U.S. Department of Energy
Advanced Research Projects Agency – Energy (ARPA-E)

Request for Information (RFI)
DE-FOA-0002786
on
Stimulating Geochemical Reactions in the Subsurface for *in-situ* Generation of Hydrogen and Helium Production

Introduction

The purpose of this RFI is to solicit input for a potential future ARPA-E research program focused on enabling technical advances which could lead to subsurface chemical reactors and gas separations. ARPA-E is seeking information to test the hypothesis that the subsurface can be used as a reactive environment to produce hydrogen at $1/kg, per DOE's Hydrogen Shot target[1], and helium with no carbon emissions.

Subsurface reactions have and do occur every day without human intervention, ranging from the mundane like abiogenic methane formation to the exotic like nuclear fission. The subsurface has a number of features which could make it amenable to performing chemical synthesis including hot temperatures (200-400+°F), high pressures, and catalytically relevant metals contained in rocks.

It is already known that geothermal heat is a significant source of renewable energy. There are several initiatives devoted to resource discovery and development through the DOE's Geothermal Technology Office which aim to use this thermal energy to produce electricity or to provide hot water and space heating. However, it may be possible to use this thermal energy for chemical synthesis. Typical deep geothermal temperature ranges (175-400°F) overlap well with chemical and other high-temperature processes (*Figure 1*).

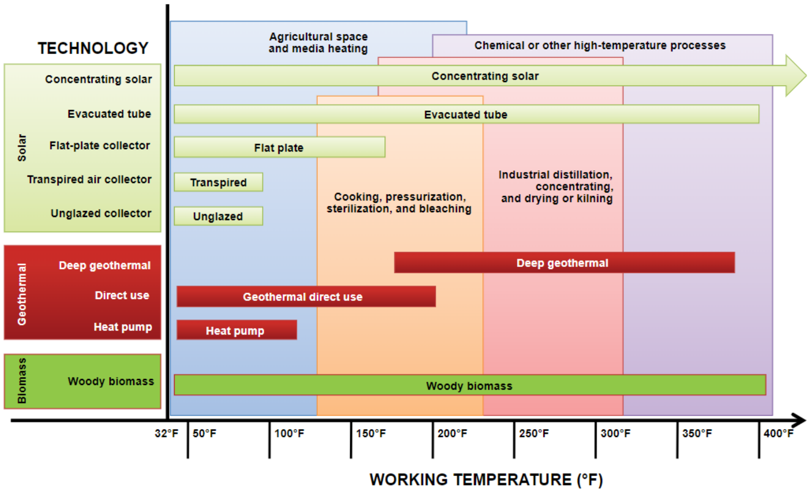

Figure 1. Typical ranges of renewable energy technologies compared with heating needs across industrial sectors. Graph obtained from EPA: https://www.epa.gov/rhc/renewable-industrial-process-heat (Accessed on March 11, 2022).

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[1] Hydrogen Shot | Department of Energy

In addition to warm thermal conditions, the subsurface is characterized by high pressures. The pressure gradient at depth is related to hydrostatic pressure change (10 kPa/m). Pressures relevant to typical industrial processes can be accessed at depths that are well within the normal range of subsurface activities today. For example, a typical Haber Bosch process is done at pressures of 400 atm: approximately the same pressure found at a depth of 2 km. Finally, rocks may contain metals which are catalytically relevant for several industrial chemical processes. Nickel-iron alloys are frequently found in rocks and both nickel and iron are common catalytic metals in industrial processes. In this RFI, ARPA-E seeks to test the hypothesis of whether the temperature, pressure, and metals in the subsurface could be exploited for chemicals synthesis.

ARPA-E is specifically interested in information to understand the technical potential of stimulating hydrogen generation in hard rock and hydrocarbon-rich basins. Within the context of hard rock, hydrogen is naturally produced via radiolysis where radioactive decay interacts with water to produce hydrogen and oxygen or via serpentinization where mafic and ultramafic rocks containing iron react with water in an oxidation-reduction reaction; the iron is oxidized and the water reduced to produce hydrogen and oxygen. Estimates of annual natural hydrogen production rates in terrestrial seeps place these rates equivalent to anywhere from 0.1-33% of today's global hydrogen production from fossil fuels[2]. Exact production rates are unknown, thereby contributing to the large variation in estimates, but it is clear that hydrogen-forming reactions occur in old, Precambrian rock which constitutes approximately 70% of the global continental crustal surface area. ARPA-E seeks information regarding the technical potential to stimulate hydrogen-forming reactions in old Precambrian rock as a way to produce clean hydrogen, using the subsurface as a georeactor.

