



Science behind Natural Hydrogen and its Potential Application

Eiichi Setoyama

Hydrogen Use and Demand



Figure 2.19 Global hydrogen and hydrogen-based fuel use in the NZE

NZE: Net-Zero Emission

Effi Energy & Geoscience Institute

From IEA (2021, Net Zero by 2050)

Sources of Hydrogen (Colors of Hydrogen)



Low-emission H2: 0.7% in 2021

(IEA, 2022, Global Hydrogen Review)



Natural Hydrogen



- Mali discovery (originally a dry water borehole in 1987; gas analysis in 2012)
- Prinzhofer et al. (2018) on the Mali discovery
- 1st hydrogen borehole in the US (2018)
- Zogonnik (2020, Earth-Science Reviews)
- "Hidden Hydrogen" in Science (Feb 2023)
- H-NAT2023 (Nov 2023, Australia)



Natural Hydrogen



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Natural Hydrogen

Natural Hydrogen (a.k.a. Native Hydrogen)

Naturally occurring hydrogen that is not produced through industrial processes

- includes Geologic Hydrogen found in subsurface

High concentration of Natural Hydrogen reported from: **Ocean**

• Mid-ocean ridge, Hydrothermal vents

Surface

• Volcanos, Seeps, Geysers

Subsurface

• Soil, Hydrocarbon reservoirs, Evaporite deposits, Aquifers, Crystalline basement, Mineral mines, Coal mines, Hydrothermal systems, etc.



From Milkov (2022, Earth-Science Review)



Motivation behind Natural Hydrogen Research

Low Carbon footprint

- Yellow H₂ (Solar): 3.6 kg CO₂eq./kg H₂ (Kanz et al., 2021)
- Blue H₂ (SMR + CCS): 8.9 kg CO₂eq./kg H₂ (Lewis et al., 2022, NETL)
- Gray H₂ (SMR): 16.4 kg CO₂eq./kg H₂ (Lewis et al., 2022, NETL)

Low Water footprint (potentially)

- Blue H₂ (SMR + CCS): 24 litter/kg H₂ (NETL, 2022)
- Electrolytic H₂ (net zero USA): 10–80 litter/kg H₂ (Grubert, 2023)



Figure 5. Variation in GHG intensity as a function of H_2 concentration, with remainder gas being either pure CH₄ (red), 66% N₂/33% CH₄ (yellow), or pure N₂ (green)

From Brandt (2023, Joule)



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Cost

- Natural H₂: < \$1/kg H₂ (Gaucher et al., 2023, European Geologist)
- Blue H₂: \$1.64/kg H₂ (Lewis et al., 2022, NETL)
- Green H₂: \$5/kg H₂ (US DOE, 2021) to \$6/kg H₂ (Gaucher et al., 2023)

Levelised cost of hydrogen production by technology in 2021 and in the Net Zero Emissions by 2050 Scenario, 2030 and 2050



From IEA (2022, Global Hydrogen Review 2022)



Where and how much natural hydrogen?

Global geologic hydrogen resource potential estimate using a box model (Ellis and Gelman, 2023, IMAGE2023 abstracts)

- 1,000s to 1,000,000,000 Mt of H₂ in place
- Mean value in 10s of million Mt of H₂ in place
 + 10s to 100s Mt of H₂/year

Local estimate examples

- 5 Mt of H₂ in the Bourakébougou field, Mali
- 1.3 Mt of H₂ in the Yorke Peninsula, Australia
- 5-10 Mt of H₂ in the Monzón field, Spain
- 46 Mt of H₂ in the Lorraine Basin, France





Application of Natural Hydrogen



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Natural Hydrogen Exploration





Natural Hydrogen Exploration: Seeps



From Malvoisin & Brunet (2023, Science of the Total Environment)



From Zgonnik et al. (2015, Progress in Earth and Planetary Science



Modified from Moretti et al. (2022, International Journal of Hydrogen Energy)



Natural Hydrogen Exploration: Source/Generation

Hydrothermal alteration

Water + Iron-rich rock + Heat

- Serpentinization of mafic–ultramafic rocks
- · Hydration of siderite (sedimentary basins) and biotite in felsic rocks

Radiolysis

Water + U, Th, or K-rich rocks/evaporites

Mechanoradical generation

Water + Silicate minerals + Faults (orogenic belts, continental rifts, etc.)

