

## Perspective

# Natural hydrogen resource exploitation must confront the issue that certain gas compositions are undesirable in terms of environmental sustainability

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### Abstract:

Exploration for natural hydrogen subsurface accumulations (“white” hydrogen) is justified based on supply requirements for expanded hydrogen-based energy systems. However, there are some key issues that require more detailed assessment before the exploitation of such resources can be justified from resource availability, environmental and sustainability perspectives. Three key issues of concern are: lack of large porous and permeable reservoirs containing hydrogen found to date; avoiding leakage of hydrogen from surface and subsurface production facilities; and finding sub-surface hydrogen reservoirs not substantially contaminated with methane or carbon dioxide but ideally almost pure hydrogen accompanied by commercial volumes of helium. The perspective presented explains why these issues are important and why the energy industry, academia and governments need to focus more on them if expanded hydrogen-based energy systems are to be developed to contribute to net-zero global emissions from the energy sector by 2050.

## 1. Introduction

In recent years, the value of locating and potentially exploiting naturally occurring subsurface hydrogen resources (so-called “white” hydrogen) has been recognised. This is because they potentially offer an alternative to generating hydrogen from natural gas via steam methane reforming (SMR; so-called “grey” hydrogen) and avoid its associated carbon emissions (Sadeq et al., 2024). SMR is the most commercially viable method of generating hydrogen on an industrial scale. Although electrolysis of water to generate “green” hydrogen can avoid generating greenhouse gas emissions (GHG) it is inefficient and expensive at industrial scales. Even when the SMR process is burdened with the costs of carbon capture and storage (CCS) it can produce “blue” hydrogen more cheaply than “green” hydrogen at industrial scales, when applying existing technologies. Hence, natural, or “white” hydrogen

resources have the potential to provide hydrogen at relatively low cost and without releasing substantial GHG to the atmosphere (Zgonnik, 2020). However, there are some technical and environmental problems associated with the exploitation of subsurface natural hydrogen that need to be addressed and overcome:

- 1) Locating commercially viable resource volumes in porous/permeable reservoirs.
- 2) Avoiding leakage of the highly mobile and reactive hydrogen molecule from such reservoirs to prevent contamination and safety concerns.
- 3) Finding resource accumulations with minimal contents of GHG.

To date natural hydrogen resources have not been found located in large porous and permeable reservoirs. Only one small, low porosity reservoir in Mali is currently being pro-

duced. This may be a consequence of limited historical exploration being focused specifically on finding hydrogen. Large hydrogen accumulations might not survive over geological time scales but are degraded due to abiotic mineral interactions and biotic reactions into other compounds. Known surface seeps of hydrogen do result in alteration/degradation of soil and vegetation (Larin et al., 2015). Hydrogen seepage and leakage from buried pipelines, wellbores, and underground hydrogen storage (UHS) facilities should not be underestimated. In the seeps evaluated natural hydrogen is not the dominant gas due to contamination with CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub> or helium (He) (Etiopie, 2023). It would be costly to separate hydrogen from such contaminants while avoiding the release of CH<sub>4</sub> and CO<sub>2</sub> to the atmosphere. Key stakeholders (industry, academia, and governments) are not focusing sufficiently to overcome the mentioned challenges.

## 2. Sources of natural hydrogen

There is a diversity of biotic and abiotic sources of natural hydrogen (Gregory et al., 2019; Klein et al., 2020). While biotic processes are dominant close to the earth's surface abiotic processes are geologically driven (Zgonnik, 2020). The main abiotic processes are:

- 1) Oxidation/reduction during the weathering and metamorphism of iron-rich oxides silicates and carbonates, with Fe<sup>2+</sup> converted in various ways to Fe<sup>3+</sup> (e.g., serpentinization of Fe<sup>2+</sup>-rich mafic minerals).
- 2) Fe<sup>2+</sup> in the magnetite of banded iron formations converted by anoxic water at low temperature to form Fe<sup>3+</sup> maghemite (Geymond et al., 2023).
- 3) Water molecules split by radiolysis in various geological setting where radiogenic minerals rich in uranium, thorium, and potassium, such as hydrated portions of granites and organic-rich shales (Ball and Czado, 2022). Some helium is also generated as a biproduct of radioactive decay in such formations (Parnell and Blamey, 2017).
- 4) Oxidation of Fe<sup>2+</sup> ions by dissolved water during magma chamber degassing particularly along mid-ocean ridges (Wang et al., 2023), but with limited potential to accumulate in reservoirs.
- 5) Mylonitization in tectonically active zones where faults and fractures impact silica-rich sedimentary formations releasing free silicon radicals that combine with water to form silanol (SiOH) plus hydrogen (Sato et al., 1986).