Another avenue that ARPA-E is exploring for producing hydrogen in the subsurface is by cracking hydrocarbons. Today, hydrogen is predominantly produced from hydrocarbons at the surface, either from steam methane reforming (76% of hydrogen production) or coal gasification (23%)[3]. However, these processes are associated with significant carbon emissions, ranging from 9 tons CO_2 per ton H_2 in steam methane reforming to 19 tons CO_2 per ton H_2 in coal gasification. Minimizing the carbon footprint from hydrogen production in these instances will require retrofitting current processes to capture and sequester significant amounts of carbon, increasing the cost of hydrogen production overall and adding complexity to the process. ARPA-E is seeking insight to test the hypothesis that it can be more economical to produce hydrogen from fossil fuels in the subsurface, keeping the carbon in place and extracting only hydrogen at the surface (*Figure 2*). Producing hydrogen this way mitigates adding a separate carbon capture and sequestering step, but it is not clear if this is technically feasible or if it has the potential to be more economical than hydrogen production from fossil fuels with carbon capture and storage at the surface.

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[2] Zgonnik, V. The Occurrence and Geoscience of Natural Hydrogen: A Comprehensive Review. *Earth-Science Reviews*. **2020**, *203*, 103140. Sherwood Lollar, B., Onstott, T. C., Lacrampe-Couloume, G., Ballentine, C. J. The Contribution of the Precambrian Continental Lithosphere to Global H_2 Production. *Nature*. **2014**. *516*. 379-382. International Energy Agency. *The Future of Hydrogen Seizing Today's Opportunities.* June 2019.

[3] International Energy Agency. *The Future of Hydrogen Seizing Today's Opportunities.* June 2019.

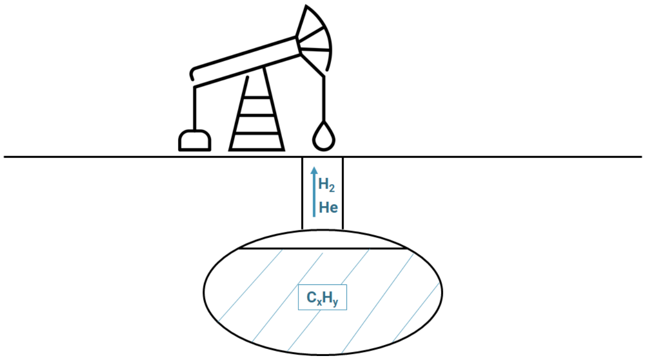

Figure 2. Hydrogen production from fossil fuels in the subsurface, keeping carbon in place while extracting only hydrogen.

To an extent, a version of this idea has already been investigated via underground coal gasification (UCG)[4]. Much of the development in UCG has historically been concentrated in Russia and China, though the US Department of Energy sponsored a total of 30 experiments between 1972-1989. One key result from DOE's coal gasification program was the development of the Controlled Retracting Injection Point (CRIP) process at Lawrence Livermore National Laboratory. Since this time, DOE involvement in underground coal gasification has been limited. ARPA-E recognizes that this technology is among the most mature for producing hydrogen-rich gases from fossil fuels in the subsurface with companies already trying to commercialize this technology. However, for the purposes of this RFI, ARPA-E is primarily interested in information for non-combustion routes to produce hydrogen from fossil fuels in the subsurface.

As shown in *Figure 2*, ARPA-E is also interested in approaches that enable the extraction of helium without co-production of hydrocarbons. Helium has a wide array of applications that impact the energy sector, including semiconductor manufacturing, electronics, quantum computing, and is a critical cryogenic coolant in everything from MRI equipment to fusion to scientific instrumentation[5]. Helium exists in the subsurface because it is a byproduct of uranium and thorium decay in the same radiolysis reactions that produce hydrogen or because it migrates up through the crust from the Earth's core. It is among the rarest elements in the Earth and due to its low molecular weight, helium regularly escapes the Earth's atmosphere where it is swept away by solar winds. Today, helium is primarily co-produced with natural gas when concentrations are above 0.3%. Between the privatization of the US's federal helium stock and the recent geopolitical fallout with the Russia-Ukraine war, securing global helium supply chains are of critical concern. While helium production cannot be stimulated in the same way as hydrogen in the subsurface, ARPA-E is interested in information on the potential of zero-emissions helium extraction without co-production of hydrocarbons.

