The Hydrogen Economy: Can it be based on Mineral (Natural) Hydrogen?

Dr Michael C Clarke, MPESA, CPEng, FIEAust, FAusIMM, RPEQ (Mining & Chemical)

Consulting Engineer, Infrastructure Development & Resource Management
METTS Pty Ltd, Gold Coast. Queensland, Australia

Email: michael.clarke@metts.com.au

Abstract

The world has been eagerly seeking to have hydrogen as the principal energy carrier and energy source. Government leaders, world identities and gradually the general populace have come to the consensus that something must be done to rein in real (or perceived) climate change. Can finding and developing natural hydrogen resources be a realistic possibility and make significant contributions to the world economy?

There have been natural gas finds in Australia that have hydrogen as a constituent. One find in the Northern Territory had hydrogen at over 10% but most finds there had only trace hydrogen. Natural hydrogen can occur with helium and a sequential production path for both gases will be discussed in the talk and the accompanying paper. Other ways of producing hydrogen are by reforming methane and/or partially oxidising coal or lignite with steam. The 'other ways', however, produce carbon dioxide that would need to be sequestered if the processes were claimed to be 'green'.

Financial assistance from government, environmental quangos and 'green' entrepreneurs has been promised to support the development of the Hydrogen Economy. Will research be able to overcome the major technical and safety hurdles that are associated with hydrogen and the Hydrogen Economy? Only time will tell!

Introduction

White, Gold, Natural, Native, Geologic or Mineral Hydrogen are names for hydrogen that originates from deep in the earth and that under normal conditions permeates to the earth's surface and thence the atmosphere (eg Boreham et al, 2021). It should be noted that hydrogen and helium are the only two elements that we can be certain are lost to the earth (Catling and Zahnle, 2009). In this paper it is called mineral hydrogen, since it is a gaseous mineral.

Hydrogen is often a component of natural gas (NG). It may be in trace concentrations or (occasionally) in higher concentrations. In higher concentrations it has caught the attention of that part of the community that is hoping for a hydrogen revolution to avert the energy crisis that is threatening world stability.

The world has been eagerly seeking to have hydrogen as the principal energy carrier and an energy source. World leaders, opinion makers and gradually the general populace have come to consensus that something must be done to reign-in real (or perceived) anthropogenic climate change. They believe that hydrogen will be the key to decarbonisation. However, can finding and developing hydrogen resources that will satisfy the assumed demand for hydrogen without carbon emissions be achieved? Will using the whole or fragments of the conceptualised Hydrogen Economy become a technical and economic reality?

Mineral Hydrogen: is it ever a major, high concentration, high volume natural gas constituent?

In many parts of the world there have been natural gas finds with substantial concentrations of mineral hydrogen, as shown in Figure 1. One find in Mali, West Africa, is of particular note: gas from the Bougou 1 well was analysed at having 97.4% H_2, 1% N_2 and less than 1% methane (Prinzhofer et al, 2018). Detailed estimates of that well's resource size and extended productivity are not available, although the mineral hydrogen was used to power a regional village for over four years. A major find with similar gas analysis of Bougou 1 is what is sought by gas explorers.

In Australia, Geoscience Australia has published a detailed paper of where mineral hydrogen has been found. Concentrations of helium have been found in some wells that also contain hydrogen (Boreham et al., 2018; 2021); do they point to a complex dual gas formation system in some instances?

There have been NG finds in the Northern Territory that have hydrogen as a constituent, with one find having over 10% hydrogen and the other just a trace, as shown in Table 1. Note that the relatively low methane counts in both analyse and the very high nitrogen and helium concentrations. Overall these are relatively poor fuel gases.

