Hydrogen, Helium and Nitrogen: A short paper, Oct 2021

Valuable Gases that can be a Constituent of Natural Gas

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Abstract

Natural Gas (NG) was the Cinderella of Petroleum until the 1970s when its value as a high energy and readily transportable fuel was recognised. The high energy primarily came from the methane content of the NG, with some NG resources containing useful concentrations of heavier hydrocarbons, that included ethane (C_2H_6), propane (C_3) and butane (C_4) and boosted the energy of the basic methane. The United States led the world in developing NG resources, building NG infrastructure and offering a relatively cheap coal-gas substitute to domestic, commercial, and industrial customers. Some NG resources also had significant percentages of petroleum condensate, a C_5, C_6 and C_7 mix that can be converted to gasoline.

NG finds also contained other gases besides the hydrocarbon fuel gases. These could be valuable, as was found with having recoverable helium, occasionally valuable where markets could be developed if not existing (e.g. carbon dioxide and hydrogen sulphide), and some could be essentially valueless like nitrogen. A salutary property of natural gas is that it is an industrial commodity; some finds of NG can remain as 'stranded resources' if required commercialisation logistics and infrastructure are not economically and/or technically feasible.

The advent of new demands being made for helium such as super-conductivity through ultra-low cryogenics (<4K) and inert gas flooding in electronic component manufacture has seen the price of helium escalate. Helium has become a valuable 'rare earth'.

The possibility of natural hydrogen (NH) as another NG constituent is real. Could NH, being mineral hydrogen (obtained from the earth) be a significant and reliable source for the hydrogen for the proposed Hydrogen Economy (H-E)? This is being looked at by proponents of H-E as potentially the saviour H-E concept. For nitrogen, the proximity of indirect demand nodes for 'cold' can be investigated.

Introduction

Helium has a worth but no internationally recognised market. Trading in crude helium, that being helium that is say 70% pure, is a feature of the US Government's monetisation of its strategic stocks. Other national resources (e.g. from Algeria, Qatar, Russia and Australia) are also in play. From these helium gas sources, plus helium increasingly produced by other developing international sources, a limited number of 'specialist gas producers' will process, store and market a number of helium products. These products being gaseous commercial grade gas (say 70 - 90% He), balloon gas, compressed gaseous A Grade (>99% He) and A Grade Liquefied He (say >99·995% He). Prices are adjusted according to the cost of processing, products logistics and product demand. Helium is however a valuable commodity with landed prices being >15 times the landed price of methane (NG).

The overall play is gas analysis, gas processing and separation, development of gas utilisation scenarios and gas supply logistics; a co-play is removing finds from the 'stranded gas' category to the 'development ready' category, thence to the production category with monetisation.

Helium, its nature, occurrence and monetisation

Helium is a noble gas with multiple isotopes. There are two stabile isotopes, ^{4}He and ^{3}He, with ^{4}He being by far the most prolific isotope, and in fact being an alpha (α) product of Uranium (U) and Thorium (Th) decay. ^{3}He is a rare isotope that comes from primordial (big bang) sources or is man made during the production of thermonuclear weapons. ^{4}He consisting of two protons and two neutrons does not decay; however some ^{4}He can be assumed to also be produced from primordial (big bang) sources, since this isotope is common in the universe. The juxtaposition of these two isotopes will be discussed later.

Types of Helium Traps that may be encountered

Two types of helium traps have been recognised; these are different in terms of trap volumes and shapes, helium concentrations, the presence and concentrations of associated gases, the presence (or absence) of evaporites (salt), the appropriate technologies and logistics of development, and the resource/reserve economics.

Type I: Relatively large methane resources, where the He is a minor co-target

Type I is an extensive dome (anticline) formation that becomes a trap for a host of gases that will likely contain very significant methane, varying concentrations of other H-Cs, plus low, but useful concentrations of helium (and possibly hydrogen); e.g. the Pas North gasfield Qatar is a Type I occurrence with 0·04% He.