The source, transport, and trap model for hydrogen and helium reside on a continuum of upstream fundamentals from the oil and gas and hard rock mining industries. On one end of this continuum resides H-He generation from hard rock sources (e.g., serpentinites and U-Th-rich granitoids), and the

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[4] Shafirovich, E. and Varma, A. Underground Coal Gasification: A Brief Overview of Current Status. *Ind. Eng. Chem. Res.* **2009**, *48*, 7865-7875.

[5] Kimani, Alex. The Helium Boom is about to Take Off in 2021. April 3, 2021. *Global Investment Daily*. https://globalinvestmentdaily.com/the-helium-boom-is-about-to-take-off-in-2021/. (Accessed March 28, 2022).

other from hydrocarbon-related source rocks (e.g., hot shales). Therefore, unique technological pathways for in-situ hydrogen and helium production exist in various geologic contexts with opportunities and challenges. Technical pathway opportunities for successful H-He recovery with no carbon emissions are still governed by structural geologic controls (e.g., faults), P-T conditions, and temporal relations. However, technical challenges and needs for economically successful H-He recovery include:

1. Successful hydrogen production by anthropogenic stimulation of source rock, other geologic mediums, and/or other materials.
2. Catalytic approaches for *in-situ* hydrogen production from hard rock or hydrocarbon deposits.
3. H-He surveying to monitor subsurface conditions to optimize well production, limit H-He subsurface diffusion, and prolong the life of the well.
4. Casing materials that limit H-He diffusion or degradation.
5. Successful H-He well production (e.g., a H-He selective membrane).
6. Parasitic losses of hydrogen in the subsurface that reduce its persistence.

Topics Not of Interest

This potential program is focused on novel technologies that enable stimulating chemical reactions in the subsurface. Approaches not of interest include:

- Work focused on basic research aimed at discovery and fundamental knowledge generation.
- Combustion-mediated underground hydrogen formation.
- Technologies that are primarily used in exploration activities which was the focus of a prior ARPA-E RFI (DE-FOA-0002599).

Please carefully review the REQUEST FOR INFORMATION GUIDELINES below. Please note, in particular, that the information you provide will be used by ARPA-E solely for program planning, without attribution. **THIS IS A REQUEST FOR INFORMATION ONLY. THIS NOTICE DOES NOT CONSTITUTE A FUNDING OPPORTUNITY ANNOUNCEMENT (FOA). NO FOA EXISTS AT THIS TIME.**

Purpose and Need for Information

The purpose of this RFI is solely to solicit input for ARPA-E consideration to inform the possible formulation of future research programs. ARPA-E will not provide funding or compensation for any information submitted in response to this RFI, and ARPA-E may use information submitted to this RFI without any attribution to the source. This RFI provides the broad research community with an opportunity to contribute views and opinions.

REQUEST FOR INFORMATION GUIDELINES

No material submitted for review will be returned and there will be no formal or informal debriefing concerning the review of any submitted material. ARPA-E may contact respondents to request clarification or seek additional information relevant to this RFI. All responses provided will be considered, but ARPA-E will not respond to individual submissions or publish publicly a compendium of responses. **Respondents shall not include any information in the response to this RFI that could be considered proprietary or confidential**.

Responses to this RFI should be submitted in PDF format to the email address ARPA-E-RFI@hq.doe.gov by **5:00 PM Eastern Time on July 11, 2022.** Emails should conform to the following guidelines:

- Please insert "Response to Hydrogen-Helium Geochemistry - <your organization name>" in the subject line of your email.

- In the body of your email, include your name, title, organization, type of organization (e.g. university, non-governmental organization, small business, large business, federally funded research and development center (FFRDC), government-owned/government-operated (GOGO), etc.), email address, telephone number, and area of expertise.
- Responses to this RFI are limited to no more than 10 pages in length (12-point font size).
- Respondents are strongly encouraged to include preliminary results, data, and figures that describe their potential processes.

Questions

ARPA-E is interested in surveying stakeholders interested in *in-situ* geochemical reaction stimulation and chemical separations. The questions posed in this section are classified into several different groups as appropriate. Please provide responses and information about any of the following. Citations are encouraged as appropriate. Please use metric units.

