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**Technical  
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Paper**



## **Solution Mining for Geologic Hydrogen**

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**SMRI Fall 2025 Technical  
Conference  
29-30 September 2025  
Wichita, Kansas, United States**

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### Abstract

Geologic hydrogen has been proposed to be the least expensive and least carbon-intensive form of hydrogen by the US Department of Energy's Advanced Research Projects Agency for Energy (ARPA-E). In addition, the US Geological Survey has suggested that broad areas of the United States are prospective for geologic hydrogen production. While there is active exploration in many locations around the world for hydrogen accumulated in conventional subsurface reservoirs (i.e., sandstones and limestones), there is also significant research into methods for stimulating hydrogen production from hydrogen "source rocks" (e.g., mafic and ultramafic rocks) largely by trying to accelerate the process of serpentinization. The technologies and workforce needed to operationalize these stimulation systems fit naturally into the core competencies of the solution mining industry, presenting new opportunities for growth. Current research is examining the effects of different fluid chemistries, temperatures, and pressures; the effects of microbes and catalysts; the use of steam and carbon dioxide as working fluids, as well as the effects of different technologies for inducing fractures in the subsurface to maximize reactive surface areas. This presentation will review the proposed stimulation systems within the context of the geochemistry of natural hydrogen production processes (i.e., serpentinization, radiolysis, deep degassing, cataclasis) and the mineralogy/petrology of source rocks to provide a guide with respect to what systems might work best in which types of deposits. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

**Key words:** Geologic hydrogen

### Introduction

After decades of falling or declining energy demand in the United States, current forecasts suggest that energy demand is expected to grow significantly over the next several decades due to the deployment of hyperscale data centers across our economy. At the same time, geologic hydrogen (hydrogen naturally or artificially produced from underground) has been suggested to be cheap, abundant, and a low carbon-intensity. *Cheap* because it can produce hydrogen at costs near, at or below the US Department of Energy's 2030 goal of \$1/kg. *Abundant* because broad areas of the US have been suggested to be underlain by prospective geology. And *low carbon intensity* because it can produce hydrogen with a lower carbon intensity than other common hydrogen production processes like electrolysis or steam methane reforming. The concept of geologic hydrogen is commonly describe as having two major subtypes: natural hydrogen and stimulated hydrogen. **Natural hydrogen** accumulates naturally in a subsurface trap similar to how other natural gasses (e.g., methane, helium) form, migrate, and are trapped underground. Natural hydrogen will likely require similar technology and methods as are available in the

current oil and gas industry. *Stimulated hydrogen*, on the other hand, involves engineering the production of hydrogen from hydrogen source rocks (e.g., iron-rich igneous and metamorphic rocks), essentially accelerating the natural process of source rock maturation. Numerous methods have been proposed to accomplish this stimulation, many of which are identical or similar to solution mining. This paper will describe those methods and where they might be applied.

## Natural Hydrogen Systems

Hydrogen has been identified in surface seeps (Zgonnik, 2020; Milkov, 2022). It has also been encountered in the subsurface during drilling for over 100 years. Dozens of pathways have been observed for hydrogen generation in the subsurface (summarized below from reviews by Zgonnik, 2020, and Milkov, 2022) that fall into several major categories (Table 1). Hydrogen produced by these processes can be trapped underground, seep to the surface, and/or be consumed in the subsurface by biotic and abiotic processes.