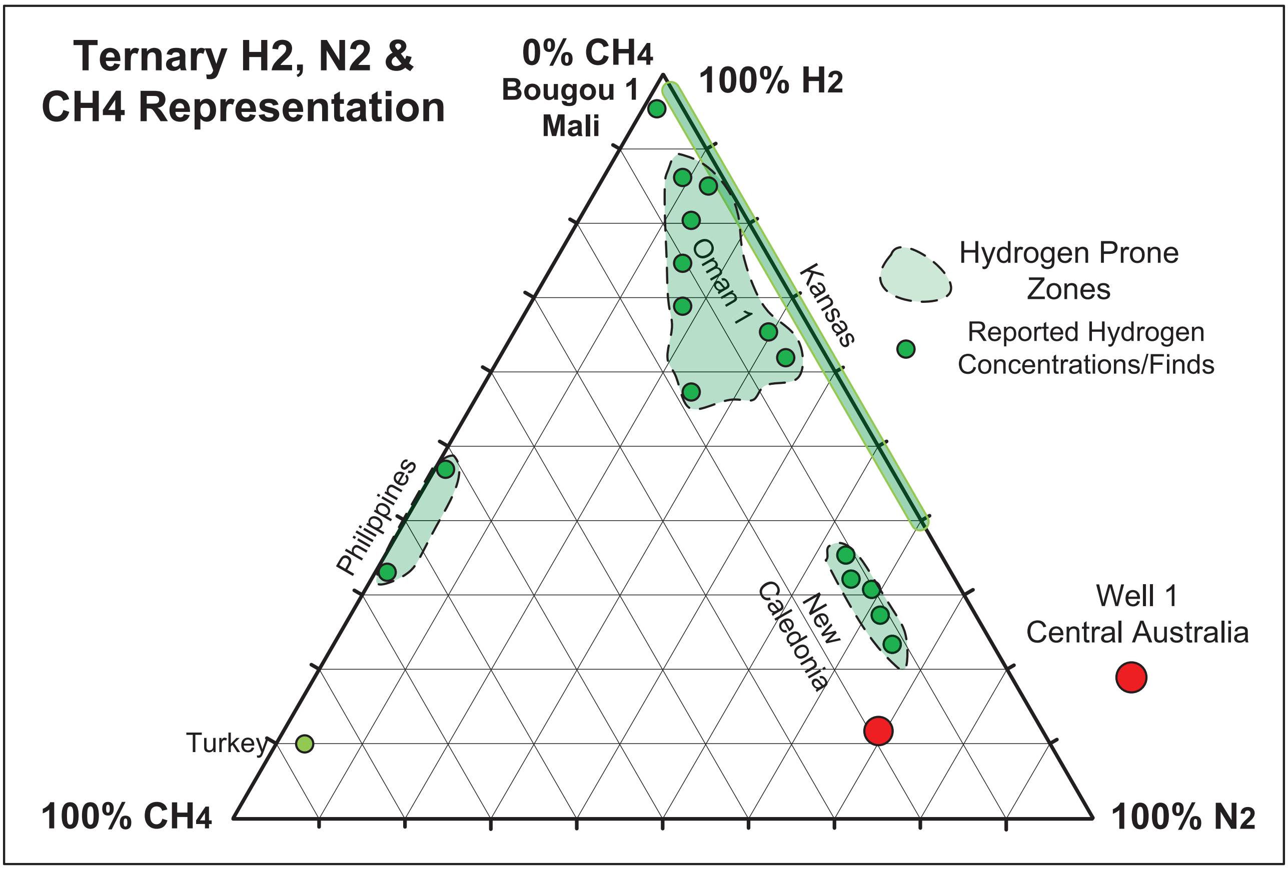

Figure 1. Ternary diagram of hydrogen-prone areas and finds (modified after Prinzhofer et al, 2018).

	MOUNT KITTY 1	MAGEE 1
Component	Mole %	Mole %
Helium	9	6·24
Mineral Hydrogen	11	0·03
Nitrogen	61	43·87
Methane	13	33·49
Ethane	4	6·41
Other hydrocarbon	NA	3·41
Total	**98**	**100·00**

Table 1. Analyses of natural gas finds in Central Australia. Data sourced from Central Petroleum 2010-2014 in Boreham et al (2021).

Separating the gases, can it be achieved? Yes, but at a cost

Cryogenics give a good separation of the gases, as graphically indicated in Figures 2a and 2b. Here each gas is extracted according to its boiling point, with the separation of hydrogen from helium being the last separation and most probably being undertaken in an expanded helium plant.

The questions that must be asked here concern the economics of the separation and the logistics required to take the product gases to market.