Although some natural hydrogen-rich gases have recorded hydrogen of ~ 20% most do not contain >3.5% hydrogen (Milkov, 2022). However, in 2024, testing of the Ramsay well (Southern Australia) sampled zones with high hydrogen purity (up to 95.5%) and other zones containing up to 17.5% helium (FCW, 2024). Clearly, a substantial amount of abiotic hydrogen is being generated, particularly in diffuse forms, within the Earth's crust (shallow and deep) on an ongoing basis from a range of geological settings, providing substantial exploration potential. The exploration focus needs to target well-sealed, porous/permeable reservoirs situated close to identified sources of hydrogen generation to facilitate replenishment delaying that hydrogen being degraded into other gases.

The microbial processes involved in biotic natural hydrogen are complex, involving both production and consumption (Piché-Choquette and Constant, 2019). Although various types of hydrogen oxidizing microbes (aerobes and anaerobes) consume hydrogen in the subsurface forming water, sulfates and nitrates as biproducts, other microbes generate hydrogen, mainly using the enzyme hydrogenase in fermentation, and other processes not involving oxygen (Gregory et al., 2019). Some of these processes are being replicated in laboratories to test their suitability for commercial hydrogen manufacture (Khetkorn et al., 2017). Hydrogen-producing and methane-producing (methanogens) bacteria co-exist in relatively shallow, carbon-rich formations such as coal and organic-rich shales, although most of the hydrogen produced in such conditions is transformed into CH<sub>4</sub> (Su et al., 2018). It is estimated that up to about ninety percent of the abiotic hydrogen generated and seeping to the surface is biotically consumed (Boyd et al., 2024). Microbial processes pose risks of consumption of some hydrogen stored in UHS facilities (Smigan et al., 1990) involving methanogenesis and the production of some hydrogen sulfide (H<sub>2</sub>S) causing pyrites precipitation (Amid et al., 2016). H<sub>2</sub>S traces in stored hydrogen also pose safety risks and incur additional sales gas purification costs.

## 3. Environmental Impacts of hydrogen leakage

A natural hydrogen cycle of production, consumption, and seepage to the atmosphere leads to a near steady-state of seasonally varying, hydrogen concentration ranges being perpetuated in the Earth's atmosphere and surface soil. However, much uncertainty exists regarding how easily that steady state might be disrupted by a rapidly expanding hydrogen-based energy system, particularly by increased hydrogen leakage from well bores, surface and subsurface storage, and transportation facilities.

Hydrogen is not a direct greenhouse gas but through its indirect atmospheric reactions generates relatively short-lived, but potent GHG impacts compared to CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub>. It does this indirectly by generating ozone, methane, and water vapor in the atmosphere (Forster et al., 2021). From a single pulse of hydrogen, the atmospheric impacts are only significant for about two decades (Paulot et al., 2021). When long-term GHG impacts are considered the role of hydrogen tends to be underestimated (Ocko and Hamburg, 2022), but this is a mistake with growing hydrogen supply chains associated with continuous leakage of hydrogen, albeit at low rates. In fact, the impact of persistent and growing hydrogen emissions (natural and anthropogenic), which partly accumulate in the troposphere and partly in the stratosphere is far from insignificant (Paulot et al., 2021). Warwick et al. (2022) applied a methodology combining hydrogen's indirect GHG impacts on both stratosphere and troposphere more suited to gases with shorter-term GHG impacts. They calculated that the global warming potential (GWP100) of hydrogen over a 100-year period was 11±5 (relative to the GWP benchmark of 1 for CO<sub>2</sub>). Forster et al. (2021) compared the calculated radiative efficiency of hydrogen with those of CO<sub>2</sub> and CH<sub>4</sub> indicating that hydrogen's indirect global warming potency (on a unit

mass basis) was  $\sim 200$  times that of  $\text{CO}_2$  and greater than that of  $\text{CH}_4$ . These figures highlight that even small percentages of hydrogen leaking continuously into the atmosphere can have damaging climate impacts.

Ocko and Hamburg (2022) evaluated the climate impacts and GHG emissions avoided for a range of hydrogen leakage rates from green hydrogen generation facilities, and a range of hydrogen and  $\text{CH}_4$  leakage rates from green hydrogen generation facilities. Their results were compared with the GHG emissions from a generic SMR grey hydrogen generation facility. The climate outcomes varied substantially between different leakage rate assumptions. Blue hydrogen facilities with high leakage rates (10% for hydrogen; 3% for methane) generated higher climate impacts than the grey hydrogen plant. Part of the reason for this is the inefficient  $\text{CO}_2$ -capture capabilities ( $\sim 64\%$ ) of existing CCS technologies (Wei et al., 2024). Green hydrogen facilities with optimistically low hydrogen leakage ( $\sim 1\%$ ) avoided the climate impacts of grey hydrogen facilities over all time scales assessed. A blue hydrogen facility with very low leakage rates (1% for both hydrogen and  $\text{CH}_4$ ) achieved approximately the same climate impacts as a green hydrogen plant with 10% hydrogen leakage, essentially reducing the climate impacts of a grey hydrogen facility in less than one decade. There are clear benefits to reducing hydrogen leakage from all hydrogen supply chain infrastructure, regardless of whether the hydrogen comes from white, green, or blue sources.

