Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Non-intermittent, Solar-thermal Processing to Split Water Continuously via a Near-isothermal, Pressure-Swing Redox Cycle

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DOE Project Award # DE-EE-0010729

Wednesday, May 8th, 2024

Project ID # P208

DOE Hydrogen Program 2024 Annual Merit Review and Peer Evaluation Meeting

NREL Transforming ENERGY
BERKELEY LAB Bringing Science Solutions to the World
Sandia National Laboratories
INL Idaho National Laboratory
Lawrence Livermore National Laboratory

Project Overview

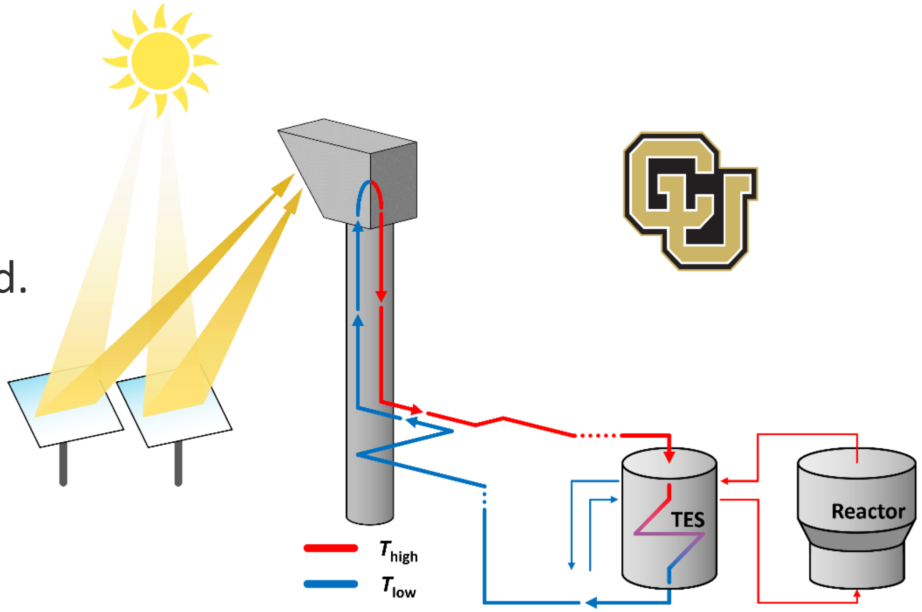
Project Partners

PI: Prof. Alan (Al) Weimer, University of Colorado Boulder
Britt Boughey, OMC Thermochemistry
Prof. Aldo Steinfeld, ETH Zürich
National Renewable Energy Laboratory (NREL)

Award #	EE0010729
Start/End Date	10/01/2023 – 9/30/2025
Project Funding*	$1.25M (DOE + Cost Share)

Project Vision

Conventional solar receiver-reactors that rely on direct irradiation and, consequently, affixed solids encounter difficulties with transport, durability, and power density when evaluated beyond the laboratory scale. By decoupling the reactor from the solar receiver and designing a process that leverages flowable powders, efficiency and scalability issues that have long challenged solar thermochemical hydrogen (STCH) production technologies can be readily abated.



Project Impact

Identify a path that, for the first time, results in both efficient and scalable production of hydrogen via solar thermochemistry, ultimately enabling DOE technical targets (i.e., $1/kg for a 50,000 kg H_2 day^{-1} plant) to be met.

** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach – Summary

Project Motivation

- 63% of Q_{solar} in record $\eta_{solar\text{-}to\text{-}fuel}$ demonstration was attributed to sensible heating of the solid
- Unlike attempts to recuperate the sensible heat rejected during temperature-swing operation, techniques for implementing highly effective (i.e., ≥ 95%) gas-gas heat recovery are already established
- Recent innovations in material selection and pressure-swing operation have warranted further investigation into the isothermal (and near-isothermal) STCH cycle

Barriers

- We have elected to implement our STCH cycle in a fluidized bed reactor configuration in an attempt to emulate how existing commercial-scale technologies that involve thermochemistry often operate. Can a gas distributor that can tolerate temperatures near 1673 K be developed? Can we avoid slugging at this scale?

