REVIEW ARTICLE

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Can the hydrogen economy concept be the solution to the future energy crisis?

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ABSTRACT

The Hydrogen Economy concept is being proposed as a means of reducing and eventually decarbonising the world's energy use. It looks to hydrogen as being a replacement for methane (natural gas) and generally as a way of removing all fossil fuels from the energy supply. The concept, however, has at least four flaws, as follows: (1) hydrogen has significantly different properties to methane; (2) hydrogen has properties that create significant hazards; (3) hydrogen has a very small initiation (activation) energy; and (4) liquid hydrogen cannot readily replace liquefied natural gas (LNG). Hydrogen's hazards will prevent it from being accepted in a societal sense. To the question 'Can the Hydrogen Economy concept be the solution to the future energy crisis?', the answer is 'no'. Hydrogen has and will have a role in world energy but that role will be limited to industry. For the future we need an advanced electric economy.

ARTICLE HISTORY

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KEYWORDS Hydrogen Economy Hydrogen hazard; reliability; power dispatchability

1. Introduction

Hydrogen has considerably less energy on a volume/volume basis than methane; however, it produces no direct carbon emissions. So an economy with hydrogen as the means of producing, transporting, storing, reticulating and using energy would be a carbon-less economy. A major question is where would you get a hydrogen supply that could meet demand with no carbon release?

Only water and energy are produced by the simple chemical reaction at the core of the H-E:

 $2H_2 + O_2 \rightarrow 2H_2O + ENERGY \Delta H^\circ - 484 \text{ kJ/mol}$ (1).

The concept of H-E was proposed by Ulf Bossel and Baldur Elaisson in January 2003 (Bossel and Elaisson 2003), in an AFDC published report, 'Energy and the Hydrogen Economy'. Bossel and Elaisson recognised the challenges of getting hydrogen into a packaged form where it could be transported from a production site to a use location. Two choices of transport they considered were compressed gas and cryogenic liquid, neither of these options being comparable to natural gas transport in terms of costs and technical challenges.

Bossel and Elaisson (Bossel and Elaisson 2003) estimated that the 'energy consumption of a (hydrogen) liquefaction plant could not drop much below 30% of the higher heating value of the liquified hydrogen'. So using a process that relies on liquefying, as is used in turning natural gas into LNG, is not valid when applied to hydrogen. They went on to state '[p]ipelines that transport hydrogen are inefficient and suffer from diffusion losses, brittleness of pipeline materials and seal leaks'. That is a valid point. There are however, 700 miles of hydrogen pipeline already in existence (Melaina, M W, O Antonia, and P. Penev. 2013), and US Office of Energy Efficiency & Renewable Energy reference quotes 'almost 1600 miles' (OEE&RE 2021); so we know that hydrogen carrying pipelines exist and are probably being built or extended.

To understand what hydrogen may be able to provide it is useful to have a comparison of energy content between hydrogen and methane (natural gas).

Note: This article had to be re-set in a full-page format to allow the ready linking between the narrative and the figures.

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Notes on Publication

This article was web initially published on 4th April 2022 by The Institution of Engineers, Australia and Taylor & Francis (T&F) in the Australian Journal of Multi-Discipline Engineering (AJMDE). There have been some alterations to the document regarding the reorganisation of sections and headings. Further the AJMDE format was two columns, a format that had to accommodate numerous figures as well as two tables in limited space. To achieve a more 'open read' I have put the article's content into a single page format.

The narrative has not been changed in content and neither has the Tables and Figures, with the exception of a correction in the first line of the Introduction, where **weight/weight** was replaced by **volume/volume** with the permission of the publishers, 27th October 2044. Apologies for this mistake.

Additions after the conclusion of the AJMDE article have included:

A Glossary of Terms plus Seven Updates.

The AJMDE article (Taylor and Francis) is at: https://www.tandfonline.com/doi/full/10.1080/14488388.2022.2046325?src=

A friend and colleague of many years, David Paul Wagner, BA, Dip Ed, Grad Dip Lib, a highly literate person, who was in the publishing business, assisted this 'old enginerurr' with 'spellin' and blooper removal; thank you Paul.

Dr Duncan Seddon, a fuels industrial chemist and a friend and colleague of many years, is thanked for his informative discussions and helpful suggestions.

I thank Mr Sivaraman Thulasiraman and his TMUL publishing team for their assistance and their willingness to remove the occasional blooper that escaped earlier excision.

I would like to thank the editor of AJMDE, Dr Mahmoud Efatmaneshnik, for his assistance in working through the T&F publishing system and his inputs to editing.

A Glossary of Terms has been added post the end of the original article. Multiple updates are also included after the Glossary of Terms. Additional updates may be included in this version (here) of the paper on the METTS's website as appropriate.

Best regards, *Mike*

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

2. Properties of hydrogen and methane (natural gas)

Hydrogen has been equated by proponents of H-E as being generally similar to Natural Gas (NG) – methane. There are system losses with both gases during transport and storage and both can be liquefiednusing cryogenic technology. Hydrogen has been described by Crabtree G, Dresselhaus M and Buchanan M (Crabtree, Dresselhaus, and Buchanan 2004) as an energy carrier but it can also be a chemical precursor, as is methane. In practice however, hydrogen and methane are very different. In a highly compressed state hydrogen, say at 25 MPa, has an expansion ratio at of around 1:240 and when liquefied the ratio is 1:848, so liquid H2 is very condensed. Further properties are presented in Table 1.

Tuble 1. Energy Density (Lower Heating Value – Env). [Note				
Fuel	Specific Energy / Energy Density			
Hydrogen	10.8 MJ/m ³ at 20°C @ 1 Bar			
	120.0 MJ/kg at 20°C @ 1 Bar			
	8.5 MJ/L Liquid <20 K			
Methane - NG	35.8 MJ/m ³ at 15°C @ 1 Bar			
	50·0 MJ/kg at 15°C @ 1 Bar			
	21 MJ/L Liquid <111.65 K			

Table 1. Energy Density (Lower Heating Value – LHV). [Note 1]

There is great variation in the components of Natural Gas: some resources are almost entirely methane, some are mainly carbon dioxide and/or nitrogen. An example of a 'good' NG is methane 88.8%, ethane 7.8%, propane 0.2%, CO2 1.9%, N2 1.3% and LHV SE 35 MJ/m³. This gas is a dry gas (low C2+ hydrocarbons) and meets the pipeline standard for CO2 content (<2%CO2); with a reduction in CO2 to less than 50ppm it would be suitable for LNG. N.B. For domestic use this gas could be blended with hydrogen up to 15% H2.

From the volumetric specific energies (MJ/m³) a system that uses methane to move energy will be over three times more efficient than one that uses hydrogen; this fact is a major challenge for the Hydrogen Economy concept. The hazards associated with the H-E concept are another major hurdle that will be addressed later in this paper.

3. The meaning of Hydrogen Economy

H-E proponents often use a graphic, such as Figure 1, in the form of a rosette to show/demonstrate what they consider Hydrogen Economy means. A simplified rosette (from what was first used by the US NERL as a graphic in Oct 2011 and adopted by WIKI as an explanation of H-E (Ruth 2011)) without detailed graphics of say transport, production etc is shown adjacent.

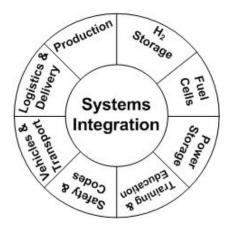


Figure 1. A basic representation of the hydrogen economy

An important inclusion is Systems Integration that will be required since practically the whole energy system will be changed by the full acceptance of H-E.

Many schematic representations have been produced. They show the sequential production (with agglomeration of sources), the transport and storage, and use of hydrogen; Crabtree G et al. (Crabtree, Dresselhaus, and Buchanan 2004) produced a basic schematic which has been expanded and edited in Figures 2 and 13.

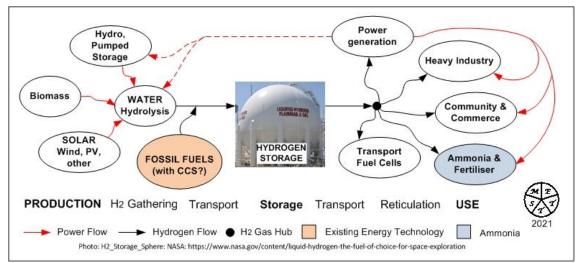


Figure 2. The Stages of the Hydrogen Economy Progression Production: H2 Gathering, Transport, Storage, Transport (post Storage), Reticulation, and Use

The cardinal points in the progression (Figure 2) are:

- Production, making hydrogen by any available method that is economically feasible,
- Gathering and agglomerating all sources of H2,
- Transporting H2, possibly by different means pre and post storage, whilst respecting its innate hazards,
- Storage, a crucial and hopefully leak free stage,
- Reticulation, the sending out of H2 to customers (a sensitive stage where community has a say),
- Using H2 in industry and commerce, but not in urban situations, and
- Hydrogen-fed Fuel Cell Electric Vehicles (HFCEVs), a special sub-case of use requiring very extensive (and expensive) hydrogen reticulation systems using pipelines or road tankers.