Degassing of magmas

Water + Hydrogen sulfide

Oxidation of magnetite to hematite

Water + Banded iron formations

Overmaturation of organic matter

Organic matter + Heat (Ro > 3.5%)

Deep-seated hydrogen from the Earth's core and mantle

Stored in the mantle and core

Not produced in the mantle or the crust by chemical reactions



From Klein et al. (2020, Elements)



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Exploration targets: Basement areas with Fe-rich and/or uranium-rich rocks, such as Precambrian continental crust



Natural Hydrogen Exploration: Migration

- Diffusion and Advection
- Fractures and Faults as conduits
- High solubility of H₂ at depth
 - Long-distance migration as solute is also possible

Biotic and abiotic consumption of hydrogen

- Biotic: Methanogens (CH₄), Sulfate reducers (H₂S); Homoacetogens (CH₃COOH), Iron reducing bacteria (Heinemann et al., 2021, Energy Environ. Sci.)
- Abiotic: Redox reactions with Fe-bearing minerals, H₂S production, CH₄ production, through HC formation



Figure 7. Conceputal model of the H_2 cycle in the Sao Francisco Basin. (a) Interpretated seismic section (Martins-Neto, 2009). (b) Zoom of the upper part of the Bambui sequence. (c) Possible presence of a karst structure according to the presence of sinkholes (Figure 2). (d) Calculated solubility of H_2 in H_2O vs. depth (Bazarkina et al., 2020 [59]).

From Donzé et al. (2020, Geosciences)

Exploration targets: Deep faults



Natural Hydrogen Exploration: Reservoir and Seal

Seal/Trap

- Aquifers
- Igneous/metamorphic rocks
- Evaporite layers (e.g., Monzó-1, Spain)
- Clay (Athabasca, Canada)

Reservoir

- Sandstone
- Siltstone
- Igneous/metamorphic rocks
- Evaporite layers
- Carbonate rocks



Bourakébougou field, Mali

From Bendall (2023, Scientific Reports)



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Bourakébougou field, Mali



Exploration/Production Technology Readiness Level

TRL Native H₂ Exploration/Production



Modified from Gaucher et al. (2023, European Geologist)

Figure 1: Evaluation of the technology maturity using the Technology Readiness Levels (TRL) method.



Enhancing Natural Hydrogen Production



8 Direct

It might also be possible to tap the iron-rich source rocks directly, if they're shallow and fractured enough to allow hydrogen to be collected.

9 Enhanced

Hydrogen production might be stimulated by pumping water into iron-rich rocks. Adding carbon dioxide would sequester it from the atmosphere, slowing climate change.

Chemical, Biological, Mechanical, Thermal, etc.

From Hand (2023, Science)

ET G Category 1. Stimulation

The proposed model must be able to do one or more of the following:

1a. Increase reaction rate by $>10^5 \times$ over the rate found in the native ore being evaluated at an equivalent starting *T* and *P* (generic rate reported as 5×10^4 kgs⁻¹ for 1 km³).¹¹³

1b. Increase the rate of other target H_2 producing mineralogical processes to produce a *comparable amount of H*₂ to **1a.**



U.S. Department of Energy Announces \$20 Million to Explore Potential of Geologic Hydrogen

ARPA-E Unveils Two Initiatives Focused on Low-Cost, Low-Greenhouse Gas Emissions Hydrogen Production

Exploratory Topics (DE-FOA-0002784)

09/07/2023

Production of Geologic Hydrogen Through Stimulated Mineralogical Processes

Topic Issue Date	September 7, 2023
Deadline for Questions to <u>ARPA-E-CO@hq.doe.gov</u>	5 PM ET, October 13, 2023
Submission Deadline for Full Applications	9:30 AM ET, October 24, 2023

A. Topics of Interest

The following is a non-exhaustive list of technologies that are of interest for ET G. Applications can address one or more technologies:

- Stimulation and generation: Technologies which enhance the natural rate of serpentinization or other equivalent hydrogen producing geochemical reactions (*e.g.*, reduction of iron bearing minerals in banded iron formations, clinkers).
- *Modeling approaches:* Methods and tools to predict the viability of subsurface resources for stimulated hydrogen generation, inform reservoir management, or assist with stimulation efforts.
- Characterization: Methods and tools to map subsurface and ocean floor resources (e.g., ultramafic formations or other candidate formations) and quantify physiochemical properties of interest, specifically total Fe content, Fe(II) concentration, Fe(II)/Fe(III) ratio, specific surface area, permeability, or other parameters relevant to stimulated hydrogen generation.



Summary

- Demand for Hydrogen
- Application of Natural Hydrogen
- Natural Hydrogen System and Exploration

Next steps

- Natural Hydrogen layers on EGICONNECT (publicly available) by the end of 2023
- Natural Hydrogen updates on EGI LinkedIn account
- EGI Living Atlas of Natural Hydrogen (GIS + Wiki)





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Natural Hydrogen Exploration: Reservoir and Seal

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Reservoir

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Athabasca, Canada From Truche et al. (2018, Earth and Planetary Science Letters)

Exploration targets: "Traditional"+ Ignerous/metamorphic rocks and aquifers

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