Key Impact

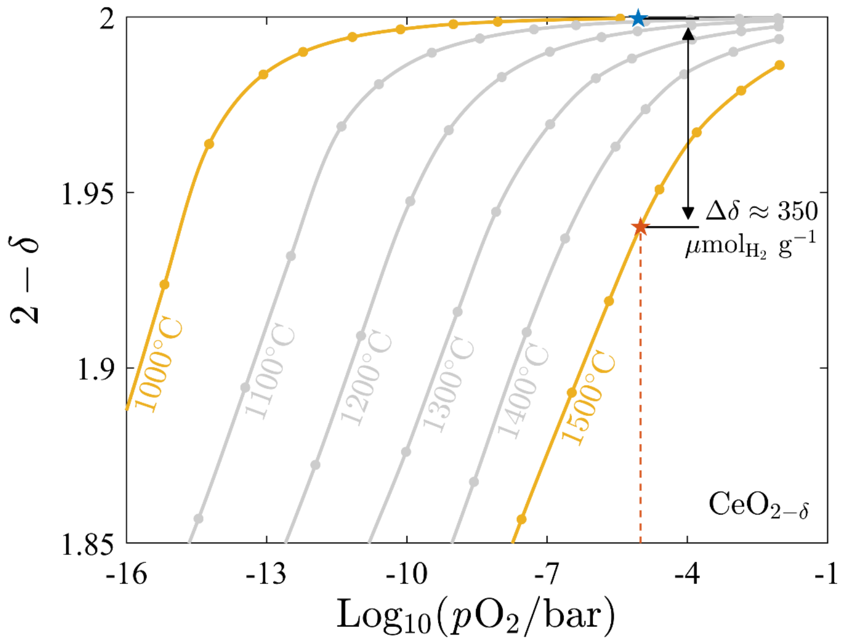
Metric	State of the Art	Expected Advance
Active Material	$CeO_{2-\delta}$	$(Fe_{\zeta}Al_{1-\zeta})_{3-\delta}O_4$
Reactor Design	directly-irradiated affixed structures	decoupled reactor involving flowable powders
$\eta_{solar\text{-}to\text{-}fuel}$	6%	> 10%

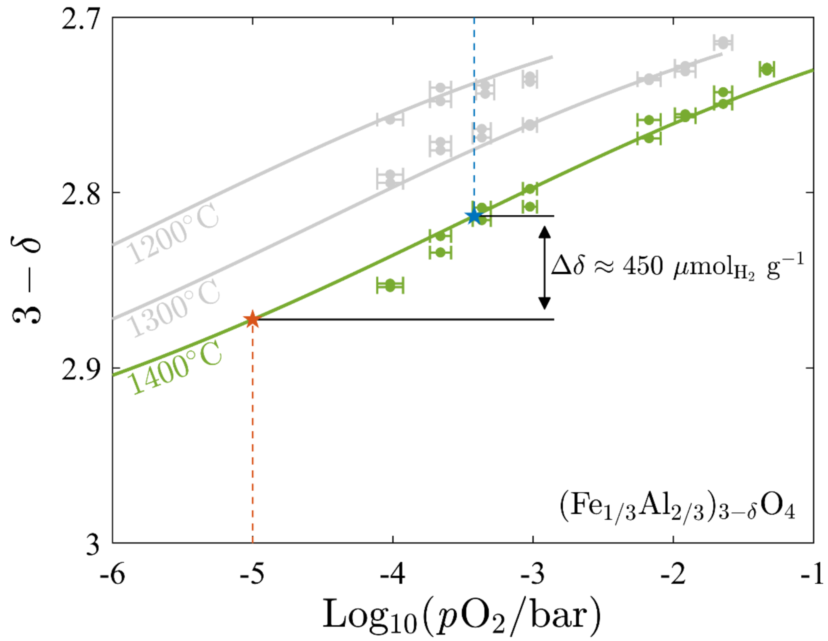
Partnerships

- Britt Boughey (OMC) – technology-to-market development
- Prof. Aldo Steinfeld (ETH Zürich) – resource and access to experimental facilities
- Zhiwen Ma, Janna Martinek, and Alon Lidor (NREL) – techno-economic analysis and multiscale modeling
- Al Lewandowski (Consultant) – solar field design