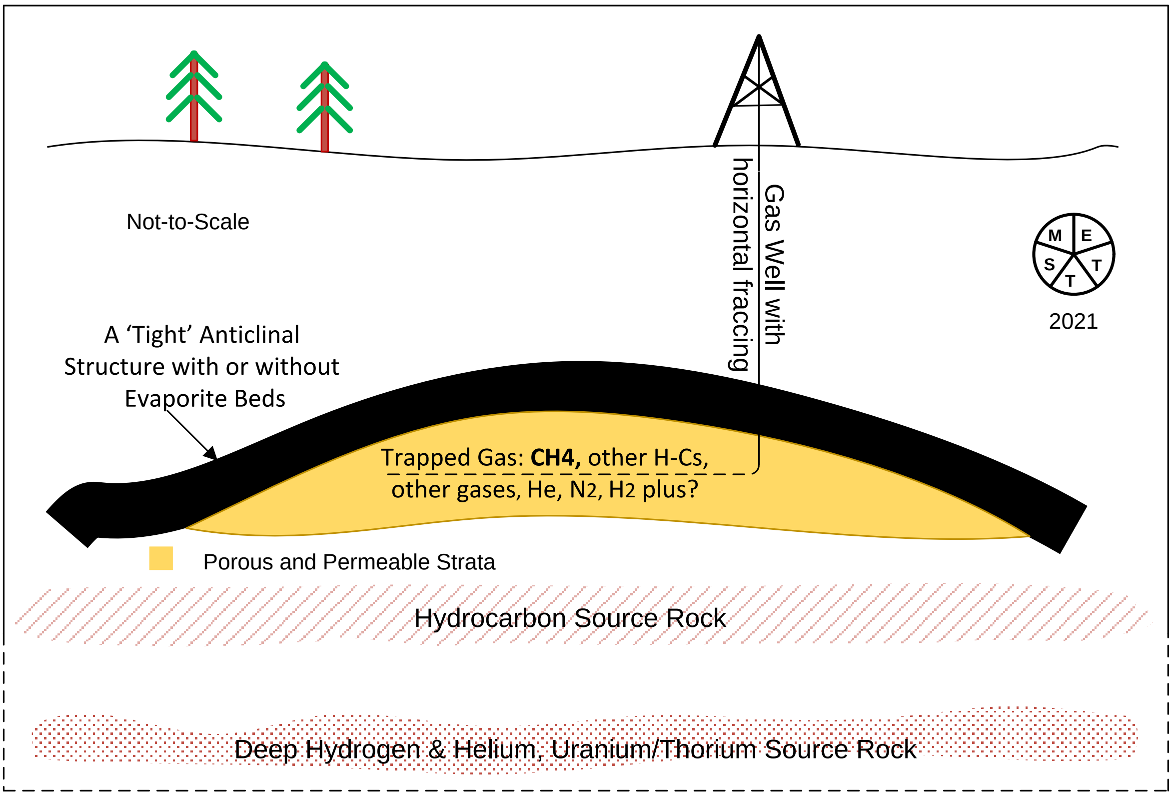

Figure 1. Helium (and potentially hydrogen) as a deep source produced from the decay of U/Th.

If both helium and hydrogen are present, a process (probably cryogenic distillation) will be required to produce a helium product (a Rare Earth commodity) and hydrogen (an industrial commodity). The relative values are likely to be lopsided. N.B. Trace hydrogen is a nuisance when high grade helium production is the target of exploration and down-stream processing; it will require that an hydrogen oxidation step be included in the separation/cleaning process.