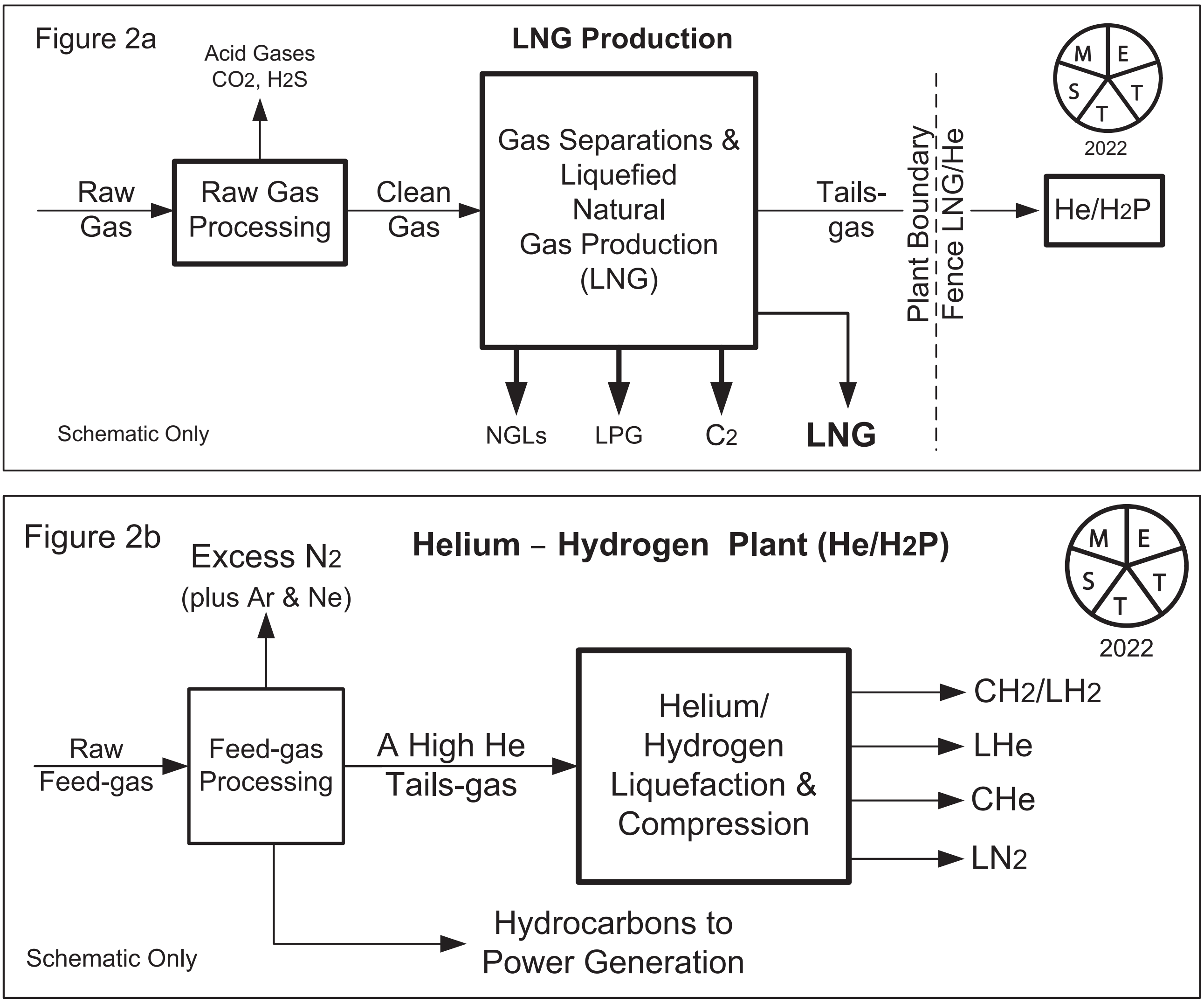

***Figure 2. (a)** LNG Production with Off-gas Delivery to a Helium– Hydrogen Plant. **(b)** Products, including Hydrogen, from Tail-gas Processing. CH2 Compressed Hydrogen, LH2 Liquid Hydrogen, LHe Liquid Helium, CHe Compressed Helium, LH Liquid Nitrogen.*

A major economic differentiation of hydrogen and helium.