Approach – Innovation

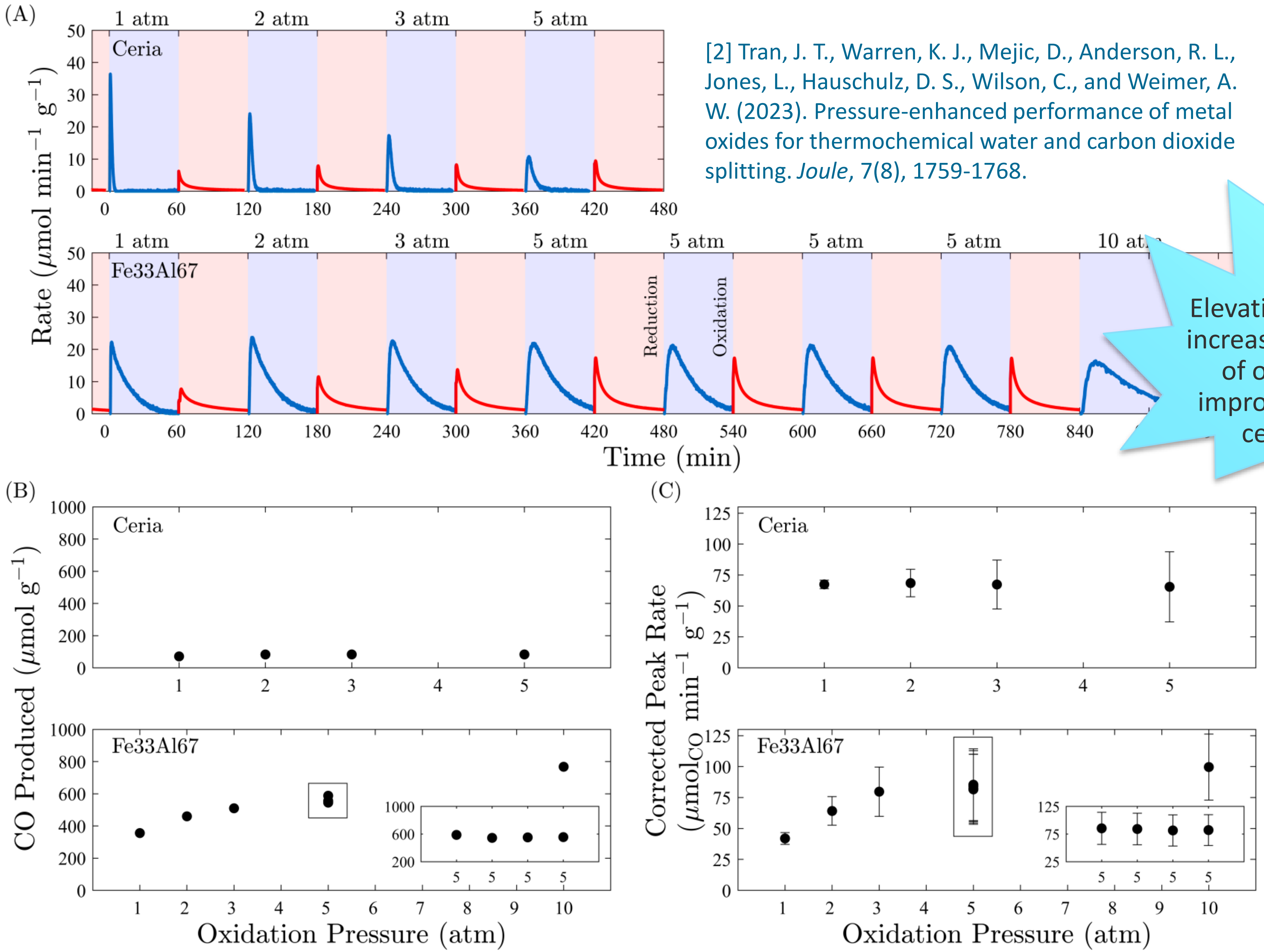
- The University of Colorado Boulder has been involved in the field of solar thermochemical hydrogen production since 2006, with one of the lab’s most significant contributions stemming from the discovery that iron-based redox intermediates, once incorporated with alumina, are capable of splitting water with exceptional performance and robust stability.





