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NEWS AND NOTES

Geological Hydrogen: A New Carbon-free, Clean Energy Vector

P. V. Sukumaran
Deputy Director General (Retd.), Geological Survey of India, Sukrutham, Ambika Road Kotekar Post, Mangalore 575022
E-mail: pvs341950@gmail.com

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Energy is the critical component of a country's economic progress. The per capita energy consumed by a country is an index of its economic well-being with most of the economically advanced countries at the forefront. Today this energy comes essentially from fossil fuels such as petroleum, natural gas and coal, all of which are greenhouse gas-emitting fuels. Combustion of fossil fuels has released 735 billion tons of CO_2 into the atmosphere since the industrial revolution and is directly held responsible for global warming ever since. The share of fossil fuels in today's energy usage is roughly 80% and is the source of two third of the world CO_2 emissions. This is an alarming situation as global temperature rise continues to register an upward trend. Despite earnest efforts by scientists, technologists and industries to seek alternative green energies it has not been possible to limit burning of fossil fuels. This dependence on naturally occurring carbon-based fuels is unlikely to be brought under control in the near future given the rising demand, and alternative carbon-free energy sources are nowhere near being commercially competitive in order to curb fossil fuel consumption.

To decarbonise the industries, the major emitter of greenhouse gases, plans have to be initiated to promote production of carbon-free fuels. The 2015 Paris Agreement envisages containing "the increase in the global average temperature to well below 2°C above pre-industrial levels" and pursue efforts "to limit the temperature increase to 1.5°C above pre-industrial levels". In order to avoid catastrophic consequences of human-induced greenhouse warming and to meet the Paris Agreement scientists and technologists are searching for alternative, sustainable and cleaner energy sources. Unfortunately, the choices are limited; nevertheless, H_2 gas may be one of such alternatives as H_2 burning produces only water and does not emit any harmful gases. Besides, molecular H_2 is the most energy-rich gas, a kilogram of H_2 holding as much energy as 4 litres of gasoline. But there are hurdles in producing carbon-free H_2 on an industrial scale. Currently 95% of the H_2 consumed around the world comes through the industrial production process of Steam Methane Reformation (SMR) in which CH_4 gas is made to react with steam at high temperature and pressure producing H_2, but also CO_2 as a by-product. SMR process releases 10 to 12 tons of CO_2 per ton of H_2 produced and so this is not green H_2 *sensu stricto*. SMR process can be sustainable only if the emitted CO_2 is captured and stored cost-effectively so that it does not add up to atmospheric CO_2 load.

As a chemical raw material, H_2 has many industrial applications: in the production of synthetic ammonia required for the manufacture of ammoniacal fertilizer; synthesis of methanol (or methyl alcohol), and in petroleum refining by hydrogenation reaction. It is also an important rocket fuel in space exploration, in propulsion systems in transportation such as ships, space- and aircrafts, submarines, etc. The demand and consumption of H_2 are obviously increasing. H_2 can also be produced on industrial scales by splitting water into its chemical components H_2 and O_2 using electrical energy. This is a process which requires significant volumes of pure water, often a rare commodity, besides critical materials and energy, all of which is not a very profitable proposition. Further, to make water electrolysis sustainable and the H_2 so produced truly green electric power should come from renewable sources such as solar and wind energy but again there is a cost barrier. The current strategy is mainly to promote H_2 production by water electrolysis using renewable sources of energy.

H_2 is an energy vector and source at the same time. The term "energy vector" refers to "an energy-rich substance that facilitates the translocation and/or storage of energy in any physical form with the intention of using it at a distance in time and/or space from the primary production site". H_2 can burn and release energy without emitting greenhouse gases and can also store electrical energy that can be harvested through hydrogen fuel cells. It is the most abundant chemical component of the universe (75%), and together with helium makes up 99.99% of the chemical ingredients of the universe. Thus, although H_2 is virtually inexhaustible the element rarely exists in its native form on earth, whereas when combined with oxygen it is quite abundant as water molecule from which it can be produced by electrolytic splitting. CH_4 can also be split into C and H_2 in the absence of O_2 in a method known as pyrolysis, using plasma technologies but that also requires heat or electricity and again relies on the availability of primary energy sources. The extraction of natural H_2 originating from geological sources circumvents all the above-mentioned hurdles associated with H_2 production. Currently the production cost of natural H_2 is 2 to 10 times cheaper than industrial production processes. It is an abundant and inexpensive source of truly green H_2. Could naturally occurring, zero-carbon H_2 play a crucial role in future energy sector? Being a non-polluting fuel, natural H_2 emanating from geological formations (geological hydrogen) could soon revolutionise the energy scenario and play a vital role in decarbonising industries. With the discovery of abundant geological H_2 in all continents of the world a sunrise industry based on natural H_2 is poised to make a landmark in the green energy sector.