I. Subsurface Hydrogen Stimulation

i. General

    i. What is the expected energy balance (energy put into system to stimulate hydrogen production versus energy content of hydrogen produced)?
    ii. What co-production opportunities might exist (e.g. geothermal with hydrogen production)?
    iii. What state-of-the-art models are there to simulate hydrogen-forming reactions *in-situ*?
    iv. What is known about the water interaction with underground steel pipelines and well casings which may result in anthropogenic hydrogen production?

ii. Electrochemical

    i. Are there electrochemical processes that would be suitable for the subsurface (e.g., Is subsurface saline water electrolysis for hydrogen production conceivable)?

iii. Biologically-mediated

    i. What are the important hydrogen-forming and hydrogen-consuming microbial communities? In what subsurface environments can they be found?
    ii. How would hydrogen-producing and hydrogen-consuming microbe interactions be addressed to ensure sustained hydrogen production?
    iii. How would you address or exploit biofilms or other byproducts that might be associated with microbial activity?
    iv. How fast do hydrogen-producing microbes work?
    v. How does the presence of CO_2 or sulfides impact biologically-mediated hydrogen formation? What else is required to boost hydrogen production rates?
    vi. How would the limits for biological life limit the application space for biologically mediated approaches?

iv. Hydrocarbon cracking

    i. How might the anticipated cost of keeping carbon in place via subsurface gas separations compare with surface carbon separation and sequestration costs for current alternatives (e.g. steam methane reforming with carbon capture)?

    - ii. What alternative non-combustion methods exist that can provide a controlled thermal source to crack hydrocarbons in the subsurface? What temperatures are required? What is the achievable temperature in the subsurface and how does that compare to temperatures required to crack hydrocarbons?
    - iii. How might host geologic formations be leveraged for catalytic dehydrogenation of hydrocarbons?

  - v. Water-rock reactions (serpentinization)
    - i. Are there examples or potential routes for the catalysis of the reaction of water with Fe_2O_3 or iron(II) silicates to form hydrogen?
    - ii. Are there alternative oxidation/reduction reactions to serpentinization which may produce hydrogen and what types of minerals woud be involved?
    - iii. What changes to the rock permeability and porosity might be expected if performing serpentinization reactions? How might these changes impact production over time?
    - iv. What are typical rates of reactions as a function of temperature, pressure, rock type, other reactants, etc… What are the controls that could be leveraged to accelerate serpentinization?
    - v. Can serpentinization be done concurrently with carbon mineralization reactions? How does the presence of CO_2 impact hydrogen generation?
    - vi. What is the production potential of hydrogen based on the occurrence of iron-rich mafic and ultramafic rocks in the US?
    - vii. What impact does alteration of olivine (e.g., chlorite, bowlingite, iddingsite) have on hydrogen production from water-rock interaction?
    - viii. Do you anticipate the formation of alteration halos around the source of fluid injection? If so, what is the anticipated impact on hydrogen production?
    - ix. Could underground mines set in ultramafic rock be repurposed for *in-situ* hydrogen production?
    - x. Can some known temperature facilitate serpentine dehydration to olivine, and if so, can we recycle the same reservoir rocks for hydrogen production? Is there a method to retain the iron(II) silicate component of the olivine from the serpentine dehydration?
    - xi. How does surface area impact water-rock reactions and how might this impact subsurface hydrogen generation?

- *II. Gas Separations*
    - i. The classification of the two primary methods to purify and separate hydrogen is based on physical and chemical principles, such as absorption, adsorption, phase changes, chemical reactions, and permeation through membranes. The methods employed are based on practicality (i.e., operation conditions). Since *in-situ* hydrogen production may provide a unique opportunity to utilize the geothermal and geopressure gradient during gas separation, what H-He purification and separation processes can be employed in the subsurface and at what cost?
    - ii. What are the anticipated technical challenges for performing gas separations *in-situ?* How might those impact the production rates of hydrogen and helium?
    - iii. Are there gas membranes that could be applied as-is or will *in-situ* gas separations require a step change in the state of the art?

III. *Technologies*

- i. What tools are available to measure resource potential, production rates, fraction left behind, formation health monitoring? How would they need to be modified to address the different resources or production phases?
- ii. Surface exploration geochemistry has been applied in traditional oil and gas exploration. Are there new technologies that could be developed to adapt and enhance existing surface methods to specifically target hydrogen seep detection? Could remote sensing (e.g. drone, satellite, etc.) techniques be developed for surveying broad areas for hydrogen seeps?

IV. Other

- i. Are there other considerations or potential routes to subsurface hydrogen generation and helium production not explicitly addressed in the questions above?