[1] Warren, K. J. and Weimer, A. W. (2022). Solar thermochemical fuels: Present status and future prospects. *Solar Compass*, *1*, 100010.

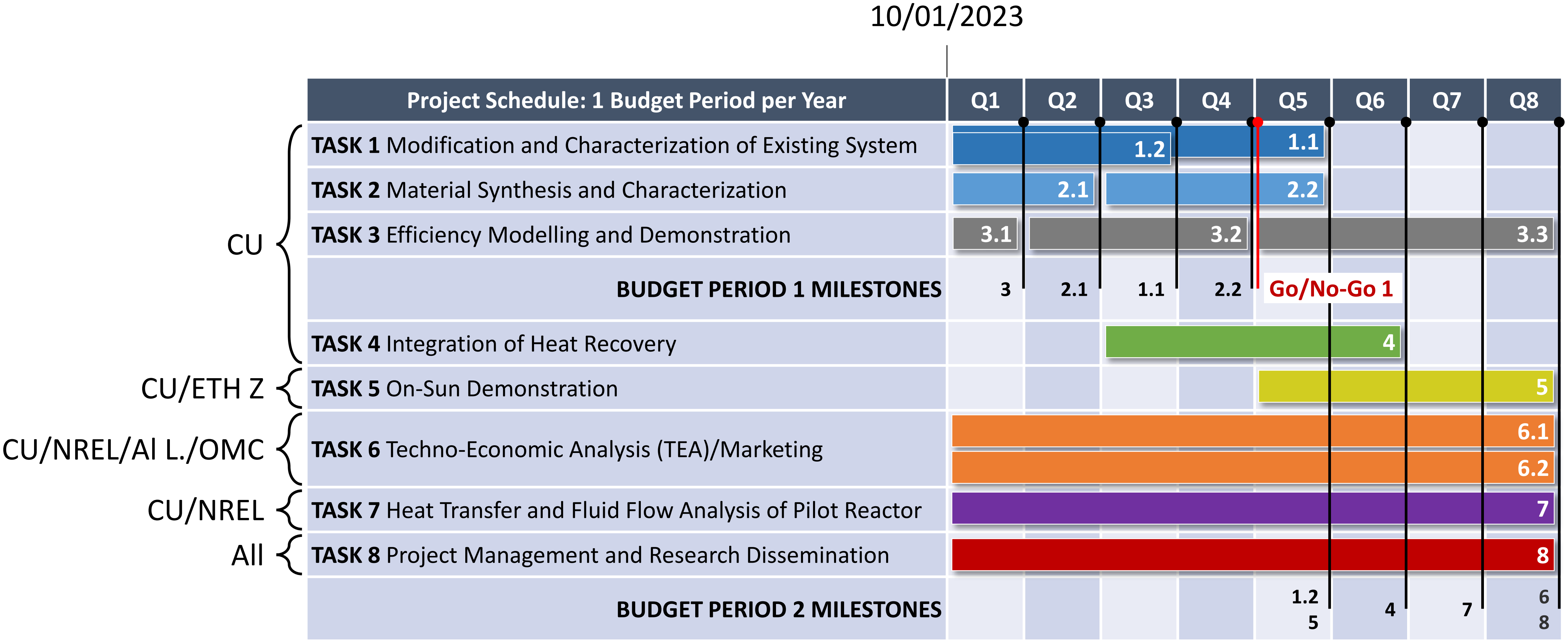
Approach – Innovation



[2] Tran, J. T., Warren, K. J., Mejic, D., Anderson, R. L., Jones, L., Hauschulz, D. S., Wilson, C., and Weimer, A. W. (2023). Pressure-enhanced performance of metal oxides for thermochemical water and carbon dioxide splitting. *Joule*, 7(8), 1759-1768.