- **Fluid alteration** pathways involve the production of hydrogen from the physical and/or chemical alteration of subsurface fluids. **Deep degassing** involves hydrogen trapped in the mantle since Earth accretion to seep to the surface along crustal-scale faults. **Igneous activity** emits hydrogen into the air or ocean associated with oxidation of hydrogen sulfide gas. Lower pressures lead to higher partitioning of sulfur into the vapor phase where it can react with water to make hydrogen. **Hydrothermal fluid cooling and depressurization** can cause hydrogen to exsolve. Cooling and depressurization of **Groundwater mixing** can produce hydrogen.
- **Iron Oxidation** pathways produce hydrogen from the oxidation of Fe<sup>2+</sup>-bearing minerals. **Serpentinization** involves the alteration of iron-rich ultramafic rocks (e.g., peridotites, and dunites). **Basic Magma Oxidation** affects mafic magmas. **Magnetite Oxidation** in magnetite-rich igneous rocks or banded iron formations. **Biotite Hydration** in igneous rocks and **Siderite Hydration** in sedimentary and metasedimentary rocks can cause hydrogen formation and Fe<sup>2+</sup> is oxidized.
- Other **Mineral Alteration** pathways cause the production of hydrogen from the physical and/or chemical alteration of subsurface minerals. **Ammonium Mineral Oxidation by Sulfate** can produce hydrogen from evaporites rich in anhydrite. Hematite and magnetite interacting with hydrogen sulfide can cause **Pyritization** and hydrogen release. **Metamorphic Hydrolysis** can produce hydrogen when high temperatures split the water molecule. **Clay Mineral Dehydrogenation** can yield hydrogen when a fluid containing cations more readily substituted into a clay mineral lattice are introduced, liberating hydrogen.
- **Radiolysis** pathways generate hydrogen from water via ionizing radiation from naturally occurring minerals (those containing uranium, thorium, and potassium chiefly). **Water Radiolysis** has been observed in places like the natural fissioning “reactor” at Oklo, Gabon (Savary and Pagel, 1997). Radiolysis has been observed to produce hydrogen in both continental and oceanic crust, though production rates have been observed to be higher in continental crust (Klein et al., 2020). Hydrogen generation rate increases with (1) radionuclide concentrations, (2) concentration of other dissolved species, (3) availability of porewater, and (4) permeability, (Dzaugis et al., 2016; Klein et al., 2020). By interacting with organic matter in the subsurface, radiolysis can also produce hydrogen by **dehydrogenating organic molecules** and **polymerizing methane**.
- **Mechanical alteration** can produce hydrogen via two pathways. **Mechano-radical hydrogen** formation occurs when silica-bearing rocks are fractured, creating a surface with silicon radical that can dissociate water (Wakita et al., 1980; Hirose et al., 2011) and a recent estimate has suggested it is the largest source of natural hydrogen (Lefeuvre et al., 2025). Higher water-rock ratios, higher specific surface area, more acidic pH, lower temperatures, and higher grinding energy have been shown to increase hydrogen generation rate (Kita et al., 1982; Hirose et al., 2011; Lefeuvre et al., 2025). While hydrogen generation rate can vary based on lithology, during experiments even marble (a metamorphic carbonate) produced hydrogen (Hirose et al., 2011). In a similar fashion, mechanical breakdown of phosphate can cause **phosphine hydrolysis** that can yield free

hydrogen. The **breakage of fluid inclusions** in rocks can release hydrogen trapped at the time of magmatic cooling.

- **Organic matter alteration** can produce hydrogen as organic matter, kerogen, coal, oil, or natural gas are subjected to ever higher temperatures during burial as well as the presence of other chemical constituents in the subsurface, like sulfur. **Methane Decomposition** under metamorphic conditions to yield H<sub>2</sub>. **Methane Oxidative Coupling** has been observed to produce hydrogen in the lab in the presence of free oxygen and certain metal oxides. **Kerogen Formation, the maturation of Petroleum or Coal**, and **Thermal Decomposition of Organic Molecules** can yield hydrogen as longer organic molecules are broken down into shorter ones. **Thermochemical Sulfate Reduction** can also produce hydrogen as sulfur is incorporated into hydrocarbons.
- **Microbial activity** can also produce hydrogen via the pathways of **fermentation, nitrogen fixation, anaerobic carbon monoxide oxidation, phosphite oxidation**. Microbial activity has also been proposed as a major sink for natural hydrogen (Beller and Hurst, 2009; Müller and Huber, 2016; Liu and Wang, 2018) and specifically for radiolytic hydrogen (D'Hondt et al. 2009) and mechano-radical hydrogen (Hirose et al., 2011).
- **Anthropogenic activity** can produce subsurface hydrogen during the processes of **drill bit metamorphism** (when the temperatures and pressures found in the near drill-bit environment alter subsurface minerals or organic matter to release hydrogen) or via the **oxidation/corrosion of steel** in the well (e.g., well casing).

### Stimulating hydrogen production

While the list of processes in Table 1 is lengthy, it is likely that it is not complete and new natural processes will yet be discovered in the future. However, it does serve as a useful starting point because most companies and research laboratories seeking to stimulate subsurface hydrogen generation endeavor to accelerate one or more of these processes (Table 2). Because many of these activities are in the early stages of research and development, publicly available information is largely in the form of press releases, company websites, conference abstracts, and grant awards.