As well as having very different physical and chemical properties the helium and hydrogen (and the other gases) have very different economics. Hydrogen is an industrial fuel, energy carrier and chemical reagent, whilst the helium is a critical mineral. Removing the carbon dioxide could be a major cost if venting to atmosphere was not allowed. The fuel gases (including the hydrogen) could be used to run the gas separation and compression units. Nitrogen could be used as a 'cold' transfer agent (Clarke, 2020).

The Magee and the Mt Kitty plays will likely succeed if the helium is in sufficient recoverable quantities to install and run the separations plant, the ancillary power plant and the required helium logistics. Given the remote locations of the finds, the value of the other gases, including hydrogen, will only be significant if very large resources are revealed and profitable logistics are created. Information on the operational co-production of helium and hydrogen in plants is needed for this to be developed in 'high-graded' areas.

Sources of Helium and Hydrogen

The stable isotopes of helium are ^{3}He and ^{4}He. ^{4}He appears to be mostly a product of uranium and thorium decay in the earth's mantle and crust. ^{3}He was most likely formed in the Big Bang and is distributed through the earth; anthropogenic production of ^{3}He is via spalling lithium in high intensity flux reactors to create thermonuclear fuel. ^{4}He is also a left-over from the Big Bang as well as being a product of U/Th decay in the earth's core and occurs in concentrations many orders of magnitude higher than ^{3}He (Ballentine and Burnard, 2002). Therefore, the helium, both ^{3}He and ^{4}He, emanating from earth's surface must be from mixed sources. This point is useful in planning NG exploration programmes.

MOLECULE/ATOM	MOLECULAR/ATOMIC MASS	ATMOSPHERIC ABUNDANCE	BOILING POINT
H_2	2·016	0·55 ppm	20·3 K
^3He	3·016	0·000137% of 5·2 ppm	3·2 K
^4He	4·003	5·2 ppm	4·2 K

Table 2. *The Properties of Hydrogen and the Two Stable Helium Isotopes.*

^3He has less mass than ^4He and a smaller atomic diameter. Hydrogen, a two-proton element, is also extremely small; the progression of H_2, ^3He and ^4He through the earth and thence to space may be in tandem. Comparative properties of the three particles in the atmosphere are presented in Table 2.

The ratio of ^3He to ^4He has become of interest to some geoscientists; understanding the ratio may assist with selecting formations for helium exploration. Note that ^3He is a very extremely expensive cryogenic research tool. We know that there is primordial helium in the earth. A question that should be asked:

Is there primordial hydrogen in the earth or is there only secondary hydrogen produced by the destruction of water and other hydrogen containing molecules such as hydrocarbons?

The Reaction of Water and Ferrous Minerals to Produce Ferric Minerals and Hydrogen

The simple reaction is: Ferrous Ions plus water → Ferric Ions plus Hydrogen (Moretti and Webber, 2021). The authors go on to discuss how hydrogen produced in this manner can result in "Fairy Circles", being where vegetation has been destroyed and where hydrogen seeps to the surface. The authors also go onto state "For H_2 we still lack knowledge and there are few wells dedicated to (hydrogen) exploration … ". The authors also postulate that, "natural hydrogen is available at globally relevant volumes"; only time will tell!

The Cracking of Hydrocarbons to Produce Solid Carbon and Hydrogen

Hydrogen is produced by high temperature cracking of methane from volcanism or subduction friction, as shown in Figure 3. Carbon is also produced but being a solid it does not migrate like hydrogen. Helium may or may not be a significant inclusion, depending on the presence of regional uranium and thorium. Nitrogen may be present through the destruction of organic biomass or from primordial sources. The cracking of hydrocarbons is dependent on heat and catalysis, with carbon allotropes determined by conditions of source and geohistory.

A Geological Source of both Hydrogen and Helium

With the potential of having a Hydrogen Economy with its replacement of carbon-based fuels with hydrogen, another source of hydrogen and in fact helium exists. For the petroleum explorationist it provides another reason for undertaking both helium and hydrogen analyses on natural gas finds.