For every H-E project the above stages would need a full Environmental, Social and Governance (ESG) analysis as well as a full safety audit. If Green Credits are to be earned when moving from a carbon economy to a hydrogen economy, then green credits auditing would also be required.

4. Transporting, reticulating and 'organising' hydrogen

Transporting hydrogen by pipeline and road is already well established. However, it comes with significant hazards and losses of gas through permeation through steel and composite materials. Transport by ship is still at the early demonstration stage, see Figure 3a.

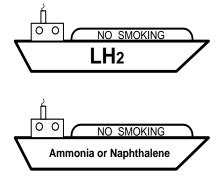


Figure 3a. LH2 by sea. This is still in the demonstration stage. The challenges will be very much to do with materials (steel, other metals composites and flexible tubing), plant (couplings, pumps and compressors, and heat exchangers) and innovative design.

Figure 3b. LH2 'carriers' by sea. Hydrogen can be incorporated into ammonia or a 'cyclic hydrocarbon' producing naphthalene, and then recovered at the destination port. Ammonia will only deliver 18% of its load as H2, and naphthalene 6% of its load as H2. This author believes that neither of those options appear to be financially feasible.

4.1. Reticulation of hydrogen

Reticulation, the dispatch of H₂ to users and customers from a hub, will involve the negotiation of engineering, scheduling and supply management, business, and community relations issues. The engineering includes the supply to customers' inlet nodes, metering, training of customers' labour forces on the use of H₂, and possibly the training of the health, environment and safety inspectorate.

The scheduling will require liaison with customers to understand their supply and use scenarios and help them understand their need for an immediate stand-by supply and working with those customers on the likely cost of using H2 purchased from the hub. The biggest challenge could be to convince the populace that the potential hazards of H2 can be managed and that it is safe for the reticulation system to pass close to their premises.

Using hydrogen in industries other than ammonia production and oil refining will require education and training for staff, management and regulators. It was observed that when gas suppliers switched from coal gas to natural gas in the 1960s and 1970s, considerable effort in educating all interested parties was required. H2 will require a much greater effort.

4.2. Agglomerating resources of hydrogen and power demand

Agglomerating the electrical outputs from multiple generation plants and devices with different and variable outputs will be challenging. Gathering the outputs of multiple hydrogen production plants will likewise be challenging. The PV cells, and batteries connected to those cells, will be producing DC power, which will be immediately available for electrolysis, whereas wind, hydro and biomass will likely be providing AC power that will need to be rectified. See Figures 11 & 13.

4.3. Producing sufficient hydrogen: the biggest challenge

The Hydrogen Economy will require access to vast quantities of hydrogen and those quantities would be far greater than the present demand for natural gas (NG). To meet expectations the hydrogen should be sourced without co-production of carbon dioxide (if CO₂ is co-produced provision should be made for Carbon Capture and Sequestration – CCS). Using an electrolysis technology to reverse the hydrogen oxidation reaction produces hydrogen without carbon:

$$H_{2O} + ENERGY \rightarrow H_{2} + \frac{1}{2}O_{2}$$
 (2)

Using PEM (Proton Exchange Membrane), an advanced water hydrolysis technology, the above equation can be rewritten with the energy inputs shown. (Shiva Kumar and Himabindu 2019)

H2O + Electricity (237·2 kJ/mol) + Heat (48·6 kJ/mol)
$$\rightarrow$$
 H2 + ½O₂ (3)

The total energy required by a PEM hydrolysis plant is 285.8 kJ/mol (0.08 kWh/mol). One mole of H2 weighs ~2 grams. N.B. Reliable electrical energy would also be required for pipeline gas compressing, possibly liquefying, and then compressing hydrogen for storage. Hydrogen systems, especially seaborne, will be very energy demanding. Figure 4.

4.4. The advent of the Hydrogen Vehicle

Where hydrocarbons can be substituted by hydrogen, a reduction in CO₂ emissions, particulates and nitrogen oxides emissions to the atmosphere will occur. Where hydrogen is used in a combustion engine (reciprocating pistons or gas-turbine) particulates will be formed from lubricant combustion and emitted through the exhaust, and, given the high temperatures of hydrogen flame, some nitrogen oxides will also be in the exhaust.

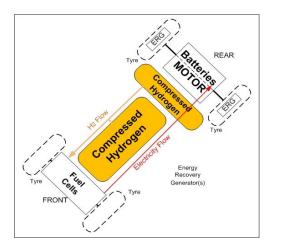


Figure 4. For Hydrogen Fuel Cell Electric Vehicles (HFCEVs) the emissions will be different. A feature of the operation of H-E is the swapping of energy between chemical energy (H2 gas and battery), electricity and mechanical energy.

Here the fuel cells convert chemical energy to electrical energy, while the motor/generator can use electricity for locomotion or recoup mechanical energy as electricity to the battery. Convenient independent battery charging provides an additional energy input. This is useful in start-up. Dual fuelling, with hydrogen and electricity, is evident in hydrogen fuelled vehicles such as the Toyota Mirai.

4.4.1 A Fueling Demand Comparison between HFCEVs and Electric Vehicles (EVs)

Electricity reticulation is available across very large parts of the globe for supplying electricity including recharging EVs, albeit that some electrical grids must be strengthened if EVs become a popular way of travelling. Reticulation of compressed H2 to large parts of the globe has barely started and may never exist outside a few wealthy regions such as California. At this juncture fuel cells fed by hydrogen are not going to be a major environmental saviour, whether or not they are part of motor vehicle technology.

5. The existing hydrogen industry

Ammonia is one of the most important basic chemical feeds to the chemical engineering industry. It is the key to the input of nitrogen into carbon, hydrogen and oxygen chemical systems, and is the source of nitrogen for amines, nitrates, nitrites and nitro and other organic and inorganic compounds and chemical groups. Since World War I nitrogen has been sourced from the atmosphere according to the exothermic equation:

N2 + 3H2 \rightarrow 2NH3 Δ H° –92 kJ/mol Haber-Bosch Process (4)

In oil refining, hydrogen is used for hydrogenation of heavy oil constituents and sulphur removal from crude. Hydrogen used in ammonia production and oil refining is usually derived from steam reformed methane:

$$CH4 + 2H_2O \rightarrow 4H_2 + CO_2 \text{ (including water-shift)}$$
 (5)

Hydrogen is likely to have an increasing role in the iron/steel industries (and a lesser role in cement being only heat supply). Smelting with hydrogen is possible with the potential biomass sources of carbon providing for iron carbide (cementite) production. But how plentiful and how expensive will the biomass needed for the world's steel production be and can it fully replace coke? Would carbon produced by methane splitting be suitable for low carbon smelting?

6. Comparative costing of the hydrogen economy and the existing carbon economy

A paper by Pinsky R et al, Comparative Review of Hydrogen Production Technologies for Nuclear Hybrid Energy Systems, 2020 (Pinsky et al.), provides proximate production costs for multiple hydrogen production technologies Pinsky R et al. (2020). These figures provide one aspect of a cost-benefit analysis that would be needed to progress the H-E past concept status.

7. Hazard analyses

H-E presents multiple hazards. Hazards associated with the physical, chemical, materials science and engineering nature of hydrogen can be qualitatively compared with those of natural gas (Ricci et al. 2006). A hazard of interest is the low electro-conductivity of hydrogen that can increase the propensity to generate electrostatic charges and produce sparks. On the positive side hydrogen has lower hazard for unventilated accumulations of hydrogen (hydrogen being so light that it tends to waft away), fires can likewise lift quickly into the atmosphere without seriously impinging on storage vessels and pipelines, and the hazard of asphyxiation is likewise reduced due to relative fast hydrogen dispersion (Ricci et al. 2006).

Did the engineers who undertook the Hazard Management of the Fukushima nuclear plants understand that their outer containment structures would allow for a build-up of hydrogen? Were they aware of hydrogen's broad flammability /explosive ranges with air, as well as it having a very small activation energy for ignition? Hydrogen that is released into confined spaces is a major hazard. The Fukushima hydrogen explosions set back the nuclear industry but also demonstrated the dangers of hydrogen. The memories of the exploding outer containment at Fukushima will be revived when there is another hydrogen fire/explosion.

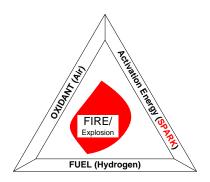


Figure 5. The Fire/Explosion Triangle

Looking at to the Fire/Explosion Triangle for Flammable Gases we find: there is a wide explosive limit for air/hydrogen mixes, with Lower Explosion Limit of 4% and Upper Explosion Limit of 74% compared methane's much tighter LEL/HEL difference 5% to 15%. Testing for hydrogen is more difficult and hazardous than for methane. Hydrogen being very light has a high dissipation rate in air if released to the atmosphere. However the high hydrogen mixing rate and LEL/HEL makes it exceptionally hazardous whenever confined.