Numerous entities are proposing or studying the acceleration of natural serpentinization reactions in ultramafic rocks via low- or high-temperature water alteration (e.g., **Anning Corporation** (Anning, 2025); **Idaho National Laboratory** (Egert et al., 2026), **Lawrence Berkeley National Laboratory** (Procopiou, 2024), **New Jersey Institute of Technology** (Ngoma et al., 2024), **Sandia National Laboratories** (M. Allendorf, personal communication), **Pusan National University** (Kim and Jeong, 2024), **Texas A&M University** (Sekar and Okoroafor, 2025)

The second most common method being researched is the injection of chemicals, carbon dioxide, or catalysts into mafic or ultramafic rocks (**Georedox** (Georedox, 2025), **Koloma** (ARPA-E, 2024), **Lawrence Berkeley National Laboratory** (Procopiou, 2024), **University of Texas-Austin** (UTA, 2024); **VEMA** (VEMA, 2025)).

Other groups are studying a more diverse array of techniques and hydrogen sources, such as:

- **Eden Geopower** is testing electrical fracturing of ultramafic rocks in Oman (Eden, 2025). Electrical fracturing has the benefit of subsequent fracturing being focused through unfractured rock, rather than fractured rock like in hydraulic fracturing.
- **Addis Energy** seeks to inject water, air, and catalysts into subsurface iron-rich rocks to generate hydrogen as ammonia (Gao et al., 2025; Addis, 2025).
- **GoldH2** has announced a successful field test of its technology to inject microbes into old oil fields to produce hydrogen from unproduced hydrocarbons (Levi, 2025). **Koloma** is researching microbial methods to produce hydrogen from ultramafic rocks (ARPA-E, 2024).

- **New England Research** (NER, 2025) and **Los Alamos National Laboratory** (LANL, 2024) seek to develop advanced hydraulic fracturing methods to produce hydrogen.
- **ProtonH2** (ProtonH2, 2025) has designed a system to inject oxygen into legacy oil and gas fields to produce a blend of syngas (carbon monoxide and hydrogen) from which pure hydrogen can be separated depending on customer specification. While their system is not carbon neutral, it does claim to sequester 15-20% of produced CO<sub>2</sub>.
- **TerraVent Environmental** (FuelCellWorks, 2025) seeks to use electromagnetic-assisted catalytic heating for converting methane to hydrogen
- **Texas Tech University** seeks to use hydraulic fracturing with electromagnetic heating (Wanambwa et al., 2024)
- **Lawrence Livermore National Laboratory** is studying methods to use short-chain organic acids to stimulate hydrogen production (LLNL, 2024).
- **New Mexico Institute of Mining and Technology** leads a team that is researching steam stimulation of ultramafic deposits for the production of hydrogen analogous to methods used for heavy oil production like steam-assisted gravity drainage (SAGD) (Czarnota, personal communication).
- **Pennsylvania State University** seeks to use inert gas dynamic fracturing and carbon dioxide stimulation (Robinson, 2024).
- **University of Southern California** is translating technology used for so-called “huff-n-puff” stimulation of shale resources (ARPA-E, 2024). This method involved a cyclic process of subsurface fluid injection, a period of permeation and chemical reaction, and finally production of the resource back to the surface.

## Discussion

Classically, solution mining is defined as an in-situ mineral extraction technique in which a solvent—commonly water, brine or dilute acid—is injected through boreholes into an underground deposit to selectively dissolve target minerals such as salt, potash, uranium or lithium (Bartlett, 2013). As the solvent percolates through the mineralized layer, it forms a pregnant solution that is pumped back to the surface via production wells. There, the dissolved minerals are recovered through evaporation, precipitation or ion-exchange processes, while the remaining fluid is often recycled for further injection.