The co-production of hydrogen and helium near simultaneously has recently been "rediscovered" during the search for hydrogen sources. Ionising radiation, including that radiation released on the production of an alpha (α) particle (a helium-4 atom) during the decay of a uranium or thorium atom, can produce hydrogen by water radiolysis (Le Caër, 2011; Boreham et al., 2021).

According to Le Caër (2011), the radiation produced from U/Th decay in an aqueous system is "reflected by Linear Energy Transfer …. . Low-LET radiation (gamma radiation, accelerated electrons and X-rays … , whereas high-LET radiation (heavy ions, alpha particles and neutrons) deposits it (energy) densely." Potentially the production of helium can trigger the production of hydrogen. Water Radiolysis can be written as follows (Le Caër, 2011):

$$H_2O \xrightarrow{\text{Ionising Radiation}} e^-_{aq}, HO^*, H^*, HO_2^*, H_3O^+, OH^-, H_2O_2, \mathbf{H2}$$

** indicates a transient radical, e- an electron.*

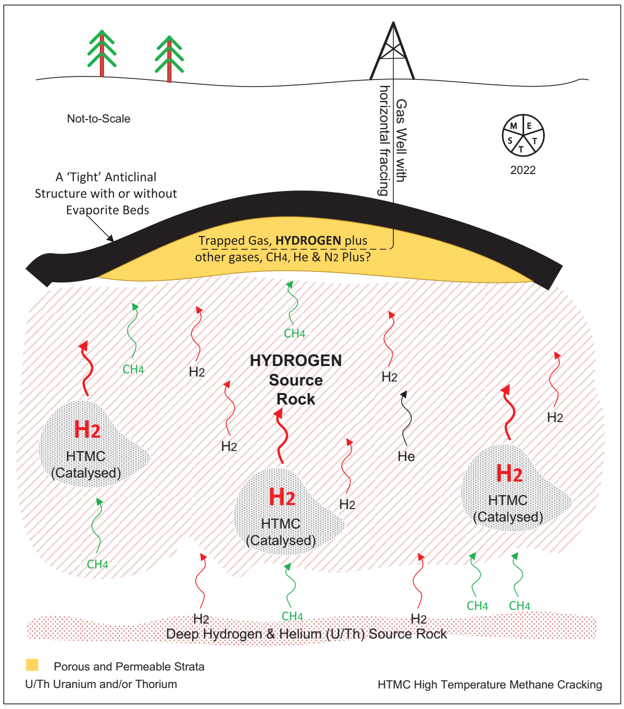

Figure 3. Schematic diagram of production of hydrogen by high temperature cracking of methane due to volcanism or subduction friction.

A Role for decaying nuclides in the production of hydrogen

Hydrogen can also be produced from the splitting of water by ionising radiation following the decay of radioactive elements. An example is shown in Figure 4.

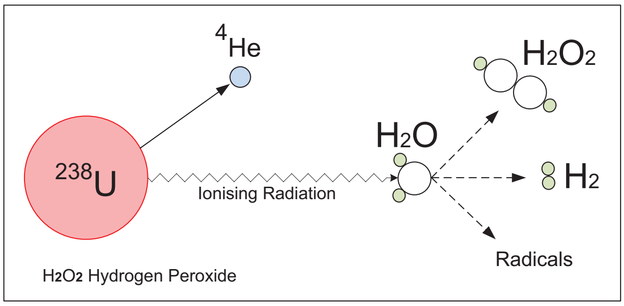

Figure 4. Ionising radiation from the decay of ^{238}U splitting water to produce hydrogen.

It should be noted that hydrogen is the only totally stable product of water radiolysis; hydrogen peroxide (H_2O_2) will decompose in the presence of many metal ions and produce free radicals.

The Energy Source for Producing Hydrogen from Radiolysis

Uranium and thorium atoms are too unstable and lose mass especially by spalling-off an alpha particle (a ^{4}He atom). The spalling will also produce a burst of energy which for ^{238}U will be 4.27 MeV*.

A Decay Energy greater than 4MeV (million electron volts) can produce hydrogen by radiolysis. Table 3 shows the decay of ^{238}U to ^{234}U producing a burst of energy of 4·27MeV. ^{234}U eventually decays to produce ^{206}Pb, a stable lead atom.

Hydrogen Sources: Is there enough hydrogen to create and maintain a Hydrogen Economy?