Undertaking Quantitative Risk (Hazard) Analyses will be at future stages of concept development through to project commissioning.

8. Another view of hazard and risk

Dr Peter M Sandman (circa 1993) developed the concept of Risk = Hazard + Outrage (Sandman 1993). Hazard with aspects of frequency, likelihood and severity can be measured. The level of outrage from a particular incident that may include political upheaval and loss of social acceptance is hard to predict. N.B. The advent of social media combined with 'fake exaggerated news' has made the blunting of outrage a greater challenge. Sandman's approach and relevance will be discussed in the concluding pages.

Ingaldi and Klimecka-Tatar (Ingaldi and Klimecka Tatar, 2020) discuss people's attitudes to energy from hydrogen and the creation of controversies as 'significant challenges for mobile [vehicle] technologies and daily life', as that applies to hydrogen introduction. Their paper discusses the attitude of respondents [to a survey] that looked at the safety of hydrogen; respondents are 'found to be not convinced that an adequate level of safety exists for energy derived from hydrogen, where safety can be understood to be technical'. The respondents also stated that 'knowledge about hydrogen as an energy source, and its production safety and storage methods, is very low'. The respondents are aware of potential hazards and if coerced to accept hydrogen have the potential for outrage.

9. Nuclear energy and the response of the nuclear industry to the H-E

The World Nuclear Association, an international body in London with responsibility for overseeing 70% of the world's nuclear power, has produced a white paper titled 'Hydrogen Production and Uses' (World Nuclear Association, 2021) that provides a wide perspective of where nuclear energy may go with respect to hydrogen production. Pinsky et al (2020) take a more focused approach in their paper, Comparative Review of Hydrogen Production Techniques for Nuclear Hybrid Energy Systems (NHES). The NHES contribution to the discussion is that nuclear power could provide electricity/energy for hydrogen production; even without economic analysis it can be assumed that hydrogen produced by fuel-cells being fed electricity from new nuclear power stations at this stage would produce expensive electricity, making electrolysis-based hydrogen production from nuclear energy also expensive.

On a basic hazard approach, the distance between nuclear power plants and hydrogen production facilities and transport systems should be considerable; a hazards analysis that takes into account international nuclear safety regulations would provide rules and regulations on distances and physical layouts.

If nuclear energy is a feasible contributor to H-E, why not simply use nuclear power generation to support an extended renewables/low carbon/electric economy (E-E)?

Low Carbon Hydrogen Sources: Options for the Renewable Energy Proponents

Blue Hydrogen, that being hydrogen produced along with carbon dioxide that is to be sent to Carbon Capture and Sequestration (CCS), has only a time limited role in H-E, as suggested in Figure 2. Sequestration, the 'S' in CCS, must be a near complete fate for the carbon, with leaks being kept within limits and gross leaks not tolerated. However, can 'forever sequestration' be guaranteed and policed?

It could be feasible to have a version of H-E that is almost solely dependent on methane and methane reforming. Such a strategy would involve a greatly increased search for methane resources. Major finds would mean endless opportunities for CCS. However, CCS opportunities at this scale would be unlikely to exist (Kindy 2021). About 90% of the world's hydrogen is produced from reformed natural gas and as of 2020, 70 million tonnes of hydrogen were produced per year (Ashcroft and Di Zanno 2021). Note 2

10. Photocatalytic hydrogen (PCH) production: a low carbon hydrogen source

Some sources of 'clean' hydrogen are small and will probably remain small due to their innate low efficiency. Li and Li (2017) point to one such example: Photocatalytic Hydrogen (PCH) Production. Its efficiency is expressed as STH%. Solar-to-hydrogen (STH) efficiency.

STH % = $\underline{\text{output energy as } H_2 \text{ gas}}_{\text{energy of incident solar light}} x 100\%$ (6)

Li and Li state that 'Up to date [January 2017], the highest STH efficiency for PEC (photo-electric-catalysis) water splitting system as reported is $\sim 2.5\%$ '. There is a long way to go before PCH/PEC becomes a major supplier of hydrogen. The reactions for PEC are:

 $2H_2O + hv \rightarrow O_2 + 4H^+ + 4e^- \text{ and } 4H^+ + 4e^- \rightarrow 2H_2$ (7) Note: hv is Photonic Radiation.

11. An alternative hydrogen source: methane cracking/splitting

Methane (and other hydrocarbons) can be split according to the following endothermic equation:

$$CH4gas \rightarrow 2H2gas + Csolid \Delta H^{\circ} = 74.8 kJ/mol$$
 (8)

Cracking methane (and other H-Cs) has been proposed in the past by groups including Kvaerner (Lu et al. 2021). Dagle et al reviewed the concept to use Liquid Metal (tin or low melting temperature alloys) to crack (split) methane into hydrogen and solid carbon products (Dagle et al. 2017). The use of molten metal such as tin as a catalyst through which a stream of methane is passed avoids catalyst occlusion that has been the challenge in previous research. The process is carried out in a heated column as shown Figure 6. The two products of the process should be pure hydrogen after separations and carbon after clean up (Msheik, Rodat, and Ananades 2021).

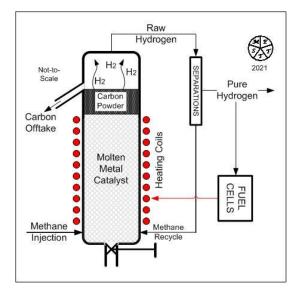


Figure 6. Molten Catalyst Methane (hydrocarbon) cracking column.

The two products of the process should be pure hydrogen after separations and carbon after clean-up.

The aggregated value of the two products will be largely dependent on the value of the carbon, that is the value of the pure allotropes that are produced. Graphene, Buckminster-fullerenes, and needle carbon have higher values than amorphous carbon and bulk hydrogen.

The suitability of the carbon product for structural and chemical uses will be crucial in seeing Methane Cracking as a major industrial process.

12. The hazards of hydrogen

12.1. Managing hydrogen as a substance: hydrogen safety and hazard reduction

Hydrogen differs from methane in many ways, having a significantly higher hazard profile. The hazards are loss of health, commercial and industrial failure, and environmental and societal loss of amenity.

Looking at the Fire/Explosion Triangle for Flammable Gases (Figure 5) we find there is a wide explosive limit for air/hydrogen mixes, with Lower Explosion Limit of 4% and Upper Explosion Limit of 74% compared methane's much tighter LEL/HEL difference 5% to 15%. Testing for hydrogen is more difficult and hazardous than for methane. Hydrogen being very light has a high dissipation rate in air if released to the atmosphere. However, the high hydrogen mixing rate and LEL/HEL makes it exceptionally hazardous whenever confined.

Some further hazards to consider:

• Hydrogen has a very low activation (ignition) energy of \sim 0.02 mJ, as compared to \sim 0.29 mJ for methane, the latter for methane being fourteen times greater, ^{Note 1}

• The activation energy can be supplied as static electricity such that rapidly released compressed hydrogen will always ignite,

- Hydrogen can permeate through steel and other confining materials causing increases in brittleness,
- Hydrogen becomes a liquid at minus 20.28 K (Propane LPG at 231.2 K and Methane 111.6 K),

• LH2 being a cryogenic fluid requires care in handling and has relatively high handling costs, requiring specialist cryogenic infrastructure and a highly trained service team,

- Hydrogen has no odour and is difficult to odourise,
- Hydrogen burns with a clear, near invisible flame,
- Mixtures of H2 and air (or O2) are detonatable (a deflagration can become a detonation), and
- •Hydrogen leaks are difficult to detect and hazardous to rectify.

Hydrogen has multiple hazards that must be managed if the Hydrogen Economy, as portrayed in Figure 2, is to be a reality.

Given the hazard profile, hydrogen introduction will incur higher insurance premiums and it will be more difficult to finance energy projects. Once they are aware of the hazards, communities likely will oppose hydrogen being introduced in their regions. Installing hydrogen reticulation grids to supply fuel for hydrogen vehicles and other uses will likely be opposed by community action groups. Hydrogen is a very difficult fuel to manage in comparison to other gaseous fuels in urban, commercial and small industrial applications.

For these reasons hydrogen is a very challenging fuel around which to build an energy export/import. For these reasons hydrogen is a very challenging fuel around which to build an energy export/import industry.

12.2. Hydrogen as an export/import fuel

In 2020, Australia became the world's largest exporter of LNG with exports worth \$AU 49 billion. It is the nation's fourth largest export and probably will be the third largest export once COVID diminishes education as an export earner. ^{Notes 3,4} LNG is a convenient and well understood cryogenic liquid. It has a Specific Energy of ~24 MJ/L (depending on composition) whilst Liquid Hydrogen (LH2) has an SE of 8 MJ/L. As a cryogenic liquid at 20 K, LH2 requires considerable energy to liquefy before loading and to regasify at the receiving port. The internal logistics gas demand is around 40% of the gas entering the liquifying plant.

