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

- Onsite
  - Other
  - Refineries
  - Iron and steel
  - Chemicals

- Merchant
  - Other
  - Refineries
  - Industry
  - Shipping
  - Aviation
  - Road
  - Buildings
  - Electricity generation
  - Blended in gas grid

Low-carbon share

NZE: Net-Zero Emission

From IEA (2021, Net Zero by 2050)
Sources of Hydrogen (Colors of Hydrogen)

Artificial
- Coal (Black)
- Natural Gas (Gray)
- Methane (Turquoise)

Renewable Energy
- Water
  - Pink (≈ Red or Purple)
  - Nuclear
- Green

Natural
- Water
- Organic matter
- H$_2$S
- White (or Gold)

+ enhancement

Low-emission H2: 0.7% in 2021
(IEA, 2022, Global Hydrogen Review)
Public interest (Google Trends)

- Mali discovery (originally a dry water borehole in 1987; gas analysis in 2012)
- Prinzofer 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** (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 H₂ concentration, with remainder gas being either pure CH₄ (red), 66% N₂/33% CH₄ (yellow), or pure N₂ (green)

From Brandt (2023, Joule)
Motivation behind Natural Hydrogen Research

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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)

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 H\(_2\) in place
- Mean value in 10s of million Mt of H\(_2\) in place
- + 10s to 100s Mt of H\(_2\)/year

Local estimate examples

- 5 Mt of H\(_2\) in the Bourakébougou field, Mali
- 1.3 Mt of H\(_2\) in the Yorke Peninsula, Australia
- 5–10 Mt of H\(_2\) in the Monzón field, Spain
- 46 Mt of H\(_2\) in the Lorraine Basin, France

Locations and geological environments of recorded hydrogen measured at >10% volume around the world.

From Bendall (2022, MESA Journal)
Application of Natural Hydrogen

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Low-carbon share

NZE: Net-Zero Emission

From IEA (2021, Net Zero by 2050)

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Natural Hydrogen Exploration

- Associated minerals/Gases
  - Gold
  - Methane
  - Helium
  - Hydrogen sulfide
  - Nitrogen

- Associated geomorphological features
  - Fairy circle
  - Seep
  - White spot

Biotic and abiotic consumption of $H_2$

Seal/Trap

Reservoir

Migration

Source and Generation of $H_2$

- Serpentization
- Radiolysis
- Overmaturation of OM
- CH$_4$, H$_2$S, etc.

Others
Natural Hydrogen Exploration: Seeps

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

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

From Zgonnik et al. (2015, Progress in Earth and Planetary Science)
**Natural Hydrogen Exploration: Source/Generation**

**Hydrothermal alteration**
Water + Iron-rich rock + Heat
- Serpentinitization 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)
Natural Hydrogen Exploration: Source/Generation

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

From Boreham et al. (2021, APPEA Journal)
Natural Hydrogen Exploration: Migration

- Diffusion and Advection
- Fractures and Faults as conduits
- High solubility of H\(_2\) at depth
  - Long-distance migration as solute is also possible

Biotic and abiotic consumption of hydrogen
- Biotic: Methanogens (CH\(_4\)), Sulfate reducers (H\(_2\)S); Homooacetogens (CH\(_3\)COOH), Iron reducing bacteria (Heinemann et al., 2021, Energy Environ. Sci.)
- Abiotic: Redox reactions with Fe-bearing minerals, H\(_2\)S production, CH\(_4\) production, through HC formation

Figure 7. Conceptual model of the H\(_2\) cycle in the Sao Francisco Basin. (a) Interpreted 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\(_2\)O 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

From Bendall (2023, Scientific Reports)
Natural Hydrogen Exploration: Reservoir and Seal

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Bourakébougou field, Mali
### Exploration/Production Technology Readiness Level

#### TRL Native H₂ Exploration/Production

<table>
<thead>
<tr>
<th>TRL Level</th>
<th>Description</th>
<th>Status</th>
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<tbody>
<tr>
<td>0</td>
<td>Discovery of H₂ at the Earth surface</td>
<td>Done</td>
</tr>
<tr>
<td>1</td>
<td>Systematic research of H₂ seepages in various environments</td>
<td>Done</td>
</tr>
<tr>
<td>2</td>
<td>Short time monitoring of sites</td>
<td>Done for 2-3 sites</td>
</tr>
<tr>
<td>3</td>
<td>Understanding of the origin of H₂</td>
<td>Done for 2-3 sites</td>
</tr>
<tr>
<td>4</td>
<td>Small-scale prototype of permanent H₂ fluxes / Numerical modelling of the H₂ permanent seepages</td>
<td>In Progress in Academia</td>
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<tr>
<td>5</td>
<td>Median-scale prototype (1200 m)</td>
<td>Hydroma (Mali)</td>
</tr>
<tr>
<td>6</td>
<td>First deep borehole (3000 – 5000 m)</td>
<td>Natural hydrogen energy LLC Desert Mountain Energy</td>
</tr>
<tr>
<td>7</td>
<td>1st deep boreholes (3000–5000 m)</td>
<td>In progress Santos (Australia)</td>
</tr>
<tr>
<td>8</td>
<td>First Exploration plan at regional scale</td>
<td>No</td>
</tr>
<tr>
<td>9</td>
<td>Prototype of Production of the first discovery</td>
<td>No</td>
</tr>
</tbody>
</table>

**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.

**ET G Category 1. Stimulation**
The proposed model must be able to do one or more of the following:

1a. Increase reaction rate by \(10^3\times\) over the rate found in the native ore being evaluated at an equivalent starting \(T\) and \(P\) (generic rate reported as \(5\times10^4\) kgs\(^{-1}\) for 1 km\(^3\)).\(^{113}\)

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)**
Production of Geologic Hydrogen Through Stimulated Mineralogical Processes

<table>
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<tr>
<th>Topic Issue Date</th>
<th>September 7, 2023</th>
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<tr>
<td>Deadline for Questions to</td>
<td>5 PM ET, October 13, 2023</td>
</tr>
<tr>
<td>Submission Deadline for Full Applications</td>
<td>9:30 AM ET, October 24, 2023</td>
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</table>

**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 serpentinitization 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 physicochemical 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)
Natural Hydrogen Exploration: Reservoir and Seal

Seal/Trap

- Aquifers
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- Clay

Reservoir

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

Exploration targets: “Traditional”+ Igneous/metamorphic rocks and aquifers