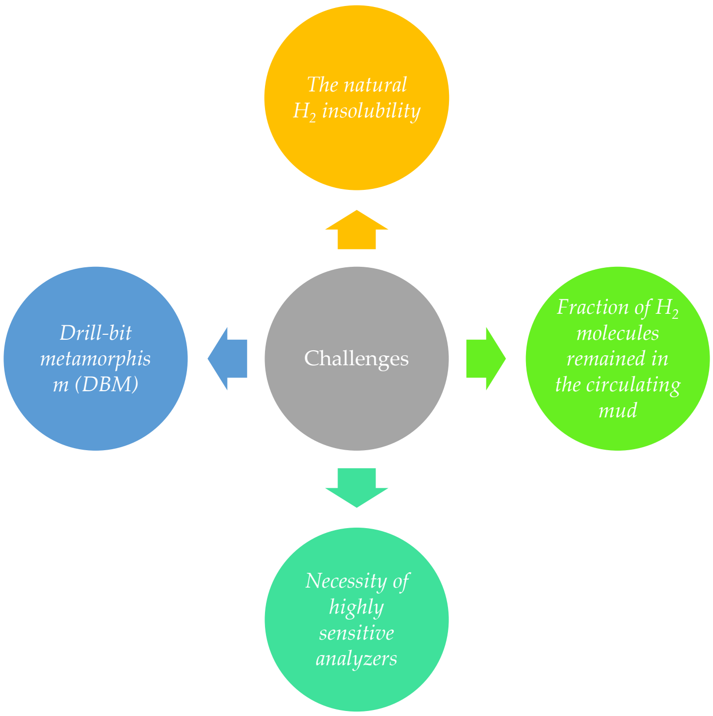

Figure 4. Four challenges related to natural hydrogen logging in the mud.

- The natural H_2 insolubility

The first challenge is that hydrogen is very insoluble when drilling through mud. Hence, a fraction of the H_2 may be degassed to the atmosphere before reaching the analyzer on the surface. To tackle this issue, an in-mud sensor can be utilized. Another alternative is to install the analyzer just before the mud is exposed to the atmosphere [81].

- A fraction of H_2 molecules remained in the circulating mud

The second issue originates from the mud circulation process. When the mud (and the mud containing H_2 molecules) reaches the ground surface, it is poured into a small open pit. Some investigations reported that the H_2 molecules require several minutes to be degassed from the mud to the atmosphere [82]. Since the mud is continuously circulating between the open pit and the wellbore inside space, the remaining fraction of the H_2 in the returning path must be subtracted from the H_2 concentration measured by the analyzer [83,84]. The authors of the current research propose the installation of an additional H_2 analyzer on the returning mud flowline. In this way, the quantity of the returning H_2 (from the open pit to the wellbore inside space) can be measured.

- Necessity of highly sensitive analyzers

The third issue is the need for highly sensitive analyzers for the measurement of H_2 concentration in the drilling fluid. As a matter of fact, the H_2 concentration may vary from a few ppm to remarkable amounts, e.g., 98% in Mali [3]. Therefore, natural H_2 analyzers must cover a broad spectrum of H_2 concentrations. Moreover, another requirement is to repeat the measurements in a short-period cycle; the reason is that the natural H_2 comes out from the fractures or faults that may intersect the wellbore just in a thin plane. Thus, the measurement cycle time must be as short as possible to avoid the skip of measurement of any potential H_2 flow. Sometimes, the fault may be the only single connector between the wellbore and the subsurface origin of natural H_2.