13. Natural Hydrogen

13.1 Mineral hydrogen extracted from natural gas

Hydrogen, as water, is a major component of the earth and also is part of the geology of the earth. Some of the hydrogen within the earth is tied up in hydrated minerals and is released in water–rock interactions involving iron. Klein, Bach and McCollom (Klein, Bach, and McCollom 2013) state '[h]ydrogen forms during the oxidation of ferrous iron in olivine and orthopyroxene to ferric iron in secondary minerals through reaction with water'. This can be represented by the general reaction:

$2FeO + H_2Oaq \rightarrow Fe_2O_3 + H_2$ (9)

So hydrogen is produced by the oxidation of ferrous ions to ferric ions over geological time. Is this hydrogen stored in geological formations or does it migrate to the atmosphere and thence into space?

13.2. The relationship of hydrogen and helium

The following gas analyses are for two natural gas wells drilled in Central Australia and are interesting due to the presence of (a) very high helium content, (b) natural hydrogen presence (in one case very high and in the second only nuisance value) and (c) high nitrogen and moderate methane contents.

	Well 1	Well 2
Component	Mole %	Mole %
Helium	9	6.24
Natural Hydrogen	11	0.03
Nitrogen	61	43·87
Methane	13	33.49
Ethane	4	6.41
Other hydrocarbons	NA	3.41
Total	98	100.00

Table 2: Analyses of NG Finds in Central Australia

The gas analyses are very high in helium. So if the discovery is confirmed, both finds would be developed as Helium Resources. Well 1 has little fuel gas content; Well 2 is also poor in fuel gas. If the Well 1 hydrogen was recovered and mixed with the available hydrocarbons (H-Cs), that fuel could be used in an on-site captive power plant. The 0.03% hydrogen in Well 2 would be a contaminant that would have to be removed from the helium. Nitrogen could be a useful by-product from both wells.

The hydrogen content of the Well 1 find could potentially be removed from the bulk of the gas using adsorption technology (PSA) with either the use of the hydrogen as a component fuel gas (as stated above) or it could be flared. The feasibility of separation of the hydrogen would depend on the efficiency of the process in separating out hydrogen without losing significant helium. That could be a challenging task. The Well's gas analyses demonstrate how variable the products of natural gas can be. What started as an exploration for hydrocarbons found potential value in a speciality gas, helium, and for Well 1 possibly hydrogen as well.

13.3. Other natural hydrogen finds

Recently there has been an increasing effort to 'discover' natural hydrogen. These efforts, that include collecting and documenting information on past finds, have brought considerable success in understanding what concentrations of hydrogen are possible in natural gas finds. Prinzhofera, Tahara and Diallob (Prinzhofera, Tahara, and Diallob 2018) have recorded the finds in Figure 7.

Finds such as those described in Figure 7 point to the need for petroleum explorers to undertake thorough sets of gas analyses of petroleum wells.

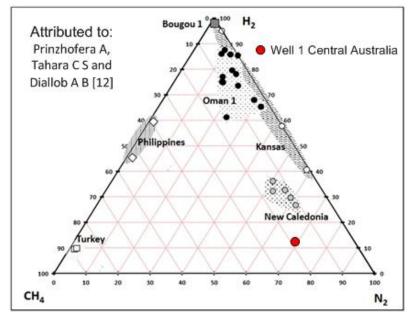


Figure 7. Adjusted natural hydrogen analyses for multiple natural gas wells.

Of particular note is the Bougou 1 well (Mali) with an analysis of 97.4% H2, 1% N2 and less than 1% methane. Detailed estimates of that well's resource size and extended productivity were not made. The natural hydrogen was used to power a regional village for over four years.

A major find with the gas analysis of Bougou 1 would be welcomed by gas explorers.

13.4. Radiolysis of water to co-produce hydrogen and helium

In Figures 8 and 9 the process of radiolysis producing both hydrogen and helium are presented. The helium is an alpha particle that is spalt off a uranium or thorium atom or daughter atom. The co-production of Hydrogen and Helium near simultaneously has recently been 'rediscovered' during the search for hydrogen sources. The question of what are the relative migration (permeation) rates of the H₂ molecules and the He atoms should be explored.

In a paper by Sophie Le Caer (Le Caer 2011), 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. N.B. 1.6 x 10⁻¹³ Joules = 1MeV

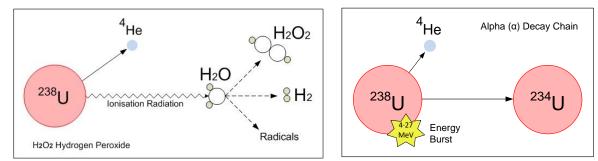


Figure 8. The spalling of a uranium atom

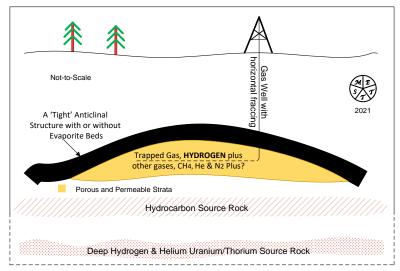
Figure 9. Energy from atom splitting

The co-production of He (a high value relatively rare mineral/atom) and H₂ (a bulk relatively low value element) offers a new opportunity to gas and oil explorationists. There may be some difficulties with the separation of helium and hydrogen and that will be a challenge for petroleum industrial chemists.

13.5. Making a resource of 'googles; of individual decay/ionisation events

Hydrogen and helium are very small particles that once 'liberated' can permeate through almost any material. Once formed they migrate through the geological formations and then on reaching the atmosphere, continue their journey into space. Helium will go through the earth and its atmosphere unscathed whereas hydrogen may oxidise to water on the way.

That both hydrogen and helium can exist in the same strata where there is a sealing formation is indicated in Table 2. Sealing strata often include evaporites such as salt being laid down with tight shales in an expansive anticlinal structure (a Type 1 sealing structure) or in smaller (but often richer in helium) structural traps (a Type 2 structure) with massive salt/evaporites. The Qatar gasfields are examples of Type 1 traps and the US helium gasfields Type 2 traps. The smaller Type 2 system tends to be self-sealing if faulting occurs since the evaporites tend to be plastic under high pressures and temperatures.



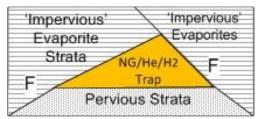


Figure 10b.Type 2 Gas Trap with 'near impervious' evaporites. F = Faulting

The plastic evaporites will seal structural faulting. The traps are not absolute in that they slow the flux of gas through the strata allowing for build-up of hydrogen and helium.

Figure 10a Type 1 Anticlinal Gas Trap

There may exist very large anticlinal formations that hold hydrogen (and helium) that have the potential for development. If high hydrogen giant/very large Type 1 type traps exist, failures of explorers to make finds over the last 60 years should be examined. Perhaps explorers did not analyse for hydrogen or perhaps they simply never explored those potential sites. As to exploring for natural hydrogen/helium, this should be done as a sub-activity of NG exploration. If major finds of 'concentrated' natural hydrogen are made, then the exploration priorities can be changed.

The finds of highly concentrated hydrogen bearing natural gas in Mali and Kansas (Figure 7) do not come with measured resources. The Bougou 1 well(s), Mali, may have supported local power generation for a relatively short production period but that resource appears to have little in common with what is suggested in Figure 10a. Perhaps additional exploration in Mali and Kansas (were the Kansas finds made whilst exploring for helium?) of Type 2. Figure 10b style of play could find locally useful resources of hydrogen. That is to be tested.

14. Gas separation, Separating the hydrogen, helium, fuel gases and other gases such as nitrogen and carbon dioxide

It is known that hydrogen and helium co-exist with a mix of other gases, some of which are valuable and some not so. Hydrogen is an industrial bulk gas with an existing price related to the demand for ammonia and its use in oil refining. Helium has no conventional market but trades at fifteen or more times the price of NG (methane), a bulk gaseous fuel.

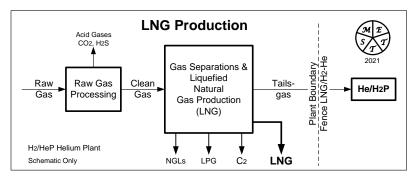


Figure 11. Gas separations with hydrogen being separated either in or before the helium plant.

The price of hydrogen will depend on the demand, with some 'authorities' suggesting that price doubling or trebling will be possible post COVID and once H-E starts to eventuate. The process sheet shown in Figure 11 would likely be more suitable to a Type 1 development. The helium (and hydrogen) separation plant that processes the tails-gas could be a relatively standard cryogenic unit. To a large extent recovering and processing natural hydrogen will be a new challenge and finding a market/destination for remote finds of natural hydrogen will create many a quandary, in that the transport of a hazardous gas will be expensive and carry risk. Natural hydrogen would need to be discovered in multi-trillion cubic feet (TCF) quantities to satisfy the demand side of H-E (see Figure 2).