Type II: Relatively small Helium rich resources, where the He is the main target

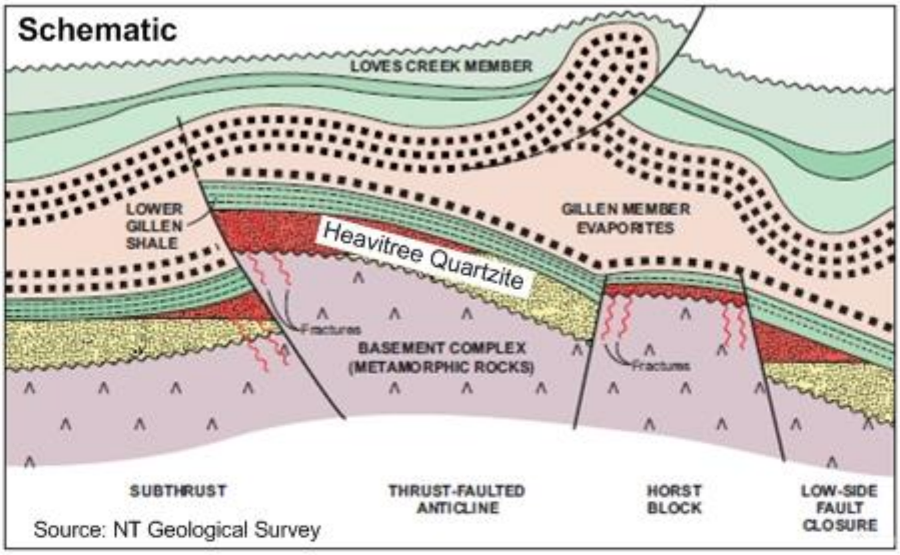

Figure 2. In Type II He plays the He is trapped by the presence of evaporites (salt) and tight shales. In the Amadeus Basin (Central Australia) the Heavitree Quartzite and fractures in basement rock act as gas receivers.

The evaporites also act as sealants where faulting occurs.

Such finds, resources and reserves exist in the United States (the source of the original commercial reserves), the Amadeus Basin and in the Virginia region (OFS) of South Africa. The evaporite sealants SLOW the helium migration from the crustal, mantle and core sources (most He being alpha (α) particles from Uranium and Thorium decay) through the atmosphere (5•2 ppm) to be then lost into space.

In Australia Type II finds have been made that have very high He counts (Magee 6% and Mt Kitty 9%), whilst in the Virginia region (OFS) South Africa finds have been made that are 1 – 4•5% He. Some of these finds have useful hydrocarbon (usually methane) concentrations; all finds have associated nitrogen. The American Helium fields have multiple occurrences, with finds having 0•3% He or greater and are traditionally considered as He plays. Industrial grade He (~70%) is often the product of Type II processing in the US.

Table 1: Analyses of NG Finds in Central Australia[1]

	Mount Kitty	Magee-1
Component	Mole %	Mole %
Helium	9	6·24
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

These gas analyses are very high in helium; if the discovery is confirmed, both finds would be developed as Helium Resources. Mt Kitty has little fuel gas content, Magee is also poor in fuel gas. If the Mt Kitty hydrogen was recovered and mixed with the available H-Cs, that fuel could be used in an on-site captive power plant. The 0·03% hydrogen in Magee would be a contaminant that must be removed from the helium. Nitrogen could be a useful by-product for both wells.

The hydrogen content of the Mt Kitty 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) 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; this could be a challenging task. The Magee/Mt Kitty 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. Such finds point to the need for petroleum explorers to undertake thorough gas analyses of petroleum gas wells.

Processing Crude NG to Achieve Maximum Monetisation by looking at all potential products

Type I occurrences can be massive fuel plays with the production of relatively small off-gas streams. The Pas Field Qatar off-gas is mainly nitrogen with a significant helium content; its hydrogen content has never been posted. Processing Qatar off-gas is relatively simple, with the products being Liquid Helium (LHe) and Liquid Nitrogen (LN_2). The LN_2 is used as a thermal buffer for LHe during transport and storage.