In today's industry, conventional gas sensors are utilized to measure the gas concentrations in the fluids. Those sensors are divided into two groups: electrochemical-based and semiconductor-based. The sensors' cross-sensitivity means that the sensor detects the concentration of a specific gas very accurately, but at the same time, it exhibits a high cross-sensitivity to the rest of the gases in the fluid [82]. Other alternative analyzers are the absorption-based sensors, which are capable of measuring the H_2 concentrations even at low ppm volumes; however, the drawback of these sensors is that they are incapable of measuring the homo-nuclear diatomic gases, e.g., H_2 in the drilling fluids [82]. Another potential analyzer is the Raman spectroscopy technique. This technique is based on the Indian physicist C. V. Raman, who won the Physics Nobel Prize for his works on light scattering in 1930 [85]. The main demerit of Raman spectroscopy is that it cannot measure low H_2 concentrations. To address this issue, Wang et al. (2020) proposed the cavity-enhanced Raman spectroscopy as a reliable method for measuring the very low H_2 concentrations in the drilling fluids [86].

- Drill-bit metamorphism (DBM)

The fourth problem is that during drilling operations, artificial H_2 gas may be generated. Such artificial H_2 is generated under two conditions: the first condition is when the drill bit penetrates into the organic, matter-rich stones such as shale sedimentations. The second condition occurs when oil-based muds (OBM) are used in the drilling of hard formations. In this condition, the interaction between the overheated mud and the bit causes the drill-bit metamorphism (DBM). Such a mechanism occurs due to the flash pyrolysis of the oil-based mud. Both laboratory and field investigations have confirmed the generation of artificial H_2 during the drilling activities. Thus, to differentiate between artificially generated H_2 and natural H_2, appropriate strategies or instruments must be applied. Otherwise, the natural H_2 concentration in the mud may be overestimated [82].

During the DBM occurrence, in addition to the H_2, other gases such as alkenes, ethane, propene, and CO are also generated; however, the concentration of the generated H_2 is much higher than those gases [82]. Using experiments on clean sandstone rocks, Strapoc et al. (2022) [82] reported a good correlation between the gas concentrations of the DBM products, e.g., H_2, alkenes, and CO. They showed that such experimental correlations can be used for back-calculation of the artificially generated H_2 in the mud. By using this technique, the artificially generated H_2 is subtracted from the naturally occurring H_2 concentration. Therefore, installing CO-analyzers and alkene analyzers on the mud flowline can be done to correct the DBM effect. It is noteworthy that the cavity-enhanced Raman spectroscopy can be utilized to measure the low concentrations of CO and alkenes in the mud. Moreover, to find reliable correlations between the H_2, alkenes, CO, and other parameters, the authors propose to utilize statistical techniques such as Monte Carlo [87] and artificial intelligence (AI) techniques, such as support vector machine [88,89].

To distinguish natural H_2 from artificially generated H_2, Keller et al. (2017) proposed the measurement of the helium concentration in the mud [90]. Despite the H_2, helium is not artificially generated during drilling operations [90]. In fact, it has very light and small molecules that are usually generated during the radioactive decay of heavy elements [91]. Hence, a simultaneous measurement of H_2 and He concentrations can clarify whether the detected H_2 is natural or artificially generated.

Keller et al. also stated that gas chromatography of H_2, He, and some hydrocarbons, including methane, ethane, and propane, is very useful for the characterization of the subsurface rocks, detection of the faults, and real-time recognition of drilling inefficiencies. For instance, a simultaneous increase in both H_2 and He concentrations can be an indicator of the increase in the porosity and permeability of rocks. Moreover, when the rocks are impermeable, the ratio of H_2/He concentration amounts to more than 1000 times [90]. If a sharp increase in the H_2 concentration is observed, the potential source is a fault. Also, when the H_2 concentration rises without He, there may be a potential for inefficient drilling issues, e.g., drill-bit overheating, mud motor failure, etc.

Such hybrid gas chromatography can be utilized instead of the expensive while drilling downhole tools. Keller et al. remarked that the accuracy of such hybrid gas chromatography is around 80%, while it costs only 10% of the downhole tools [90].

2.2.6. Underground Hydrogen Storage (UHS)

Similar to oil and gas, natural H_2 requires specific considerations such as transportation pipelines, distribution facilities, etc. One important consideration is that the exploited natural H_2 must be stored in large amounts to supply the energy requirement for urban consumers. Only in this condition natural H_2 is turned into a sustainable renewable energy source for public consumption.