The veritable rainbow of hydrogen: H_2 is an odourless and colourless gas, but in commerce various colours are used to qualify it based on how carbon-free is its production. ***Grey H_2*** refers to H_2 produced from natural gas or CH_4 by SMR process but without capturing the greenhouse gases given out in the process. ***Blue H_2*** is H_2 produced in SMR but with the emitted greenhouse gases captured. ***Green H_2*** is produced from sources other than hydrocarbons not involving burning of CO_2-emitting fuels. ***Pink H_2*** involves production through nuclear-driven processes but generates radioactive wastes. ***Geological H_2*** is designated as ***White H_2*** or gold H_2, also known as native H_2 or natural H_2 and is the most carbon-free energy source. No carbon is involved in its generation at the source nor during consumption in various end-uses.

Many readers of this article would have heard of the Chimaera flames (Fig.1A) or the eternal flames of Chimaera, near the city of Antalya, Turkey. Chimaera flares are one of the natural wonders of the world which have been burning for two and a half millennia and was said to be the source of the first Olympic torch (1896, Athens). The flames are documented by Pliny the elder in his work *Naturalis Historia*, written around 79 BCE. For a long time the perplexing flares of Chimaera were mysteries. The long held local myth about the flame is that these fires are the breath of a hybrid monster called Chimaera (described by Homer in his magnum opus *Iliad*).

Several scientific explorations in the area now confirm that the Chimaera fires are due to the ignition of natural H_2 and CH_4 emanating from ophiolite rocks underneath, where rock-water interactions generate molecular H_2 (ophiolite refers to jumbled up blocks of oceanic lithosphere thrust over continents during plate motions, an important component of which is ultramafic rock that is the chief source of H_2). Meteoric waters percolating through associated limestones of ophiolite become carbonated, and eventually the dissolved CO_2 combines with H_2 producing CH_4.

A series of recent studies confirm that emanations of natural H_2 are more widespread and common on our planet than was previously known. Following a number of discoveries in Siberia, United States, Australia, Mali, Brazil and Eastern Europe there has been an explosion in publications related to natural H_2 in the last one and a half decades. These are obvious signs of geological H_2 as a promising and renewable energy resource, unlike fossil fuels, for green energy transition in the coming years.

What then is geological hydrogen? Geological hydrogen is H_2 generated in rock formations by a process called hydrolysis where the rocks are altered by reaction with water. Rocks containing minerals wherein iron is present in ferrous (Fe^{2+}, reduced; or Mg as Mg^2) state undergo oxidation in presence of water. In the process the ferrous iron is oxidised to ferric state (Fe^{3+}, or Mg^{2+} to Mg^{3+}) taking oxygen from water, thereby freeing H_2 gas. This H_2 either becomes accumulated in suitable rock reservoirs or escapes into the atmosphere and is eventually lost to space. From a geological perspective, in fact, H_2 has been neglected because of a lack of quantitative information about geological H_2 emissions and the general assumption that this is not a potential exploitable resource. In reality, however, this is not so considering recently discovered resources worldwide. For instance, a recent find of natural H_2 in an abandoned coal mine in France has a reported resource of the order of 46 million tons (6 to 250 million tones according to some estimates). These are a pointer to the stupendous nature of the hidden geological H_2 resource.