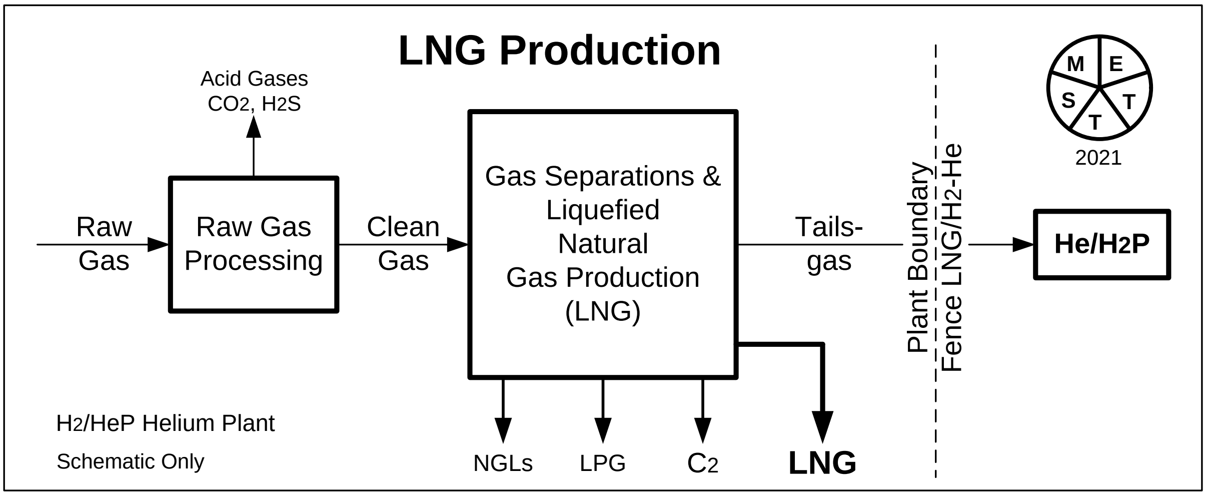

Figure 3a. LNG Production with Off-gas Delivery to a Helium (He) – Hydrogen (H_2) Plant

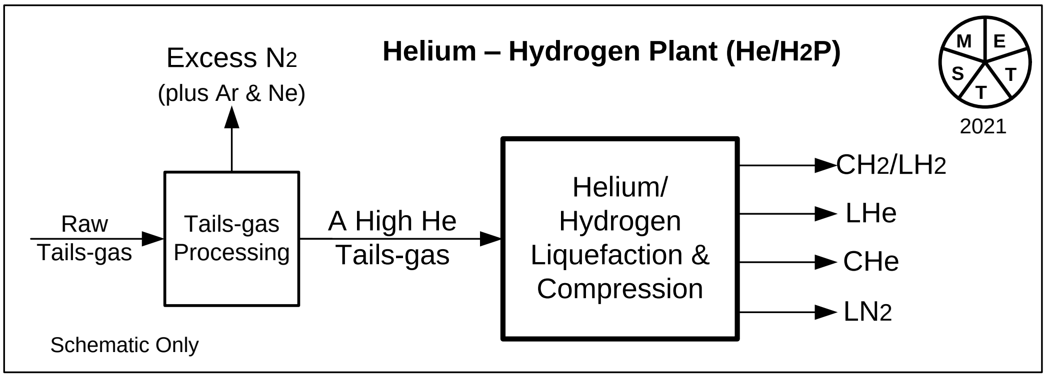

Figure 3b. Products, including Hydrogen, from Tail-gas Processing

Figure 3b is essentially the cryogenic process for separating helium from high He concentration crude NG, industrial grade helium (~70% He), recovered helium as well as LNG tails-gas. N.B. Industrial grade helium is often produced by adsorption technologies – PSA.

An appeal to Readers: If you have heard of operational co-production helium/hydrogen plants I would be very grateful for a heads-up!