Elevating oxidant pressure increases attainable extent of oxidation, thereby improving conversion for certain materials.

Approach – Innovation



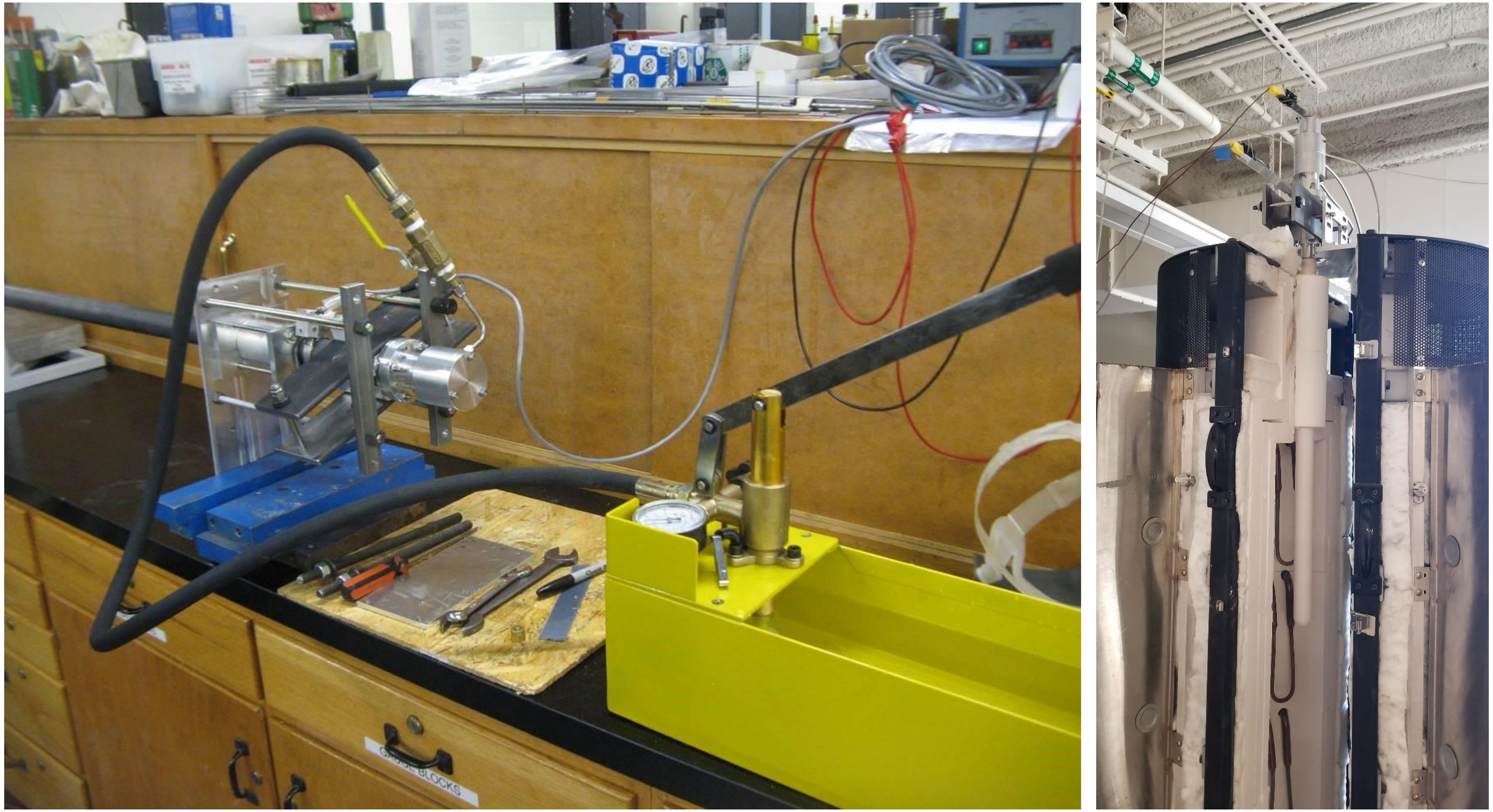
10/01/2023

	Project Schedule: 1 Budget Period per Year	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
CU	**TASK 1** Modification and Characterization of Existing System			1.2		1.1			
	TASK 2 Material Synthesis and Characterization		2.1			2.2			
	TASK 3 Efficiency Modelling and Demonstration	3.1			3.2				3.3
	BUDGET PERIOD 1 MILESTONES	3	2.1	1.1	2.2	Go/No-Go 1			
	TASK 4 Integration of Heat Recovery						4		
CU/ETH Z	**TASK 5** On-Sun Demonstration								5
CU/NREL/Al L./OMC	**TASK 6** Techno-Economic Analysis (TEA)/Marketing								6.1 6.2
CU/NREL	**TASK 7** Heat Transfer and Fluid Flow Analysis of Pilot Reactor								7
All	**TASK 8** Project Management and Research Dissemination								8
	BUDGET PERIOD 2 MILESTONES					1.2 5	4	7	6 8

Approach – Safety Planning and Culture

- This project was required to submit a safety plan to the Hydrogen Safety Panel.
  - The reviewer comments, which were received on March 8th, were addressed, and an updated safety plan is now on file.
- The University of Colorado Boulder's safety culture:
  - Derived from the PI's industry experience with the DOW Chemical Company
    - All projects must pass an internal safety review prior to experimentation, and all team members must maintain compliance with CU EH&S trainings, all of which require annual renewal.
  - For the application of thermochemical hydrogen production, no experiments can proceed until an electrochemical oxygen analyzer situated downstream of the gas manifold and reactor systems reports less than 2 ppm O_2 under baseline inert gas delivery.
    - Such high leak integrity is achieved through a wealth of experience, as well as through the use of all stainless-steel fittings/plumbing and custom-designed reactor components.