However, there are no strategies to exploit natural H_2 at the moment for lack of sufficient information about the hidden H_2. The whole subject is in its infancy and many questions about natural H_2 are yet to find satisfactory answers. Lack of knowledge on natural H_2 is due to various factors. Most of the millions of wells drilled to date are in sedimentary basins which are unlikely places for natural H_2 to be present in abundance. Being a light gas H_2 diffuses easily and quickly leaves its place of seepage. Besides, it is a very reactive gas and quickly combines with O_2 to produce H_2O. For these reasons H_2 leaves no trace in its place of origin or seepage especially if it is in low abundance. For the same reasons, explorers never focussed on detection of H_2, and geological H_2 has by and large been overlooked, and for decades geologists believed that the earth did not hold significant H_2 deposits.

A paradigm shift: The earliest record of natural H_2 seepage was by Dmitri Mendeleev, the father of the Periodic Table of Elements who in 1888 reported H_2 seeping from cracks in a coal mine in Ukraine. Later the German scientist Ernst Erdman is reported to have documented the flow of H_2 at a salt mine in Strassfurt, Germany. However, it was the discovery of seafloor hydrothermal vents in 1977 in the East Pacific Rise that paved the way for our understanding that H_2 is an important component of hydrothermal vent discharges all along the 80,000 kilometre-long Mid-Ocean Ridges. The discovery of Lost City Hydrothermal Field off the Mid-Atlantic Ridge in 2000 was another milestone where mantle peridotites exposed at the sea floor are in contact with sea water, and rock-water interactions in this geologic setting was observed to produce H_2. Thus, natural H_2 produced by water-rock interactions has been observed for a long time but on a large scale it was considered to happen mainly along the Mid-Ocean Ridges where hot newly created oceanic crust is in immediate contact with seawater. This resource of natural H_2 in the middle of the deep sea far away from the coast is currently unfavourable for any economically viable H_2 production.

The real H_2 boom, in fact, commenced with the fortuitous discovery of natural H_2 flow in a water-well in Bourakebougou village, Mali in Western Africa. An accumulation of H_2 was found here in 1987 at a shallow depth of 110 m during a water well drilling operation. One of the drillers smoking a cigarette was reportedly badly injured by an exploding flux of gas. Subsequent analysis revealed the gas to be mainly H_2. And today a natural- H_2 -based power plant here is producing electricity to lighten Bourakebougou, the first instance of natural H_2 tapping in the world. This breakthrough discovery in Mali represents a significant milestone in the natural H_2 business and is gathering momentum in exploration all over the world. Since Mali's success in tapping natural H_2 prospectors are now fanning out across the globe in vigorous exploration activities with many new finds in USA, Brazil, Australia, Eastern Europe, Namibia, Spain, Russia and so on. Thus, contrary to conventional wisdom, earth harbours vast deposits of natural H_2 that could be tapped like oil.

The earth's hydrogen factories: Natural H_2 either as free gas, as gaseous inclusions in minerals or as dissolved gas in underground waters is found in a wide variety of geological settings, both offshore and onshore. There are well-documented occurrences of natural H_2 within copper mines in Ontario, Canada, and South African gold, platinum and chromite mines, and in geothermal brines in Iceland. Natural H_2 has been documented in many super-deep wells drilled to a depth of 5 km or more such as the Kola super-deep well (12.2 km) where the gas emissions are mainly H_2-N_2-rich with an increase in H_2 recorded at deeper horizons below 8 km. Interestingly at this depth no water was encountered making it unlikely that the detected H_2 was produced by reaction with water, and in all probability it is primordial H_2 leaking from the lower mantle or outer core.

Origin of geological hydrogen: Despite H_2 being the most abundant molecule in the universe, in the earth's atmosphere it exists only in trace quantities of about 0.5 ppm. Other than this natural H_2 occurs essentially combined with O_2 (in H_2O) and with C in all hydrocarbons (methane, ethane, propane, etc). However, several natural phenomena lead to continuous generation of H_2 in the earth's crust. For instance, rock-water interaction or hydrolysis releasing free H_2 can be observed in multiple geological contexts. The reaction is fast and efficient at high temperature of ~300°C, but also possible at lower temperature. There are different naturally occurring processes in the earth's crust producing H_2 by different reaction processes. The best known are (i) hydrothermal alteration of ultramafic rocks; (ii) splitting of water molecule (called radiolysis) by radioactive energy of uranium, thorium and potassium present in rocks, (iii) bacterial fermentation of organic matter in the absence of oxygen, (iv) decomposition of CH_4 into graphite and H_2 under upper mantle