The concept of having a Hydrogen Economy, being an energy-based economy without carbon, has been promoted as the way to a renewable future (Crabtree et al, 2004). A very major challenge is the sourcing of sufficient hydrogen to meet the total demand and specific demands for energy. Some of the proposals for sourcing energy are:

- The use of photosynthesis to crack water into hydrogen and oxygen,
- A much greater reliance on hydro-power to produce endless and continuous electricity to cover the intermittent nature of renewable energy, and use the "endless" electricity in electrolysis plants to produce hydrogen and oxygen,
- Crack methane (or other hydrocarbons) to produce solid carbon and hydrogen (Kvaerner Patent, 2011),
- Reform natural gas to produce hydrogen and carbon dioxide (as is now the case) and "successfully" sequester the CO_2 (for eons) to produce Blue Hydrogen, and/or
- Find substantial and recoverable resources of Mineral Hydrogen from deep geological formations.

All the above hydrogen production techniques have great challenges in terms of meeting worldwide demand for hydrogen if the Hydrogen Economy is to become a serious proposition. In the author's opinion the Hydrogen Economy is unsustainable unless affordable H_2 exists either through finding enormous reserves of mineral hydrogen or cheap electricity is available.

Other potential 'real' sources of hydrogen that could satisfy niche demands

Of some interest is methane cracking in terms of producing hydrogen and potentially very valuable solid carbon products. Those products may include graphene, needle-carbon, pure amorphous carbon and fullerenes, whereas diamonds are an unlikely product of methane cracking. The production of a carbon prime product may provide a positive impact to lowering hydrogen pricing. The process was originally promoted by the Kvaerner Corp (Kvaerner Patent, 2011) but failed to progress due to costs. Where electricity is available at an advantageous price, the economic use of that electricity in electrolysis plants may be possible if a price is put on the oxygen co-product. That oxygen could increasingly be utilised in community sanitation that could bring major benefits to world health. Could carbon and oxygen co-products make the hydrogen economy more feasible?

NATURAL NUCLIDE	DECAY PRODUCT	DECAY ENERGY MEV	HALF-LIFE YEARS
Thorium 232	Alpha particle	4·08	1·405 x 1010
Uranium 235	Alpha particle	4·68	7·04 x 108
Uranium 238	Alpha particle	4·27*	4·468 x 109

* 4.27 MeV = 6.84 x 10^{-13} Joules

Table 3. *Nuclides, decay products, decay energy and decay half-life.*

Mineral Hydrogen: Has it real worth?

The real worth of mineral hydrogen is yet to be realised. Very large and very pure H_2 deposits that have good logistics (being transportable by pipeline as compressed gas) and ready markets will help in establishing that worth. Do they exist? Can they be found? Will they exist in situations that have acceptable logistics?

Mineral Hydrogen: Has it real worth?

The real worth of mineral hydrogen is yet to be realised. Very large and very pure H_2 deposits that have good logistics (being transportable by pipeline as compressed gas) and ready markets will help in establishing that worth. Do they exist? Can they be found? Will they exist in situations that have acceptable logistics?

Is Hydrogen a Greenhouse Gas with a serious Global Warming Potential a potential game changer?

Frazer-Nash (2022) produced a report for the British Government on the Greenhouse Gas (GHG) properties of hydrogen, questioning the hypothesis that carbon dioxide and methane are the only major GHGs and that by switching from a carbon economy to a hydrogen economy the world will be saved from a temperature-induced catastrophe (ie global warming). The Report states "there is an increasing body of evidence that hydrogen is itself an indirect greenhouse gas and recent research suggests that it has a Global Warming Potential 11 times that of carbon dioxide (over a 100-year time horizon). Hydrogen, by its nature, is hard to contain and understanding how much hydrogen could be emitted to the atmosphere in a future hydrogen energy system is important for policy development".

Producing, transporting, storing, reticulating and using more hydrogen will enrich the atmosphere with another GHG if the Frazer-Nash (2022) conclusion is correct. The benefit of reducing carbon use will be largely fossil fuel conservation, being oil, gas or coal, as against the technology demands of hydrogen. The choice of fossil fuels over hydrogen will be largely economic, not environmental or scientific. The potential for hydrogen to be a serious GHG should continue to be studied.