  - During monthly team meetings, time is reserved to address any incidents, near-misses, and key items impacting safety.

Approach – Safety Planning and Culture



Example: Custom-designed stagnation flow reactor assembly successfully passing a 650-psi (~45 bar) hydrostatic pressure test (left), prior to system installation (right). System was in commission for 18 months, operating at temperatures up to 1450°C and pressures up to 30 bar (Tran et al., *Joule*, 2023).

Potential Impact

- Unlike competing technologies, thermochemical pathways for producing green hydrogen from water can use the entire solar spectrum and have the potential to scale volumetrically (not modularly).
- Despite these inherent economic advantages, DOE’s hydrogen production cost targets of < $1/kg will not be met via thermochemistry unless more efficient technologies are developed.
  - The more efficient a process is, the less solar energy (i.e., less cost) is required to produce a unit of product.
- By designing our technology in accordance with commercially established analogues (e.g., fluid catalytic cracking) and implementing an approach that addresses the significant irreversibilities associated with, in particular, wide temperature swings, we expect to produce results that will shift the current paradigm.
- Consequently, the scope of this work is well aligned with the capabilities of the HydroGEN Consortium, which we intend to leverage to develop tools that others, should they adopt a similar plant configuration to what we have proposed, can use to gain immediate insight into how their material(s) would perform.
  - EMN nodes utilized:
    - Techno-Economic Analysis of Hydrogen Production
    - Multi-Scale Thermochemical and Electrochemical Modeling for Material Scale-Up to Component and System Design

Accomplishments: Task 1

- Milestone 1.2 (Q5; 15 months): Complete existing system modifications and computationally and/or experimentally determine minimum fluidization velocity for the as-synthesized iron aluminates. ✓