Fig.1. A. The eternal fires of Mount Chimaera at Yanartas in Antalya, Turkeya is the biggest emission of abiogenic CH_4 discovered on land so far and has been burning for more than 2500 years. Natural H_2 produced by water-rock interactions in underlying Takirova ophiolites generates H_2 that on reaction with dissolved CO_2 in circulating waters eventually produces CH_4 (image GettyiStock); **B:** Fairy circles are bare patches of soil bordered by a ring of taller grasses found dotting the desert grass lands in many countries, and are obvious signs of H_2 seeps from below. Such structures in eastern coastal plains of the USA are called Carolina Bays. Here fairy circles in Namibia's Marienfluss valley (image credit: robertharding/Alamy Stock Photo).

conditions and (v) rock fracturing and breakage of chemical bonds in silicate minerals generating free radicals and eventually H_2. Among these potential H_2 sources, hydrolysis of ultramafic rocks producing serpentinite (serpentinisation) remains by far the most studied.

Active serpentinisation is an ongoing process in many ophiolite rock assemblages in places such as Oman, Turkey, New Caledonia, Cyprus, Columbia and so on producing H_2 and CH_4. What is important to note here is that in all these cases it is the flow of H_2 and not an accumulated fossil H_2 resource that is measured, while H_2 is continuously being generated in these settings. Besides the above, large quantities of primordial H_2 are available in the earth's mantle and core where it is in combination with metals like Fe and Ni as metal hydrides. This resource has also been pondered by some researchers as a potential source of H_2.

In addition to the above geologic settings for H_2 generation, certain other occurrences of H_2 are also known though its source in these settings is not always clear: (i) H_2 is a major gaseous component (up to 30%) in ancient evaporite formations where the gas is seen trapped inside salt crystals; (ii) H_2 contents ranging from 2.9 to 40% are reported in coal-derived gases such as coal bed CH_4; (iii) H_2 seepages have been discovered in sub-circular depressions called fairy circles (Fig.1B) located in intra-cratonic basins all over the world such as the East European craton in Russia, the Atlantic coastal plain in North Carolina, USA, Namibia and Australia where absence of or sparse vegetation is very remarkable; (iv) accumulation of H_2 up to 500 ppm is reported in the clay deposits surrounding the Cidar Lake uranium mine in Canada where water radiolysis by natural radioactivity of uranium generates H_2.

Banded Iron Formations (BIF) are abundant in the cratonic areas of all continents of the world constituting the chief commercial sources of iron. Recent experimental studies have demonstrated BIF as potential source rocks for H_2 generation, and have also been confirmed by field observations of H_2 in soils in the vicinity of BIF in Namibia, Brazil, Australian and S. Africa, supporting the experimental demonstration. The mineral magnetite (Fe_3O_4) is a byproduct of virtually all chemical reactions producing natural H_2 and acts a catalyst augmenting subsequent H_2-producing reactions. Further magnetite present in BIF has about 30% Fe^{2+} sites in its crystal lattice that is amenable for oxidation in presence of water which can liberate H_2. Besides magnetite, BIF have iron carbonate (siderite and ankerite) and iron silicate minerals (stilpnomelane, riebeckite, minnesotaite, etc) that also have Fe^{2+} sites congenial for oxidation and H_2 generation. BIF are thus a newly identified source rock for H_2 production and should form targets for exploration of natural H_2.

Natural hydrogen resources: At the moment there are many uncertainties in exploitation of natural hydrogen as the subject is still in infancy stage, but the most important is a lack of scientific information about the generation and commercially exploitable accumulation of native H_2 on earth; it is also unclear if the resource occurs in a reservoir formation with a cap rock as seal similar to petroleum resources, though atleast in Mali this appears to be the situation. Besides, as a gas though H_2 moves only vertically, under confining pressures it can go into partial solution in underground water and hence can also move horizontally with water. Under such circumstances it may have a source far away from where it is observed on the surface. Another apprehension is whether it can compete with the industrial sources of H_2 such as blue and grey H_2 currently being produced commercially. Expert opinion in this field is divided but many agree that natural H_2 can be a cost-competitive future resource compared to present H_2-feedstock. However, the processes that produce geological H_2 are not fully understood while it is generated in a large range of geological settings both oceanic and continental, and also by biogenic and abiogenic processes.