Natural Hydrogen could, however, have some niche applications as exemplified in the following hypothetical case:

A NG find in the Andaman Sea is found to have 10% natural hydrogen. The off-takers of the gas do not want natural hydrogen in their gas, so are happy to allow a third party to build a gas separation plant onshore. The separated hydrogen will be sent to an adjacent ammonia plant. The ammonia plant owners and operators are happy to have a zero-carbon ammonia production facility.

It is highly probable that there will be additional demand for hydrogen, even if only relatively small portions of the H-E actually come into being. Global hydrogen demand was 'around 90 Mt H₂ in 2020, having grown 50% since the turn of the millennium', according to the IEA. (Global Hydrogen Review 2021) Hydrogen use in heavy industry outside ammonia production and oil refining will grow, with one possibility being Directly Reduced Iron. However, most of this demand for hydrogen will continue to be met from reforming natural gas.

The options for low (or nil) carbon hydrogen production will be limited due to cost, with hydrolysis being an example. There will be an ever-increasing demand for electricity from industry, commerce and communities which are aspiring to lifestyle improvements. Diverting electricity to hydrogen production will need to be justified to receive social acceptance. Failures in supply due to diversion will not be tolerated.

15. Guaranteed power dispatchability

Guaranteed power dispatchability is what communities have come to expect and will be looking for if the H-E is introduced. For industry power dispatchability is a non-negotiable expectation. The value of dispatchability is discussed in the NEM literature (National Energy Market 2021).

The introduction of the H-E will see the need for energy diversion from chemical fuels to electricity. In the near future electric vehicles (EVs), not hydrogen fuelled vehicles, will become common. (Battery Electric Vehicles (BEVs) versus Hydrogen Fuel Cell Electric Vehicles (HFCEVs) – BEVs win 2021) Although demand for non-electric 'transport energy' will still be there, and even though that includes hydrocarbons, dirty electricity (fossil fuel derived power) or intermittent green electricity, there will still be a need for increasing guaranteed dispatchable power delivered by efficient and secure power grids.

15.1. Other niche hydrogen production and utilisation scenarios

Research is being undertaken on what percentage of methane can be replaced by hydrogen in natural gas systems. Safety and technical compatibility must be understood as must the carbon footprint reduction.

Melaina, Antonia and Penev, of the US National Renewable Energy Laboratory (Melaina, Antonia, and Penev 2013) state in their report '[t]he implications of hydrogen blending vary with the concentration of hydrogen. Relatively low concentrations of hydrogen, 5%–15% by volume, appear to be feasible with very few modifications to existing pipeline systems or end-use appliances.' This work is useful in that it may allow for the use of NG containing a 'geologically feasible' concentration of H2 to be used in specific applications off the NG grids. For example, raw NG that contains 7% H2 v/v may have 10% H2 after gas clean-up/removal of CO2 and N2. This mixture may be appropriate for commercial applications. (Melaina, Antonia, and Penev 2013). Hydrolysis produces two products, hydrogen and oxygen. Oxygen has uses in sanitation, with its addition to sewage and wastewater, reducing the concentration of dangerous microbes. If oxygen is given a fair value, that cashflow will assist in supporting the use of electricity to produce hydrogen. It is noted that sanitation is not sterilisation: sterilisation requires ozone (O3) which is very power consuming to produce.

In the upstream end of the petroleum industry the exploration for helium has accelerated from the 1970s. The current interest in natural hydrogen may well see very large finds of N-H. In parts of the world that are or can be covered by pipelines, pipeline transport of H₂ seems appropriate between production nodes and reticulation hubs. Although H₂ transport by pipeline is understood, it is costly because of materials, safety and community acceptance considerations.

Replacing LNG with LH2 in seaborne transport is probably not going to happen on a large scale. The energy losses during liquification, shipping and regasification will be too great to be financially sound whilst the maintenance of specially designed tankers will be costly. Using a tied solar PV plant to supply DC power to local electrolysis plants is a niche use, with methanol (Bowker 2019) or ammonia being products.

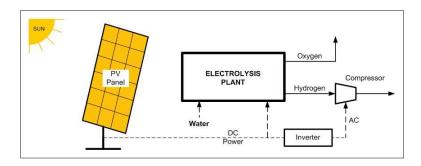


Figure 12. PV powered water electrolysis: a simplified view

If Figure 12 were part of a remote HFCEV/EV fuelling station the bulk of plant would consist of a compressed hydrogen tank farm, battery bank and bowser assembly.

The filling points for compressed hydrogen (CH2) and power on the one hand and the tank farm and battery bank on the other hand would need to be well separated due to safety concerns. The combined hydrogen and power servo would have high CAPEX and OPEX, require high security and have a significant footprint

16. Summing up the HYDROGEN ECONOMY concept

With the exception of fossil fuels with CCS, there are no other references to carbon in Figure 2. CCS is questioned regarding its role as part of the Hydrogen Economy. The sequestration of large volumes of carbon dioxide 'forever' is a monumental task.



On reviewing the H-E proponents' simple comparisons and assumptions, it is understood that they are suggesting:

- H2 could replace CH4, and LH2 could replace LNG,
- the natural gas grid could be easily converted from methane to H2,
- the same level of hazard that applies to CH4/LNG would apply to H2/LH2,
- similar combustion properties exist for CH4 and H2 such that end-use appliances need only modest modifications, and
- Community acceptance of H₂ would be similar to that experienced during the switch from town (coal) gas to natural gas in the 1960s/1970s.

This author believes that those comparisons and assumptions are misplaced, erroneous or just plain incorrect. In the first example hydrogen can never fully replace methane (and visa-versa) whilst in the third example the natural gas grid will be very difficult to convert to carry hydrogen. Researchers are trying to safely increase the percentage of hydrogen that can be blended with methane to greater than 15% (St. John 2020). There is no way that the level of hazard that is found in methane and LNG will be the same as hydrogen/LH2, since the innate chemical and physical properties of the two gases are so very different. It has taken many years to understand what is required in safe LNG storage and transport.

The confidence the promoters of H-E are exhibiting must be challenged by physics, chemistry, materials science and engineering. Also society must also be given the opportunity to be educated about what is being proposed and then be allowed to make us its collective mind.

17. The hazards, risks and social acceptance

Hazard and Risk should not the taken to be the same thing. Dr Peter M Sandman (Sandman 1993) produced the basis equation that: Risk = Hazard + Outrage.

Hazards are measurable; the pot-hole is of measurable dimensions, its physical location is known (or soon will be) and its continued existence is 'an accident waiting to happen'. Hazard has dimensions that can include, likelihood of a fall into it, the potential severity and injury from a fall, and the frequency of potential walkers to come across the pot-hole.

If there is an accident/incident outrage may be generated; if nothing is done about the pot-hole in a reasonable time, social acceptance of the performance of the local authority will be jeopardised. Fukushima is having new high tsunami walls built and new levels of safety are being introduced in the management of Japan's nuclear power plants; these measures were needed to allow limited nuclear power plants to restart.

Ingaldi M and Klimecka-Tatar D (Ingaldi and Klimecka-Tatar, 2020) discussed the 'considerable controversy' that hydrogen would incur 'in many countries'. Their study looked at (social) acceptance in Poland, the Czech Republic and Slovakia of the proposed hydrogen economy.

Questions put in their survey were: '(is) Hydrogen energy safe for People' and '(is) the use of hydrogen fuel safe'? The result of the survey was, '[t]he respondents are not convinced that an adequate level of safety exists for energy derived from hydrogen'. They suggested more education to convince the population that hydrogen is safe; the gist of the article was H-E is good, it only needs social acceptance.

Ricci et al (Ricci et al. 2006) delineated the Hazards of Hydrogen. They noted in their conclusion: 'Hydrogen as energy carrier for the future has to be viewed as an element in a complex network of technologies ranging from generation of hydrogen by various means, through different forms of distribution, down to varied end uses. It will also form part of a "socio-technical system", for there is a key human element to the safety of any technology' and '[i]f part of the expectations is that hydrogen is safe or at least as safe in similar uses as the familiar fossil fuels of the present, the public could be unnerved by a significant accidental fire or explosion associated with hydrogen in the transition to a hydrogen economy.' So H-E has to work with strong technical inputs ensuring very high safety whilst being able to answer the social uncertainty.

Ricci and colleagues point out that Industrial experience with hydrogen is frequently used to anticipate the nature of potential safety concerns arising from its use as an energy carrier and a vehicle fuel, and state that 'Industrial production and use of hydrogen as a chemical has gone on for at least 50 years, is well understood'. Industrial production using hydrogen as a chemical input or fuel can be very positive.

18. Hydrogen's potential sources and roles: some positive aspects

All is not negative with respect to hydrogen. On the production side commercial methane cracking to produce a carbon product and a hydrogen co-product is possible. If the demand for specific carbon allotropes, such as graphene, exists and the cracking process can produce those allotropes, then the cost of 'non-carbon' hydrogen could be reduced.