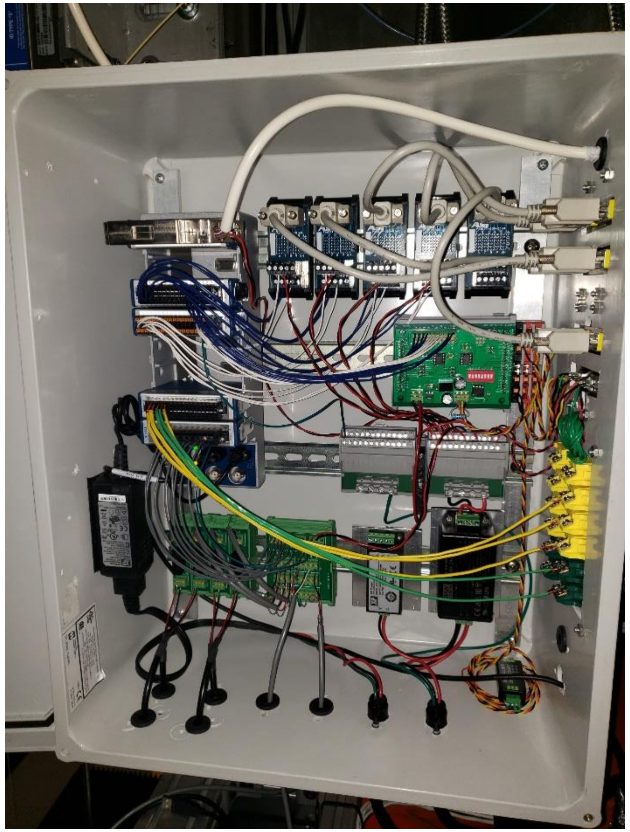


Table 1. u_{mf} as a function of temperature and gas species.			
Gas	**Particle Size**	***T* = 20°C**	***T* = 1500°C**
Ar	45 – 106 μm	u_{mf} = 0.27 cm/s (*F* = 450 sccm)	u_{mf} = 0.07 cm/s (*F* = 110 sccm)
	106 – 212 μm	u_{mf} = 1.4 cm/s (*F* = 2300 sccm)	u_{mf} = 0.4 cm/s (*F* = 640 sccm)
CO_2	45 – 106 μm	u_{mf} = 0.4 cm/s (*F* = 680 sccm)	u_{mf} = 0.1 cm/s (*F* = 160 sccm)
	106 – 212 μm	u_{mf} = 2.1 cm/s (*F* = 3500 sccm)	u_{mf} = 0.5 cm/s (*F* = 850 sccm)

Accomplishments: Task 2

- Milestone 2.1 (Q2; 6 months): Establish that, within uncertainty, …
  - (1) the elemental composition of the representative in-house sample agrees with the respective target values ✓ (also completed for the external, “large-scale” sample)
  - and (2) the percent relative change in equilibrated mass at 1673 K between oxygen partial pressures of 10^{-2} and 10^{-4} bar exceeds 0.8%.

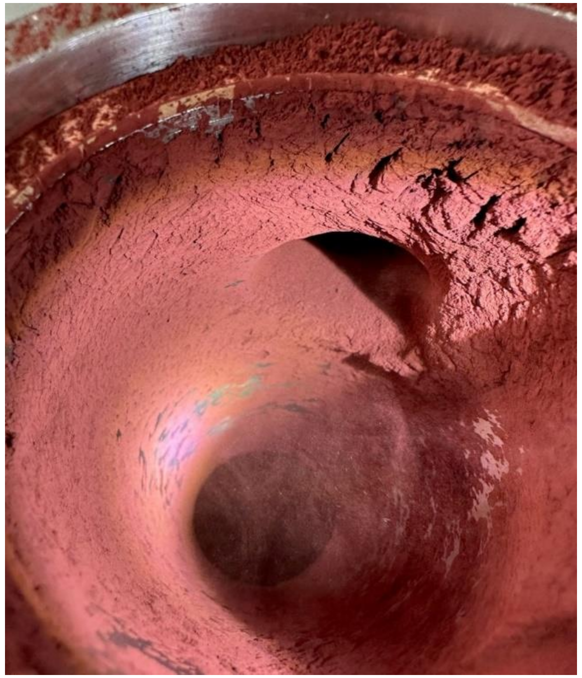


Table 2. Elemental composition of the as-synthesized iron aluminate materials (target: between Fe33Al67 and Fe47Al53) as determined by ICP-OES.