Because of the above constraints estimates of hidden H_2 resources vary significantly and do not at all indicate the potentiality of the resource. Global H_2 emissions from geologic sources are estimated to be of the order of 23 million tons per year. This is an order of magnitude higher than previous estimates but not high enough considering recently discovered worldwide diffusive seepages. According to Viacheslav Zgonnik, of Natural H_2 Energy, USA, an expert in this discipline the annual generation rate of H_2 in crustal geological settings is approximately 254±91 billion cubic metres whereas another recent estimate gives a much lower value of 31 billion cubic metres. Nevertheless, according to Zgonnik, global natural H_2 production rates have been greatly under-estimated while the most optimistic natural H_2 resource estimate is still lower than the current industrial H_2 production. For example, according to International Energy Agency world industrial H_2 production in 2019 was 4.1 trillion cubic metres whereas currently known natural H_2 resources are about 2 orders of magnitude lower than this. What is to be remembered here is that what is being measured is not the resource as a deposit but only the H_2 production rates, and that it is continuously being generated in rock formations. This is unlike other minerals resources where there is a physical resource whose dimensions can be gathered and resource estimated by drilling. Obviously currently known resources are grossly underwhelming and the real figures will become apparent as technology of H_2 exploration improves. Considering that we are virtually sitting on a H_2 iceberg and that the production cost of natural H_2 is only $1.0-0.5 per kg, far below the cost of industrial production by SMR and water electrolysis ($ 1-7.5 per kg) experts are optimistic that the natural H_2 resource can meet or even surpass the world demand for H_2 in the near future.

Limitations of hydrogen as an energy vector: Notwithstanding the fact that H_2 burning produces carbon-free, clean energy it has its own limitations as an energy vector. Given that molecular H_2 is the most energy-rich gas, at ambient pressures a kilogram of H_2 occupies 12 cubic metres of space which means H_2 requires enormous storage space. Pressurised tanks can hold more but adds weight and costs to vehicles. Liquefying would circumvent the storage problem but requires chilling the gas to -253°C that again is prohibitively expensive. Converting H_2 to metal hydrides, particularly rare earth metal hydrides would eliminate the storage issues to a considerable extent. The extremely small size of H_2 molecule (120 picometre) allows it to leak and escape while using usual kinds of plumbing systems, though fabrication of special polymers impervious to H_2 are in the process of commercialisation. For these reasons H_2 has to be consumed at the place not far away from its site of production. These storage issues along with lack of pipelines and distribution systems are the main reasons why Li-ion batteries are preferred over H_2 fuel cells in the race to electrify automobiles.

Indian initiatives: Though India has already embarked on a National Green Hydrogen Mission (NGHM, 2023) under the Ministry of New and Renewable Energy with the goal of achieving Net Zero emissions by 2070 there is no reference to geological hydrogen therein (which is presumably is due to lack of awareness). The aim of the Mission is to produce green hydrogen utilising renewable energy sources such as wind, solar, etc. from fossils fuels particularly natural gas, and electrolysis of water. Therefore, as far as the country is concerned, the author has no information if anyone has taken up any initiative towards exploring the country for this nascent resource though the geological settings of the country are very congenial and potential for natural hydrogen generation. The Archaean cratons enclosing greenstone belts with numerous alkaline plutons, faultlines criss-crossing the terrain, the ophiolite belts of Manipur-Nagaland, Andaman Islands and the Himalayan belts and mountains of BIF present in the Karnataka, Bastar, Singhbhum and Bundelkhand cratons are all ideal loci to explore for geological hydrogen. Perhaps not many including geologists and geoscience experts in sister disciplines are aware of the new developments going on around the world in this novel field of energy research. It is hoped that this article will be an eye opener to government agencies, the Geological Survey of India in particular and earth scientists in sister organisations in the country to commence exploration in this direction so that we do not lag behind others in our quest for green energy alternatives.

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