Natural hydrogen, if found in useful quantities and concentrations, may be the answer to securing hydrogen as a bulk commodity that can be used for power generation. Niche hydrogen production systems such as DC power from PV solar plants being used for hydrolysis, with the hydrogen product being used for ammonia making and with oxygen being made available for sanitation, are possible.

Pipeline transport of hydrogen between collection nodes, that are part of a natural hydrogen system, and a reticulation hub connected to heavy industry are possible and there are already hydrogen pipelines in existence.

19. An alternative to the hydrogen economy: nuclear energy

Figure 2 shows a hydro or pumped-hydro system with the energy held in water impoundments being used to produce hydrogen. Presently and in the future, pumped-hydro is used for ensuring baseload demand is met. In Figure 13 nuclear power has been added to increase the baseload supply and ensure power dispatchability and thus security. The preference for maintaining H2 supply is substituted for maintaining power supply.

There are relatively few options open for creating a new fuel economy, with the fuel also being an energy carrier. If all carriers (fuels) that contain carbon are ruled out, an Electric Economy (E-E) is the only choice. An E-E comes with significant existing infrastructure, some of which may need urgent upgrading. Regions that have an existing significant nuclear power capacity with pumped storage opportunities are limited and the E-E finance opportunities are very unevenly distributed over the globe. On the positive side an expanded Electric Economy does not come with a host of hazards like the proposed Hydrogen Economy.

Figure 13 shows what is essentially an electric generation and energy transport system. Nuclear energy is matched up with pumped-hydro since both can deliver baseload power with energy security. The traditional fossil fuels and H2 produced from fossil fuels can recede as nuclear capacity increases. Energy efficiency improvements will reduce carbon emissions and better methane management will further reduce emissions. Improvements in electricity transmission and distribution systems will also reduce greenhouse gas (GHG) production. Natural hydrogen, if available, can be used in supporting biomass in power generation.

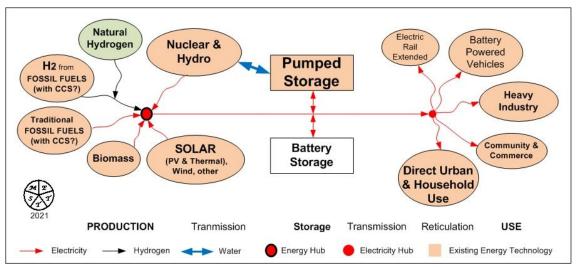


Figure 13. An Enhanced Electric Economy with Nuclear Inputs

19.1 The size and nature of new nuclear power plants (NPPs)

Many commentators are advocating large baseload Nuclear Power Plants, say 1200 MWe per unit and above, and others are advocating for Small Modular Reactors (SMRs), say ≤300 MWe each. A compromise would be pods of say 3–4 SMRs. The selection of reactor size will be dependent on demand, situation, and '9th of a kind' plant cost. SMRs will, however, often win on project deliverability given their modular format

The Eastern Australian Power Grid is not suitable for very large generation plants. By contrast US and European units can be larger since the grids are stronger and have higher population densities to service. It would be useful if the first of the SMRs were already operating as base-load (in-effect spinning reserve) to support the electricity grid of eastern Australia. For this to happen a major increase in the social acceptance of nuclear energy will be required and the availability of nuclear plant modular packages that are 5th of-a-kind (or greater) will also be required. This discussion is for the future. Nuclear energy is the only non-carbon baseload option that can maintain dispatchable power that will support renewable energy. The two energy forms are complementary.

19.2. Nuclear, hydrogen production and use, and social acceptance

Since the 1960s a social movement has developed opposed to the use of nuclear energy (Gamson and Modigliani 1989) and nuclear energy lost much social acceptance after the Three Mile Island, Windscale and Chernobyl nuclear accidents. However, in recent years sections of public and government opinion in the United States, United Kingdom, China and India have become more supportive to nuclear. That trend has continued to be true even after the 2011 Fukushima accident (Kugelmass 2020). It can be noted that the UK is progressing its replacement of nuclear power plants with new units such as Hinkley Point C, 3200 MWe (Tabuchi 2021).

The hydrogen economy is now encountering increasing scepticism and a heightened lack of social and institutional acceptance, as described by Tabuchi and researchers at the Australian National University (and the University of Queensland) (Beck et al. 2019). The ANU researchers state: 'This public sentiment is crucial and highlights the public's concern over climate change and the environment. It also foreshadows that there may be large-scale public opposition to hydrogen production methods that rely on fossil fuels and unproven CCS technologies' (Beck et al. 2019).

Zaunbrecher et al (Zaunbrecher et al. 2016) found that, although there are supportive attitudes and trust in hydrogen storage in the populace, there are misconceptions. There is a lack of information and other concerns were mentioned. The presence of the 'well-known NIMBY effect' is causing close proximity decreasing acceptance. The conclusion of the paper states, 'however, fear of risks (hydrogen related hazards), especially regarding hydrogen storage in residential areas, should be addressed adequately.' The authors suggested that social acceptance of hydrogen (storage) will be achievable if there are adequate separations between communities and hydrogen facilities.

20. Conclusion

Figure 13 shows the progression of an Electric Economy that includes some nuclear energy inputs for guaranteeing power dispatchability with nuclear energy complementing renewables. The transport and reticulation sections of the progression have been revamped and losses have been minimised. The role of hydrogen will increase especially if the production of commercial natural hydrogen can be achieved. Electricity produced from renewable sources independently of major grids will be able to take advantage of battery storage. That electricity could be a homestead supply, a small industry supply or a small mini-grid for example, township supply.

The potential for natural hydrogen finds that have high hydrogen analyses is proven. The question is now whether those potential finds have the volumes of gas with good strata permeability that can make those finds commercial. The finds would likely need to be Type 1 accumulations for major grid connection. Potentially multiple Type 2 finds when agglomerated could be a source of hydrogen for a niche ammonia plant or remote petroleum refinery. N.B. The promoters of hydrogen have promoted natural hydrogen to Gold Hydrogen, so can an ammonia plant be directly connected to a gas well? See: Gold Hydrogen P/L www.goldhydrogen.com.au In short, hydrogen as the basis of the Hydrogen Economy is not a solution to the oncoming energy crisis.

If a non-carbon H2 supply that has the size to match the methane resource, can be created, then a major energy transfer system will have been created. Hydrogen will never totally replace methane as a fuel energy carrier. Electricity will increasingly be the main energy carrier, with methane as LNG and/or piped natural gas having a lesser but still significant role.

Complementary activities to reduce carbon emissions must include the conversion of fugitive methane (Global Warming Potential 23) to CO₂ (GWP 1). Examples of opportunities are the conversion of ventilation air methane by combustion, the collection and use of agriculture biogas, and higher levels of aerobic digestion when processing human wastes. Oxygen produced by fuel cells could be used in methane oxidation, biogas conversion and enhanced aerobic digestion of wastes.

Notes

1. Acknowledgement for hydrogen properties data. Miriam Ricci, Gordon Newsholme, Paul Bellaby and Rob Flynn have produced a symposium paper titled 'Hydrogen: too dangerous to base our future upon?' Symposium Series No. 151, Crown Copyright 2006. https://www.icheme.org/media/9792/xix-paper-04.pdf The authors are thanked for their contribution to the debate.

2. Ashcroft N and Di Zanno P's article, 'Hydropower: a cost-effective source of energy for hydrogen production' was published on 1 November 2021. This author does not agree with Ashcroft and Di Zanno's conclusion that 'hydro will be one of the world's major suppliers of electricity for hydrogen production by 2050'. This author would argue that land and water for hydro will compete with land and water for agriculture, urban growth and amenity; that hydro is cyclic in terms of drought and flood cycles; and that suitable sites for hydro have already been taken for existing hydro.

3. As well as being an important industry for Australia, LNG is a very important fuel for East Asia and South Asia. Switching to natural gas has been used (and will be used) to reduce the use of coal in power generation and thus coal produced emissions.

4. Methanol is suggested as being an energy storage medium as well as being an intermediate chemical in producing dimethyl-ether and acetic acid. Methanol being produced in the following reaction:

CO + 2H₂
$$\rightarrow$$
 CH₃OH (Bowker 2019).

A question: Where do the promoters find the green carbon monoxide to produce methanol? Partially reformed biomass may be one answer, but the cost of biomass is often high and subject to seasonal fluctuations in supply. Another question: Where does guaranteed (dedicated) water come from if the whole fuels and production complex is situated in a region prone to drought?