Conclusion

Finding resources of mineral hydrogen that make sense for development in the Hydrogen Economy world seems very unlikely at this time. Petroleum explorationists searching for natural gas (of any composition) have not yet found very large (TCF) gas reservoirs with a high percentage of mineral hydrogen despite seventy years of natural gas exploration; they are either very unlucky with their explorations or more likely is the realisation that mineral hydrogen exists in relatively small and impure finds or they have been looking in the wrong geological setting.

Mineral hydrogen finds may be enough to provide hydrogen for oil refineries (for petroleum hydrogenation) and/or hydrogen for ammonia plants; these will be niche uses in niche situations. Mineral hydrogen which may be found in situations that require the bulk shipping of liquid (LH_2) for monetisation will be become stranded assets, since LH_2 will be expensive and hazardous to ship (handling of LH_2 is different from LNG; remember LH_2 is not LNG). Hydrogen will likewise be a relatively expensive and hazardous compressed gas (CH_2) to pipe. Compressed hydrogen being reticulated through an urban and commercial region will not be welcomed by hazard-averse populations.

Ending with a question: If there are massive hydrogen resources in the earth's crust, why have they not been discovered and developed?

REFERENCES

Ballentine, C.J. and Burnard, P.G., 2002. Production, release and transport of noble gases in the continental crust. Reviews in Mineralogy and Geochemistry 47, 481–538. https://doi.org/10.2138/rmg.2002.47.12

Boreham, C.J., Edwards, D.S., Poreda, R.J., Darrah, T.H., Zhu, R., Grosjean, E., Main, P., Waltenberg, K. and Henson, P.A., 2018. Helium in the Australian liquefied natural gas economy. The APPEA Journal 58(1) 209–237 https://doi.org/10.1071/AJ17049

Boreham, C.J., Edwards, D.S., Czado, K., Rollet, N., Wang, L., van der Wielen, S. Champion, D., Blewett, R., Feitz, A. and Henson, P.A., 2021. Hydrogen in Australian natural gas: occurrences, sources and resources. The APPEA Journal 2021, 61, 163–191. https://doi.org/10.1071/AJ20044

Catling, D. and Zahnle, K., 2009. The escape of planetary atmospheres. Scientific American, https://geosci.uchicago.edu/~kite/doc/Catling2009.pdf

Clarke, M.C., 2020. Making Nitrogen a Valuable Co-product of Helium Recovery from Natural Gas. PESA News, Issue 158, 3rd Qtr.

Crabtree, G., Dresselhaus, M. and Buchannan, M., 2004. Hydrogen Economy. Physics Today, Vol 57, Issue 12

Frazer-Nash Consultants, 2022. Fugitive Hydrogen Emissions in a Future Hydrogen Economy. Client: Dept of Business, Energy & Industrial Strategy, UK.

https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1067137/fugitive-hydrogen-emissions-future-hydrogen-economy.pdf

Kvaerner Patent, 2011. Hydrocarbons Cracking, Norway, N0175718C

Krasnovsky, A.A., 2007. Primary Mechanisms of Photoactivation of Molecular Oxygen. History of Development and the Modern Status of Research. Biochemistry (Moscow), 2007, Vol. 72, No. 10, pp. 1065-1080 https://doi.org/10.1134/S0006297907100057

Le Caër, S., 2011. Water Radiolysis: Influence of Oxide Surfaces on Hydrogen Production under ionising Radiation. Water, Vol 3 (1), 235–253, https://doi.org/10.3390/w3010235

Moretti, I. and Webber, M.E. (2021). Natural Hydrogen: a geological curiosity or the primary energy source for a low carbon future? Renewable Matter, https://www.renewablematter.eu/articles/article/natural-hydrogen-a-geological-curiosity-or-the-primary-energy-source-for-a-low-carbon-future

Prinzhofer, A., Tahara Cisse, C.S. and Diallo, A.B., 2018. Discovery of a Large Accumulation of Natural Hydrogen in Bourakebougou (Mali). International Journal of Hydrogen Energy V43 I42, pp 19315–19326. https://doi.org/10.1016/j.ijhydene.2018.08.193