On the other hand, stimulating unconventional hydrocarbon resources (like shale gas and shale oil) typically relies on extended-reach horizontal drilling and hydraulic fracturing (Gidley, 1992; Ran, 2020). After vertical drilling to the target shale layer, the drill bit is steered horizontally for thousands of feet within the formation to maximize exposure. High-pressure fluid—usually water mixed with chemical additives and fine proppant (sand or ceramic beads)—is then pumped down the well in multiple stages to create and prop open a dense network of fractures in the otherwise low-permeability rock. These induced fractures dramatically increase the formation’s effective permeability, allowing trapped oil and natural gas to flow back into the wellbore for recovery. Once fracturing is complete, most of the injected fluid is recovered at the surface for reuse or disposal, while the proppant remains in place to keep pathways open, boosting both initial production rates and overall hydrocarbon recovery.

Solution mining for hydrogen (or stimulated hydrogen production) shares aspects of both methods. Like traditional solution mining, producing hydrogen is envisioned as needing to inject a fluid to cause a chemical reaction with either subsurface rocks or petroleum. But like stimulating shales, the host formation may need to be stimulated mechanically or thermally to

increase permeability, and a gaseous resource is produced back to the surface. Both solution mining and unconventional hydrocarbon stimulation incorporate processes to separate produced fluids so the economic parts (e.g., oil, gas, minerals) can be marketed and the working fluids can be re-used or disposed. The variety of methods being studied in the lab or field (Table 2) go beyond even these simple descriptions to include such varied and novel processes like injecting microbes or electrical stimulation.

It is likely that given the heterogeneity in stimulatable rock types found across the globe, some of these methods will work well with some rock types, while other rock types may require new methods not yet being researched. As data from ongoing laboratory research and field trials yield new publications, we will likely develop a better understanding how to match production process with deposit rock type.

## **Conclusions**

The companies and laboratories listed in Table 2 represent some of the first groups studying engineered geologic hydrogen production as a source of energy. Despite the breadth and depth of the projects outlined above, when compared to the numerous pathways for natural geologic hydrogen production (Table 1), it is clear that there is still much room to study and optimize other methods for stimulating hydrogen production beyond the major focus on accelerating serpentinization in ultramafic rocks. Indeed, when mapped to the broad array of possible subsurface stimulation techniques (Table 3), numerous unexplored technologies are evident that may warrant further research because of the opportunity to translate existing technology, methods, and workforce from the petroleum, geothermal, and mining industries.

**Table 1: Processes known to produce hydrogen underground (cf. Zgonnik, 2020; Milkov, 2022).**

Process Family	No.	Process	Critical Ingredient(s)	Hydrogen Source
Fluid Alteration	1	Deep degassing	Pathway from Mantle	Hydrogen
	2	Volcanic activity	Volcanic Fluids	Water, H <sub>2</sub> S
	3	Hydrothermal cooling and depressurization	Volcanic Fluids	Methane
	4	Groundwater mixing	Water	Water
Iron Oxidation	5	Serpentinization	Fe in Ultramafic Rocks	Water
	6	Basic magma oxidation	Fe in Mafic rocks	Water
	8	Biotite hydration	Felsic Rocks	Water
	9	Siderite hydration	Siderite	Water
	10	Magnetite oxidation	Magnetite	H <sub>2</sub> S
Mineral Alteration	11	Ammonium mineral oxidation by sulfate	Anhydrite rocks	Ammonium
	12	Pyritization	Volcanic rocks	H <sub>2</sub> S
	14	Metamorphic hydrolysis	Heat, Pressure	Water
	15	Clay mineral dehydrogenation	Exchange-worthy Cations	Clay Minerals
	7	Metasomatism with metal hydrides from deep mantle	Ultramafic rocks	Metal Hydrides
Radiolysis	16	Radiolysis via U/Th/K minerals	U/Th/K minerals	Water
	17	Radiolytic dehydrogenation of organic molecules	U/Th/K minerals	Organic molecules
	18	Radio-polymerization of methane	U/Th/K minerals	Methane
Mechanical	19	Mechano-radical formation	Silicate rocks, stress	Water
	13	Phosphine hydrolysis	Phosphate rocks	Phosphine
	20	Fluid inclusions	Basement rocks, especially granites	Hydrogen
Organic Matter	21	Methane decomposition	Heat	Methane
	22	Methane oxidative coupling	Alkali metal or lanthanide oxides, heat	Methane
	23	Kerogen formation	Heat	Kerogen
	24	Petroleum or coal maturation	Heat	Hydrocarbons, coal, kerogen
	25	Thermal decomposition of organic molecules	Heat	Hydrocarbons, coal, kerogen
	26	Thermochemical sulfate reduction	Sulfate, heat	Hydrocarbons
Microbial	27	Fermentation	Organic Matter	Water/OM
	28	Nitrogen fixation	Organic Matter	Water/OM
	29	Anaerobic carbon monoxide oxidation	Organic Matter	Water/OM
	30	Phosphite oxidation	Organic Matter	Water/OM
Anthropo-genic	31	Drill bit metamorphism	Organic Matter	Organic Matter
	32	Steel Oxidation by CO <sub>2</sub>	Steel/Iron, CO <sub>2</sub>	Water
	33	Steel Corrosion by H <sub>2</sub> S	Steel/Iron, H <sub>2</sub> S	Water
	34	Steel Corrosion by Acid Groundwater	Steel/Iron, Acid Groundwater	Water