A potential way to accumulate the exploited natural H_2 is to store it underground. This technique is known as UHS. In this technique, natural H_2 is injected into the subsurface formations [92]. Natural H_2 can be stored in large quantities within underground structures [93]. However, there are some limitations related to the UHS. For instance, drilling operations are a major part of the UHS projects, and a close trade-off between the drilling cost, rate of penetration, wellbore stability, etc., for all possible geological formations must be reached [94–97].

Aquifers are water-saturated rocks that are more available than salt formations and depleted oil/gas reservoirs. In the vicinity of large cities, commonly, there are water sources, especially aquifers [98]. In many cases, water extraction from those aquifers leads to environmental impacts such as ground settlement or land subsidence [99]. Thus, the UHS can be a beneficial engineering application to reuse those depleted aquifers. To select an appropriate aquifer for the purpose of UHS, two points must be regarded: firstly, on the top of the aquifer, there must be an impermeable caprock to prevent the injected natural H_2 from escaping into the surrounding geological structures [92,100,101]. Secondly, the porosity and permeability of the aquifer must be appropriate to achieve a successful injection and production process. The disadvantage of UHS in aquifers is that to gain geological knowledge about the aquifers' rocks, there is a need to drill exploratory boreholes, causing more excessive costs [102]. However, sometimes, the aquifers may have been already well characterized. Another disadvantage of the UHS in the aquifers is that the injected natural hydrogen can escape from the fractures and faults within the aquifers.

The second potential geological structure to store natural H_2 is the salt caverns. The salt caverns are constructed by injection of water into the salt domes or thick salt layers. Salt formations have good geological features such as high impermeability (prevention of H_2 leakage), low reactivity with the containing H_2, and a saline environment (prevention of microbial H_2 consumption) [103,104]. Moreover, H_2 injection and production processes can be conducted through a single well, which reduces drilling costs and wellbore instability problems that impose formidable expenditures on the project [105,106]. Although salt caverns are ideal structures for UHS purposes, their construction process is environmentally unfriendly since fresh water is consumed, and brine is disposed of into the environment. It also should be noted that the capacity of salt caverns is less than that of the aquifers and the old hydrocarbon reservoirs [101].

The majority of today's UHS operations are implemented in depleted oil/gas reservoirs. These reservoirs are associated with impermeable caprocks. Moreover, geological data are also stored in previous oil/gas field developments. One source of this data is the poroelastic parameters that play an integral role in the interaction between the injected fluid (natural hydrogen) and the reservoir [107–111]. In the oil/gas sites, the required surface equipment and facilities are also already accessible on the site. These advantages have made the depleted oil/gas reservoirs fast and easy to access UHS targets [111]. Due to this matter, the UHS in the oil/gas-depleted reservoirs is cheaper than the aquifers and salt caverns [112]. It is noteworthy that the injection/production of fluids such as natural hydrogen from the depleted oil reservoirs can lead to environmental impacts [113].

Despite those advantages, there are some limitations related to oil/gas reservoirs. The injected hydrogen may reduce the compressive strength of the cement around the injection and production wells [100]. Athar et al. (2022) performed some laboratory investigations on the impact of H_2 diffusion into the cement. It was observed that when a dry cement sample is exposed to hydrogen, the hydrogen molecules diffuse into the cement texture and create some bubbles in the cement structure. This causes a decrease in the UCS of the cement of 50%, just after a week. Hence, the injected H_2 may threaten the integrity of the injection and production wells [114]. Moreover, the injected natural H_2 may embrittle the top caprock, which leads to rock instability. Another disadvantage is the possibility of a chemical reaction between the residual gas/oil and the injected H_2, which reduces the purity of natural H_2 [114]. In addition, the rock's mechanical parameters must be taken into account to properly simulate the reservoir conditions [115].