Sources of Helium and Hydrogen

Point of logic: As previously mentioned ^3He and ^4He are the stable isotopes of helium. ^4He appears to be mostly a product of uranium and thorium decay in the earth's mantle and crust. ^3He was most likely formed in the big bang and is distributed through the earth; humans produce it by spalling lithium in high intensity flux reactors to create thermonuclear fuel. Some ^4He however must also be a left-over from the big bang as well as being a product of U/Th decay in the earth's depths. So the helium, ^3He and ^4He, emanating from earth's surface must be from mixed sources. This point is useful in planning NG exploration programmes.

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

Table 2. The Properties of Hydrogen and two Stabile Helium Atoms

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	4·2 K
^4He	4·003	5·2 ppm	3·2 K

Hydrogen is likely to be react with atmospheric oxygen through photon energisation.

The ratio of ^3He / ^4He has become of interest to some geoscientists; understanding the ratio may assist with selecting formations for helium exploration. N.B. ^3He is a very extremely expensive cryogenic research tool.

So 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?' Do Figures 3a & 3b apply to Hydrogen?

The Cracking of Hydrocarbons to Produce Solid Carbon and Water

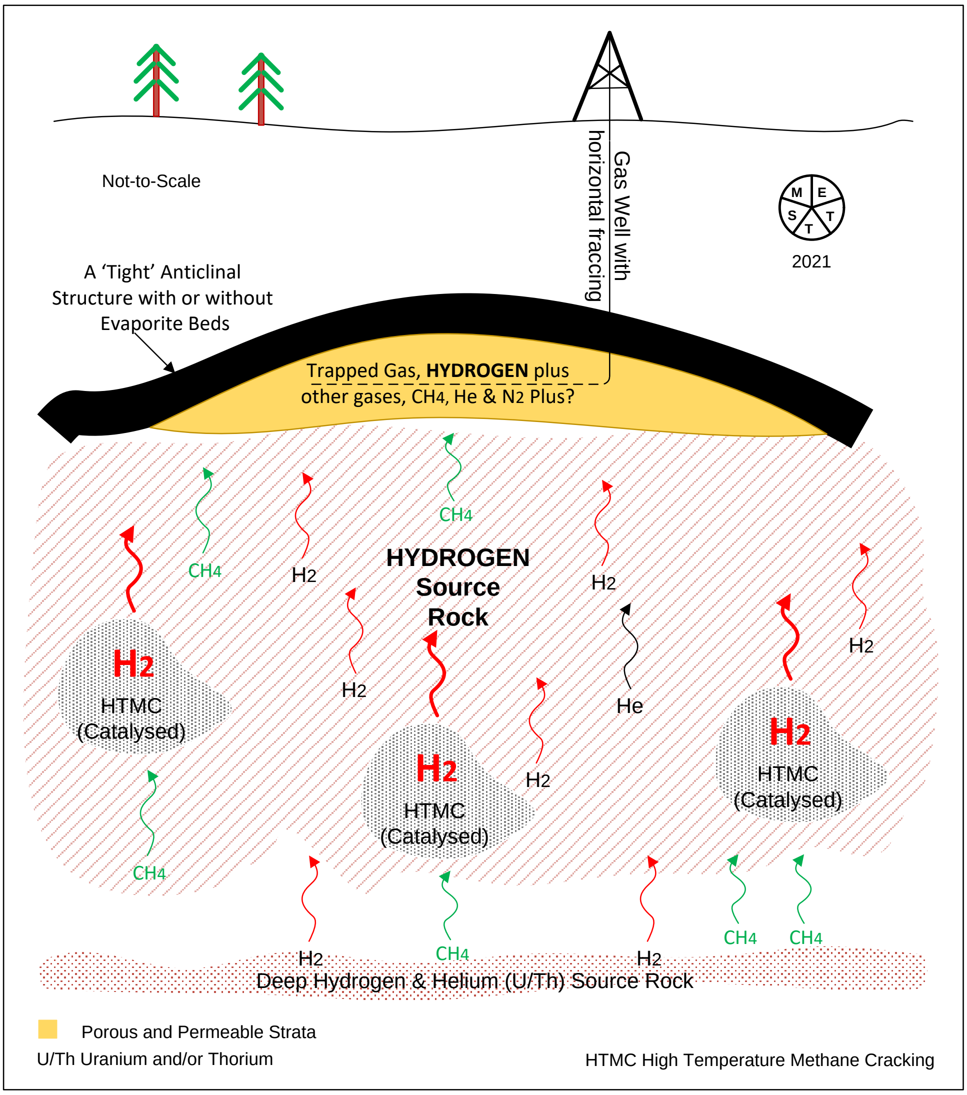

Figure 4.