**Table 2: Known processes that may produce hydrogen underground. NL = National Laboratory**

Type	Organization	Code	Technology	Source
Company	Addis Energy	Addis	Water, air, catalyst geoconversion to ammonia	Ultramafic
	Anning Corporation	Anning	Water and heat stimulation	Ultramafic
	Eden Geopower	Eden	Electrical fracturing	Ultramafic
	GeoRedox/Sage	GeoRedox	Catalyst-free water stimulation	Diverse
	GoldH2	GoldH2	Microbial stimulation of petroleum	Petroleum
	Koloma	Koloma	Geochemical and microbial models	NA
	New England Research	NER	Hydraulic fracturing	Ultramafic
	ProtonH2	ProtonH2	In-situ oxidation of petroleum to yield syngas (CO+H <sub>2</sub> )	Petroleum
	TerraVent Environmental	TerraVent	Electromagnetic-catalytic heating for CH <sub>4</sub> conversion	Petroleum
	VEMA	VEMA	Chemical stimulation	Ultramafic, BIF
Lab	Texas Tech University	TTU	Hydraulic fracturing with electromagnetic heating	Petroleum, Ultram.
	Idaho National Lab	INL	Water and heat stimulation	Ultramafic
	Lawrence Berkeley NL	LBNL	Low Temperature chemical & catalyst stimulation	Ultramafic
	Lawrence Berkeley NL	LBNL	High pressure, high temperature	Ultramafic
	Lawrence Livermore NL	LLNL	Short-chain organic acid stimulation	Ultramafic
	Los Alamos National NL	LANL	Geochemical and hydromechanical stimulation	Ultramafic
	New Jersey Institute of Tech.	NJTech	High temperature stimulation	Ultramafic
	New Mexico Tech	NMT	Steam stimulation	Ultramafic
	Pennsylvania State University	PSU	Inert gas dynamic fracturing and CO <sub>2</sub> stimulation	Ultramafic
	Pusan National Univ. (Korea)	Pusan	Low temperature stimulation	Ultramafic
	Sandia National Laboratories	Sandia	Water and heat stimulation	Ultramafic
	Texas A&M University	TAMU	Water and heat stimulation	Ultramafic
	Univ. of Southern California	USC	Huff-n-Puff stimulation	NA
	University of Texas-Austin	UTA	Abiotic catalyst and carbon dioxide stimulation	Mafic



**Table 3: Publicized stimulated hydrogen companies or laboratory research mapped to reservoir stimulation technologies.**

<b>Method</b>	<b>Technique</b>	<b>Organization (See codes in Table 2)</b>
Mechanical	Acid Fracking	-
	Electrical Fracturing	Eden
	Explosive Fracturing	-
	Hydraulic Fracturing	LBNL, NER, TTU
	Proppant Fracturing	-
Chemical	Acidization	-
	Catalysis	Addis, LBNL, UTA
	Oxygenation	ProtonH2
	Solvents/Leaching	LANL, LLNL, VEMA
	Surfactants	-
	Other chemical / lixiviant	Addis, GeoRedox, INL, Koloma, VEMA
Biological	Encourage Microbes	GoldH2, Koloma
	Discourage Microbes (Biocides)	-
Thermal	Heating	Anning, INL, LBNL, NJTech, Pusan, Sandia, TAMU
	Steam Heating	NMT
	Electrical heating	TerraVent, TTU

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