Multiple surface seeps of natural hydrogen, mainly of abiotic crustal origin, have been detected in several countries in recent years including Australia, Brazil, Mali, Namibia, Oman, Russia, Turkey, and the U.S.A. (Etiope, 2023). These features are typically associated with quasi-circular surface anomalies, many forming minor topographic depressions, either filled with water or with water-logged terrain. Outer rings displaying inhibited vegetation growth (fairy circles) are common aspects of such features. Many of these overlie relatively shallow basement cratons or ophiolite deposits, suggesting that they are most likely being generated by iron oxidation processes. Migration through basement connected faults together with advection in groundwater systems are involved in transporting and replenishing the generated hydrogen (Fitts, 2023). It is unlikely that biotic hydrogen diffusion in soil could sustain the scale associated with such hydrogen seepage in locally concentrated areas (Etiope, 2023). The observed seeps are not pure hydrogen but may contain substantial concentrations of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and He (McMahon et al., 2022), with the former two contaminant gases substantially increasing the GHG contributions of these gas mixtures.

Potential exists to inject anoxic water into relatively shallow Fe-rich formations (e.g., banded iron formations or ultramafic rocks) to induce or accelerate natural processes that generate hydrogen, termed "orange" hydrogen (Osselin et al., 2022). This can be combined with carbon sequestration by injecting  $\text{CO}_2$ -rich aqueous solutions inducing carbonate precipitation. As part of the feasibility analysis of such projects, it is important to assess the potential sub-surface and surface environmental consequences of even relatively small-scale hydrogen (and/or  $\text{CO}_2$ ) leakage from such stimulated zones. The

negative impacts on surface and subsurface ecosystems from fugitive hydrogen seepage, and its associated methanogenesis, could be substantial if they are not adequately controlled and contained.

Most of the observed natural hydrogen surface seeps are less than one hundred meters in diameter, although a few of the more than five hundred such features studied in Russia are up to three kilometers in diameter (Larin et al., 2015). The studied hydrogen seeps are typically characterized by soil bleaching accompanied by reduced plant growth microbial development, and some dead zones. Such surface environmental damage raises concern over the possible long-term consequences of hydrogen seepage/leakage, even at relatively low levels, from subsurface infrastructure (e.g., buried pipelines and UHS facilities). Ecosystem damage and reduced crop yields are potential consequences.

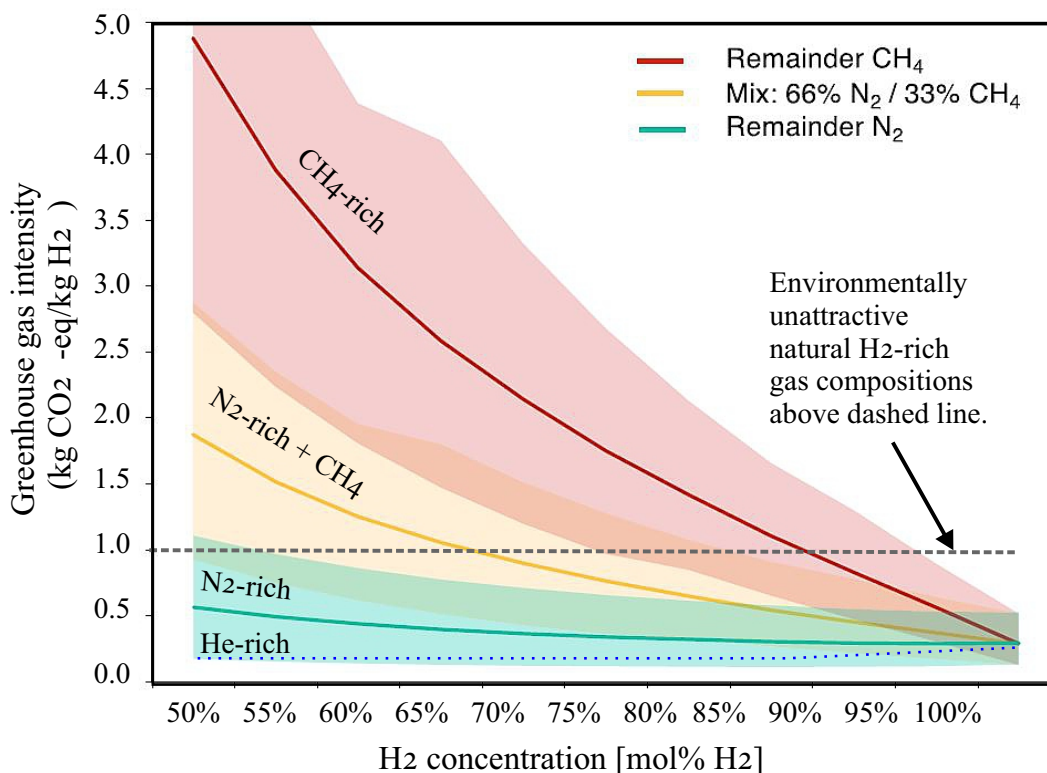
There is considerable uncertainty about the levels to which hydrogen leakage can be constrained in hydrogen supply chains (Warwick et al., 2022). Many feasibility studies assume that leakage would be constrained to the 1% to 2% levels, now achievable with best practices being enforced for methane-rich gas supply infrastructure. However, hydrogen is a much smaller, more mobile, and reactive molecule than  $\text{CH}_4$ , and is therefore likely to leak more easily than  $\text{CH}_4$  or  $\text{CO}_2$ . As the volumes of hydrogen supply chains increase, the GHG consequences of approximately 5% hydrogen leakage would likely result in substantial global warming impacts.