Hydrogen is produced by high temperature methane cracking from volcanism or subduction; carbon is produced but does not migrate like hydrogen.

Helium may or may not be a significant inclusion, this depending on the presence of regional U/Th.

Nitrogen may be present through the destruction of organic biomass or from primordial sources.

The H-C cracking will be dependant on heat and catalysis; carbon allotropes will be determined by conditions.

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. In a paper by Sophie Le Caer[2], 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.

According to Caer, 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*.' So the production of helium triggers the production of hydrogen.

Water Radiolysis can be written:[2] [* indicates a transient radical, e$^-$, an electron]

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

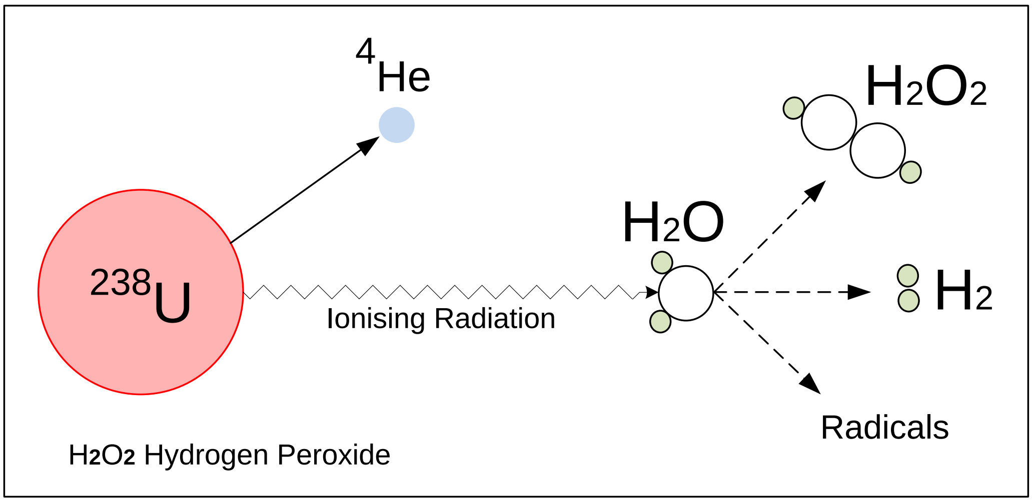

Figure 5a. Ionising radiation from ^{238}U decay splitting water.

N.B. Hydrogen is the only totally stable product of water radiolysis; Hydrogen Peroxide 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 large to be stable; they lose mass especially by spalling-off an Alpha Particle (a ^4He atom). The spalling will also produce a burst of energy which for ^{238}U will be 4·27 MeV.[3]

Table 3. Nuclides, decay products and decay energy

Natural Nuclide	Decay Product	Decay Energy MeV
Thorium 232	Alpha particle	4·08
Uranium 235	Alpha particle	4·68
Uranium 238	Alpha particle	4·27
Uranium 234	Alpha Particle	4·86

A Decay Energy greater than 4 MeV (million electron volts) can produce hydrogen by Radiolysis.

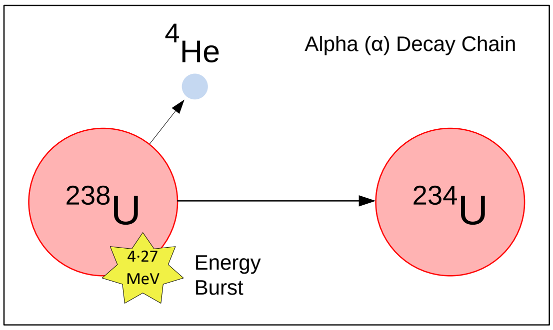

Figure 5b. The main decay links for ^{238}U.