3. Conclusions

Prior to the current decade, hydrogen was mostly needed for the production of chemical substances in petrochemical plants. To produce hydrogen, 900 million tons of CO_2 are released annually into the atmosphere through the production of grey hydrogen by a steam-reforming technique. Such an emitted CO_2 amount is equivalent to the CO_2 emitted by the global aviation industry. Therefore, this huge amount of steam reforming-derived emissions, along with the depletion of hydrocarbon reservoirs and global warming issues, have changed our traditional attitude toward hydrogen. This occurred especially when the commercial applicability of natural hydrogen as a carbon-free energy source was proved in Bourakebougou in Mali in 2012. Hence, the traditional misconception about the rarity of natural hydrogen sources is not further valid.

In this research, some of the major detections of natural hydrogen in different countries were described. The main detection methods were related to the ophiolites, Precambrian rocks, oil and gas fields, and salt rocks. Nevertheless, this does not imply that only these structures hold natural hydrogen resources. The precise assessment of these resources remains uncertain due to the absence of comprehensive studies. The previously mentioned findings, in reality, were incidental outcomes during projects primarily focused on exploring hydrocarbons, water, minerals, coal, and similar resources. Consequently, in order to identify potential natural hydrogen resources, it is imperative for various countries or international organizations to implement a thoroughly organized strategy.

Natural hydrogen reserves are found in association with a diverse spectrum of geological formations, from ultramafic rocks to sedimentary rocks. However, natural hydrogen is a colorless and odorless gas, which makes the potential seeps and leakages tough to be visible. To discover potential natural hydrogen resources, appropriate exploratory surveys must be adopted to detect fairy circles, underground seismic activities, and freshly activated faults. For instance, geophysical methods can be used to monitor the hydrogen concentrations in aquifers and to plot the H_2 concentrations with depth in different geological regions. Such surveys may reveal the potential hidden bonds between the natural hydrogen presence and other rock characteristics. Furthermore, such H_2 plotting can be deployed in the prediction of earthquakes, hydrocarbon resources, different minerals, etc.

Currently, a notable absence of dependable instruments persists to accurately measure the levels of natural H_2. This deficiency extends to even the deepest human-drilled boreholes utilized in oil and gas exploration. The origin of this problem can be traced back to the difficulties associated with assessing the natural H_2 content present within the drilling fluid. In this research, four primary challenges in the precise recording of the concentration of H_2 in the drilling fluids were detected and elaborated. They included the natural H_2 insolubility, the fraction of H_2 molecules remaining in the circulating mud, the necessity of highly sensitive analyzers, and the drill-bit metamorphism (DBM) issue. To mitigate these challenges and accelerate humankind's access to potential natural hydrogen sources, an international synergy appears to be imperative. Such a synergy must outline the development of H_2 detection sensors, the establishment of simpler and more exact measurement standards, equipping the geoengineering sampling devices with hydrogen measurement tools, etc. Moreover, as large accumulations of natural hydrogen are envisaged to be in deep rocks, the development of hydrogen-discovery deep drilling methods is of paramount importance in the future.

Successful underground hydrogen storage plays a pivotal role in advancing the utilization of hydrogen as a clean and efficient energy carrier. To ensure the viability of underground hydrogen storage, several key necessities must be addressed. First and foremost, geological suitability is a critical factor. Identifying geologic formations capable of securely containing hydrogen is paramount. Depleted natural gas reservoirs, salt caverns, and aquifers are among the potential storage sites. These formations possess the physical attributes required for safe hydrogen containment, such as impermeable rock layers that prevent leakage and suitable porosity for holding substantial volumes of hydrogen. Furthermore, rigorous safety assessments and risk management strategies are imperative. Hydrogen, being a small and highly reactive molecule, can pose unique challenges in terms of containment and potential leakage. Robust safety protocols must be established to prevent accidents, ensure the protection of nearby communities, and minimize environmental impacts. Technological innovation is another key necessity. Developing advanced storage and monitoring technologies is essential to optimize the efficiency and reliability of underground hydrogen storage.

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