#### 4. Life-cycle analysis of natural hydrogen supply

Provisional life-cycle analysis of the potential GHG impacts of future natural hydrogen production systems (Brandt, 2023), involving a well production site and a gas processing/ purification facility, suggest high sensitivity to the produced gas composition (Fig. 1). That study focused initially on a benchmark gas composition of 85% hydrogen with contaminant gases including  $\text{N}_2$  (12%) and  $\text{CH}_4$  (1.5%). It assumed well productivity rates and reservoir depths of methane-rich gas reservoirs in the U.S.A. Those simulated gas composition and assumptions resulted in a GHG intensity (mainly from fugitive hydrogen leakage) of 0.4 kg  $\text{CO}_2$ -eq/kg  $\text{H}_2$  produced. However, as  $\text{CH}_4$  concentrations in the gas were increased the GHG intensity increased rapidly (Fig. 1). Those results imply that gas compositions with less than about 85% to 90% hydrogen, particularly those rich in  $\text{CH}_4$  would have substantial GHG consequences. By contrast, gas compositions of hydrogen and the inert gas helium would have reduced GHG impacts. Hence, exploitation of hydrogen plus helium gas compositions should have the lowest GHG footprint and could benefit from two distinct revenue streams.

#### 5. Conclusions

There are clear commercial and cost justifications for exploration and eventual exploitation of relatively cheap-to-produce natural subsurface hydrogen reservoirs. That resource could supplement environmentally sustainable supply from industrially produced hydrogen derived either from fossil fuels



**Fig. 1.** Simulated greenhouse gas intensities for potential field development sites of different hydrogen-rich natural gas compositions based on life-cycle analysis. The blue dotted line for hydrogen-helium mixtures is an estimate added to emphasize the environmental benefits associated with developing such reservoirs. Modified from Brandt (2023).

combined with carbon capture and sequestration (SMR-CCS; commonly termed “blue” hydrogen), or by the more expensive electrolysis of water powered by renewable energy (commonly termed “green” hydrogen). However, the exploitation of natural hydrogen resources is hampered by substantial logistical and environmental challenges that need to be confronted by industry and industrial regulators. The three most difficult challenges to overcome are:

- 1) finding subsurface reservoirs with sufficient volume, porosity and permeability capable of flowing and recovering substantial quantities of hydrogen to the surface.
- 2) avoiding fugitive seepage/leakage of hydrogen from surface and subsurface production infrastructure to minimize its green-house gas impacts and potential ecosystem damage.
- 3) finding subsurface reservoirs with gas compositions that are rich in hydrogen (>85%) with very low contamination by CH<sub>4</sub> and CO<sub>2</sub>, and, ideally, with commercial quantities of helium.

To overcome these challenges targeted exploration, research and regulation are required. Targeted exploration needs to focus on natural hydrogen sources least likely to be contaminated with CH<sub>4</sub> and CO<sub>2</sub>. Targeted research needs to focus on developing new or modified technologies and materials that can reduce hydrogen leakage from pipelines and hydrogen storage facilities (above and below ground) and inhibit methanogenesis in UHS reservoirs. Targeted hydrogen-

specific regulation and legislation is required to prevent the development of environmentally unsustainable natural hydrogen resource compositions. Surface and subsurface monitoring for hydrogen leakage from natural hydrogen production and storage should be mandated with penalties applied for excessive hydrogen leakage rates.

### Acknowledgements

Substantial hydrogen exploration efforts are ongoing around the world. Their results should provide valuable clarifications regarding the compositions and distribution of such resources.

### Conflict of interest

The author declares no competing interest.

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