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Dr Michael C Clarke, FIEAust, CPEng, FAusIMM, MPESA, RPEQ, has qualifications and experience in the fields of mining, chemical and environmental engineering. He has worked with gases for a significant part of his professional career, including the combustion of ventilation air methane, the recovery of helium from natural gas, carbon dioxide capture and sequestration, the hazards associated with hydrogen and the combustion of methane with increased radiance. Dr Clarke has been a research engineer, consulting engineer and academic. He has been a consultant to the Asian Development Bank and upstream petroleum companies and a consultant and energy research leader to wasteto-energy developers. He holds two research degrees: a MEngSc that looked at the 'Biodegradation of Cyanide in Mine Tailings' and a PhD that examined the 'Use of Selective Flocculation in Recovering Coal Values from Coal Rejects'

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END OF AJMDE ARTICLE (CONTENT) AS PUBLISHED BY IEAust & Taylor and Francis, 4th April 2022

GLOSSARY of TERMS

AFDC	Alternative Fuels Data Center (US)	LHe	Liquefied Helium
ANL	Argonne National Laboratories (US)	LEL	Lower Explosive Limit (UEL Upper Explosive Limit)
ANU	Australian National University	LHV	Lower Heating Value (UHV – Upper Heating Value)
CAPEX	Capitan Expenditure	LNG	Liquefied Natural Gas
CCS	Carbon Capture and Sequestration (Storage)	LN2	Liquefied Nitrogen
CNG	Compressed Natural Gas	LPG	Liquid Petroleum Gas (propane and butane)
CH2	Compressed Hydrogen	mJ	milli Joule
DC/AC	Direct/Alternating Current	MJ/L	Mega Joules per Litre

DoE	Department of Energy (US)	Mt	Million tonnes
E-E	Electric Economy	NEM	National Energy Market
ESG	Environmental, Social, Governance	NHES	Nuclear Hybrid Energy Systems
EV	Electric Vehicle (BEV - Battery EV)	NG	Natural Gas
H-Cs	Hydrocarbons	N-H	Natural (mineral) Hydrogen
H-E	Hydrogen Economy	NREL	National Renewable Energy Laboratory (US)
HFCEV	Hydrogen Fuel Cell Electric Vehicle	OEE&R	E Office of Energy Efficiency & Renewable Energy US
hv	Photonic Radiation	OPEX	Operational Expenditure
ΔH°	Enthalpy	РСН	Photocatalytic Hydrogen (production)
J	Joule	PEC	Photo-electric-catalysis
К	Degrees Kelvin (temperature)	PEM	Proton Exchange Membrane (water hydrolysis
kJ/mol	kilo Joules per mole		technology)
kWh/mc	bl kilo Watt hours per mole	PV	Photovoltaic
LH2	Liquefied Hydrogen	STH	Solar-to-Hydrogen (percentage efficiency)
MeV	Mega Electron Volts (1.6 x 10 ⁻¹³ Joules = 1MeV)	TCF	Trillion Cubic Feet

POST PUBLICATION UPDATES

UPDATE 1. TESLA

Tesla's (Elon Musk's) preference for Battery Electric Vehicles (or hybrid electric/gasoline) vehicles is well known. He has described the concept of hydrogen fuel-cell (cars) as being "extremely silly". The report by CNBC¹ stated that Musk has 'a history of expressing strong opinions about hydrogen and hydrogen fuel cells'. Musk has stated. "It's just very difficult ... to make hydrogen and store it in a car". This statement is correct; having a car with fuel-cells (a source of ignition), highly flammable batteries (almost certainly Lithium-iron) and multiple tanks of highly compressed hydrogen, in a car built with a high portion of highly combustible material (essentially plastics) presents a significant mix of composite hazards. The hazards associated with BEVs are similar to those of petroleum powered vehicles.

¹See: <u>https://www.cnbc.com/21/12/06/elon-musk-has-strong-views-on-hydrogen-and-not-everyone-agrees.html#</u>

Mr Musk apparently has pecuniary interests in BEVs, however the factors behind his comments are still valid. NOTE: METTS does have any commercial interests in any vehicle technology.

BEVs do present some challenges. The use of batteries as a storage system for energy has greatly improved over the last thirty years and reportedly further advances are in the wind. However, Europe and parts of Asia will be better placed for BEVs given their relatively high population densities as against Australia, with its greater spread of communities. Batteries, distance and the remoteness of recharge/maintenance/battery waste do not mix well.

UPDATE 2. CAVERN STORAGE OF HYDROGEN

6th March 2022

The use of artificially created caverns in deep salt strata to store compressed hydrogen (CH₂) is a tried and tested means of storing great quantities of gas with 'reasonable security' against leakage. Examples of such practice exist in the south-eastern United States and in the United Kingdom where hydrogen stored in caverns is used as a back-up supply for the oil refining industry. Where suitable salt seams exist at depths of 500 – 1500 metres (ENEGIE 2021), caverns may be created my using non-entry salt extraction techniques².

²Please visit ENGIE: https://innovation.engie.com/en/articles/detail/hydrogene-souterrain-stockage-sel-cavites-mines/25906/12/1

In Figure 2 of the core article above, a cryogenic liquid hydrogen sphere is shown. This insulated sphere provides NASA with LH2 for its rocketry. Cryogenic storage of hydrogen will be a significantly more expensive exercise than salt cavern storage. Losses of hydrogen through boil-off from an insulated sphere can be expected to be costlier that slow seepage of hydrogen compressed hydrogen through salt layers. Question: Does Australia have suitable salt measures for hydrogen storage?

6th March 2022

UPDATE 3. NATURAL HYDROGEN FOR INDUSTRIAL USE

Mineral Hydrogen is discussed at some length in the Article. I can be a constituent of natural gas and in one instance in Mali was the only significant component of that NG. The Mali 'resource' was reported to be flowing gas for some years when it was used for powering a small community. In other instances, such as Well 1, Central Australia the hydrogen was present at 11% v/v (with helium at 9%). In other Australian finds and shows the hydrogen content has always been below 10% [1].

Natural Gas(es) vary greatly in their composition. In most instances both the hydrogen (and helium) are in trace amounts and for hydrogen cannot be considered to have commercial value since hydrogen is 'only' an industrial fuel/product.

In producing a hydrogen product from a NG well, the percent concentration of hydrogen must be known as well as the volumes of gas(es) that can be recovered. Within limits, say <15% H2 of the hydrocarbon content, hydrogen can be blended into the fuel gas (with residual nitrogen and carbon dioxide also being present). Note: Although hydrogen will increase the Specific Energy of the total fuel gas, it will not improve domestic and commercial use, since an increase in radiance is looked to for radiant heat transfer. This radiance increase is achieved by the addition of higher hydrocarbons (H-Cs) such as $C_2 - C_5$. If a 'pure' hydrogen is required for ammonia production and oil refining, that hydrogen will need to be separated. Any co-produced carbon dioxide from the wells will need sequestration (or carbon credits); the CO2 from H-C use will also need to be accounted for.

To understand the potential for mineral hydrogen (Gold Hydrogen) to be produced from a well and find a market the following schematic has been produced. Figure A, Paper Updates.

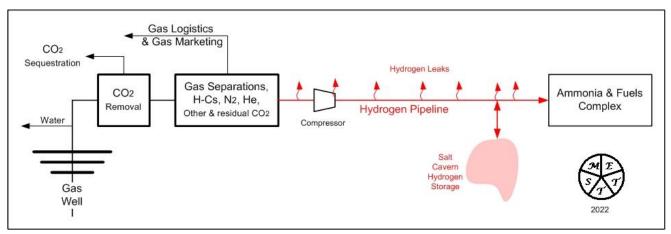


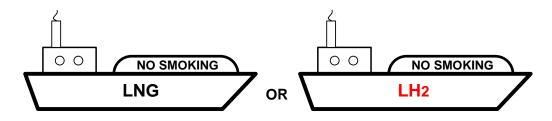
Figure A. The functions of a Gold Hydrogen extraction, processing, storage and supply line to heavy industry: Golden Hydrogen being hydrogen that is extracted from natural gas with 'no' carbon footprint [2].

Figure A includes hydrogen losses by permeation through the pipeline (and ancillary fittings). No losses from the cavern storage are considered, but valves etc that connect the storage to the hydrogen could be a source of loss. Figure A also delineates the gas extraction and processing activities from hydrogen as against hydrogen transport and storage and thence use. It is assumed that the three functional areas are in remote localities.

The actual processes in the gas extraction and processing area will be determined by the raw gas composition and the gas resource size. The materials that are used in the pipeline (and ancillary fittings) will be chosen with respect to the flows and pressures of hydrogen, the pipeline length and safety considerations. The space between hydrogen and hydrocarbons plants will be considerable post separation, and will determined by a hazards analysis.

[1] Table 2. The Hydrogen Economy Article

[2] Gold Hydrogen, a term used by Ballentine C and Gluyas J, Earth Sciences, Oxford University, Sept 2021, https://www.earth.ox.ac.uk/2021/09/gold-hydrogen-oxford-earth-sciences-in-the-times/



The question the feasibility of LH2 shipping is put in the figure above. What is common to both carriers (ships) is that they, carry a flammable liquefied gas that can create explosive mixtures with air, the gas is cryogenically liquefied and requires regasification before use. The commonality essentially ceases when 'deeper' questions regarding the materials science of the gases, the costs (and efficiencies) of liquefying, the relative safety of seaborne carriage of either gas, the social acceptance of such carriage, and the amenity and security of loading and off-take systems are considered.