N.B. 4·27 MeV = 6·84 x 10^{-13} Joules

The decay of ^{234}U will proceed eventually producing ^{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.[4] 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,
- Reform natural gas to produce hydrogen and carbon dioxide (as is now the case) and 'successfully' sequest the CO_2 (for eons) to produce Blue-Hydrogen, and/or
- Find substantial and recoverable resources of Natural Hydrogen from deep geological formations.

All the above hydrogen production techniques have great challenges in terms for meeting worldwide demand for hydrogen if H-E is to become a serious proposition. N.B. The Hydrogen Economy is a dud in terms of affordable H_2 unless some brilliant finds of natural hydrogen are made.

Persistent Geological Challenges to a Natural Hydrogen World

Figures 1 and 4 show a dome-like anticlinal structure acting as a gas trap (actually a place where the flux of hydrogen and helium from earth to space is be slowed), and exploration can 'discover' valuable NG resources; but how much of this gas will be hydrogen, nitrogen, carbon dioxide and methane as well as hydrogen and helium? What do you do with the co-produced CO_2 and CH_4? Can both gases be sequested?

N.B. Hydrogen, being an industrial commodity, has a relatively low value. If the value was artificially increased (or at least subsidised) to meet the cost of recovery, cleaning and gas separation, and hydrogen transport and reticulation, would the cost of a H-E be acceptable to society? These are big questions.

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; diamonds are an unlikely product of methane cracking. The production of a carbon prime product may provide some latitude in hydrogen pricing. The process was originally promoted by the Kvaerner Corp 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 (not sterilisation) that could bring major benefits to world health.

Natural Hydrogen: Has it real worth?

The real worth of natural hydrogen has still to be found. 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?

Nitrogen, an odd-fellow of a gas: Not entirely inert, essential to life (constituent of amino acids) and a useful industrial commodity

Pure nitrogen is usually recovered from the air using cryogenic separation (N_2 being 78% of the atmosphere). In helium production liquid nitrogen – LN_2 (77K boiling point) that is a component of NG is used as a thermal buffer in double-skinned helium transport flasks (internal flask ~44,000 litres LHe) and as a 'cold' heat exchange medium in helium production and liquefying. Nitrogen is likely to have similar roles in hydrogen production. In the production of helium excess liquid and compressed cold nitrogen are often produced. Cold nitrogen, produced in helium and hydrogen works, could be used in the food industry. The customer would be essentially purchasing 'cold'.

Conclusion

Finding resources of natural hydrogen that make sense for development in the Hydrogen Economy world seems very unlikely at this time. Petroleum explorationists, who have searched for natural gas (of any composition), have not yet found TCF quantities of high percentage natural hydrogen despite seventy years of NG exploration; they are either very unlucky with their explorations or more likely have come to the realisation that natural hydrogen exists in relatively small and impure finds.

Natural 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. Natural 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 (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.

Best of luck with your helium, hydrogen and nitrogen ventures and adventures.

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References

1. Extracted from publications produced by Central Petroleum Ltd, Circa 2010 – 2014
2. Water Radiolysis: Influence of Oxide Surfaces on Hydrogen Production under ionising Radiation. Sophie Le Caer Water, 2011, Vol 3, p 235 – 253, doi: 10.3390/w3010235
3. Calculated from extracted figures from an IAEA nuclide web interactive data spreadsheet. www.nds.iaea.org/reinsd/NdsEndsf/QuertForm.html
4. Crabtree G, Dresselhaus M and Buchannan M, Hydrogen Economy, Dec 2004, Physics Today, Vol 57, Issue 12
5. Kvaerner Patent, Hydrocarbons Cracking, Norway, N0175718C, Nov. 2011