The time and cost required to establish a LH2 fleet cannot presently be estimated since the concept is still at the early demonstration stage1, that being the construction, commissioning, the first carriage of LH2 (being loading, transportation and off-loading), the recertification of that ship post journey and the analysis of the findings of the demonstration¹. See Suiso Frontier1: www.hydrogenenergysupplychain.com/supply-chain/the-suiso-frontier/

As to quantities the gas carriers that have a capacities of > 150,000 m³ are becoming common so new LH2 ships of similar size will be looked to if for instance Australia is to supply Central Europe with the equivalent hydrogen to fill the gap that the removal of fossil fuels from the western EU will require. Note: The new LH2 fleet will not use converted existing ships or the majority of on-shore/off-shore existing plant.

Learnings from Cryogenic Carriage of HELIUM

Helium-4 and LH2 have significant differences in boiling point (BP) temperatures, being 4 K and 20 K respectively, (K Kelvin), other important BP temperatures are nitrogen, 77 K, and natural gas ~113 K. High purity liquid helium is transported in flasks that have an outer shell that contains super-cooled liquid nitrogen. A typical internal He flask holds around 40 kL of LHe². The LHe flasks/tanks are costly and fragile, however the contained LHe is a valuable critical material, unlike all forms of hydrogen that are industrial materials. Note: A flask system was being designed for railway applications using suspended spring-loaded mounts within the 40' Standard Container Frame to overcome the hazard of rail shunting forces³.

²Gardener Cryogenics: www.gardnercryo.com/helium-products ³ Per Com. Manager, Gardener Cryogenics, Darwin, circa 2011.

The brittleness of materials increases as the working temperature decreases into the cryogenic range. This requires that the cycle of loading, transport with cryogenic liquid, unloading, transport with 'empty tanks' and refilling with cryogenic liquid(s), utilise ullage to maintain cryogenic temperatures. The hazard of losing cryogenic temperature will be significant, although less with hydrogen than with helium; such loss will still create materials integrity issues. Providing the required level of ullage will come with its costs.

Costs associated with liquefying hydrogen

Energy will be required to liquefy hydrogen. The level of energy required will be a multiple of the energy required to liquify natural gas. As to regasification and storage of hydrogen as gas the costs will be greater than for the equivalent LNG regasification and storage. The plant required for regasification and storage will not be the same plant as is now used for CNG. (Salt strata suitable for caverns that can take compressed hydrogen are and will be rare and old-time gasometres not suitable.) What will those additional costs be? This will be one of the research areas that must be undertaken.

The costs of new technology are usually high. If the technology is for or part of a hazardous industry/plant then insurance will be high. The development of a LH2 fleet will trigger three distinct classes of high-level hazards, being; petrochemical, maritime and terrorist/political. It may receive a low environmental hazard rating, but this will not makeup for the heavy insurance costs from the other three classes.

The real (or surmised) hazards of hydrogen will make finding 'friendly' ports difficult; the construction of specialised ports away from urban and commercial centres will be a major priority of those who are designing the required infrastructure. Note: The Longford CNG explosion (1998) did not make 'selling' NG developments any easier for the gas industry.

The Suiso Frontier, its relevance to a potential future LH2 fleet

The small liquid hydrogen carrier (ship) has been constructed in South Korea for the purpose of proving the technical feasibility of shipping LH2 from Australia to Japan. The Suiso Frontier, of 1250 cubic metres carrying capacity, reached Australia and departed with a 75 ton (70% of its maximum load)⁴. Suiso Departs: Jan 31, 2022 ⁴www.maritime-executive.com/article/suiso-frontier-departs-australia-with-first-liquid-hydrogen-shipment

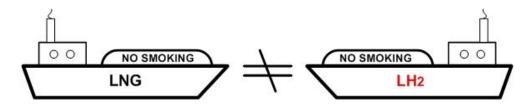
It is understood that the LH2 that was produced by lignite reforming with the co-produced CO2 being captured and sequested. Natural hydrogen produced from NG wells may come with a low carbon footprint, but will this gas be sourced in situations logistically amenable to marine transportation, thence storage and industrial use? The demonstration will prove (or not prove) that carrying LH2 is technically feasible at least for one journey, however how many loading cycles can the ship safely endure. What will be maintenance requirements of LH2 ships. Also, what will be the total logistics costs of producing, liquefying, storage, shipping and re-gasification of the LH2 and managing the flow of LH2 between producer and user.

Flexibility versus Rigidity of Ships as against LH2 tanks/containers/flasks

Ships are built with a degree of flexibility and can flex in multiple directions. For LNG, the Moss type of ship, with its individual spherical cargo (LNG) tanks, has three or four sphere tanks that are relatively independent of ship's hull⁵; other designs such as the membrane type incorporate tank flexure in the design. The increased rigidity/brittleness of materials at 20 K (as against 113 K) will be more difficult to accommodate re flexing v's rigidity. ⁵ Mitsui OSK Lines 2021. www.mol.jp/en/iroiro_fune_e/ships/03_lng.html

Conclusion

The joint venturers and government agencies participating in the Suiso Frontier project should be commended their involvement and persistence with this project. Testing required by the South Korean authorities alone took two years whilst the ship was delayed from departing South Korea by many months⁴. One of the useful findings of this demonstration will potentially be to see if the hazards of hydrogen can be reduced in hydrogen tankage. The use of existing LNG technology coupled with advanced cryogenic materials science will hopefully improve hydrogen handling on-shore. As to seeing ships of the LH2 fleet enter major Australian ports to load LH2 in equivalent tonnages to the present LNG traffic will take a long time, if ever. Note: Suiso Frontier Fire⁶. It was reported in April that a fire had occurred on the ship on the 25 January2022 whilst in Victoria.⁶ https://www.offshore-energy.biz/worlds-1st-lh2-carrier-suiso-frontier-in-a-fire-incident/.



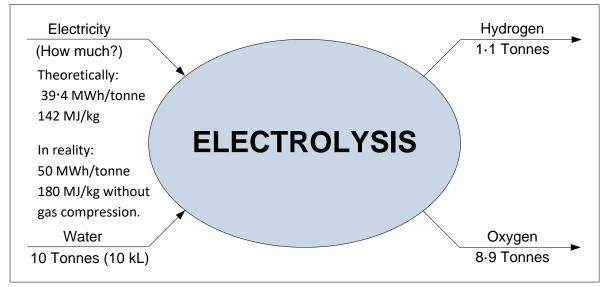
LNG shipping is not equal to LH2 now or into the foreseeable future.

Update 5. EXPLORING FOR MINERAL HYDROGEN

Over the last six months increasing interest has been shown in the possibility of there being potentially commercial finds in natural (mineral) hydrogen. A number of exploration companies have either had their natural gas orientation being switched from methane to hydrogen or have been floated with hydrogen containing natural gas being their target. The PV magazine has discussed those possibilities in their article of February 2022. <u>https://www.pv-magazine.com/2022/02/02/natural-hydrogen-exploration-boom-snaps-up-one-third-of-south-australia/</u>. Note: South Australia appears to be very prospective for hydrogen according to the SA Govt: <u>https://www.energymining.sa.gov.au/industry/energy-resources/regulation/projects-of-public-interest/natural-hydrogen-exploration/gold-hydrogen-natural-hydrogen-exploration.</u>

Hydrogen exploration is speculative in terms of likely concentrations of hydrogen in the target gas, the presence of other gases of varying usefulness (e.g. Helium would be a positive presence) or negative value (e.g. the presence of carbon dioxide and hydrogen sulphide would probably not be wanted), the ability of existing gas infrastructure to utilise hydrogen as a mixed fuel gas, and the cost of gas separation to make the hydrogen a valuable industrial commodity are all Modifying Factors that will govern project feasibility.

Update 6. UTILISING THE OTHER PRODUCT OF WATER ELECTROLYSIS – OXYGEN 22nd October 2022



The figure below demonstrates the twin products of hydrogen and oxygen from water electrolysis:

Oxygen is a major industrial commodity that is usually produced by air separation. If vast new resources of oxygen are created in the production of hydrogen, will there be a market for the co-produced oxygen? If yes, developing oxygen off-take opportunities will be an important economic project Modifying Factor.

UPDATE 7. THE HYDROGEN ECONOMY – A BOOK

30th October 2022

My friend and colleague, Dr Duncan Seddon FRACI, CChem, has produced an excellent book on the Hydrogen Economy. Duncan has included Hydrogen Economics with Case Studies as well as H-E Fundamentals and Technology. I recommend his book to you: *The Hydrogen Economy - Fundamentals, Technology, Economics,* Singapore: World Scientific Press, May 2022. www.//doi.org/10.1142/12593.