Element	**In-House (20x dilution)**		**External (10x dilution)**	
	[mg/L]	[mol mol_c^{-1}]	[mg/L]	[mol mol_c^{-1}]
Fe	645	0.34	367	0.38
Al	602	0.66	292	0.62

Accomplishments: Outlook

- Thus far, we have completed planned system modifications, produced – both internally and externally – iron aluminate powders of the desired composition, and computationally identified operating conditions that can lead to an improvement in solar-to-fuel conversion efficiency (as compared to the current state-of-the-art).

- As a result, we are well positioned to meet the Go/No-Go Decision milestone by the end of Q4.
  - Go/No-Go 1 (Q4; 12 months): Using the existing tubular reactor and at least 10 grams of iron aluminate powder, synthesized in-house via Task 2, demonstrate a production capacity greater than 550 µmol g^{-1} for 5 consecutive cycles, quantify the accompanying solar-to-fuel energy efficiency, and compare measured performance with model predictions. Then, determine the mass loading required to achieve an efficiency of 10% to inform the design of the next iteration reactor, as well as dictate the configuration of the heat exchanger to be developed in Task 4.

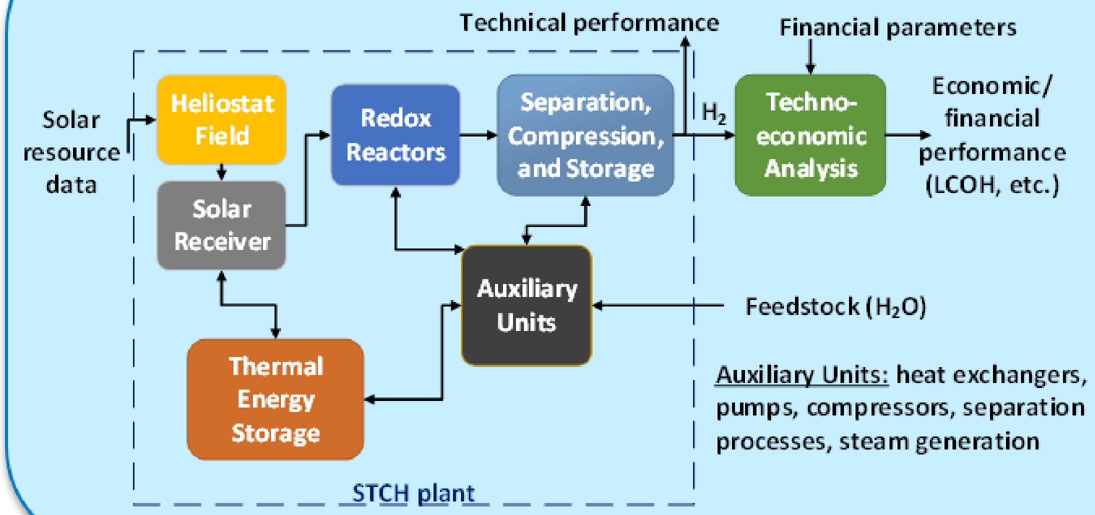
Collaboration Effectiveness

CU STCH Project Node Support (NREL)

Tasks	NREL Team Major Task Timelines	Budget Period										
NREL Task No	Breakdown Tasks 6 and 7 System and Component Modeling	Timeline in								Major Goals & Deliverables	Start Date	End Date
		BP1				BP2						
		1	2	3	4	1	2	3	4			
T1	TEA System/Component Modeling Framework Development	🟧	🟧							Down selection of configurations; PFDs of the two selected configurations	10/1/2023	3/31/2024
T2	Assist Developing Reduced Order (1D) Models (ROM) of Reduction and Oxidation Reactors		🟧	🟧	🟧					Facilitate ROM development for reactor analysis and initial assessment of reactor configuration for system integration and TEA	1/1/2024	7/31/2024
T3	Support CU Multiphysics Modeling of Lab-Scale High Flux Solar Simulator (HFSS) Reactor		🟧	🟧	🟧					Support CU HFSS reactor model development and parametric study of reactor processes	1/1/2024	9/30/2024
T4	Integrate CST/Renewable Electricity with STCH Process able to Evaluate a System Configuration			🟧	🟧					STCH-system integration and modeling methods for hybrid CST/renewable electricity with thermal storage	1/1/2024	9/30/2024
GNG1					X							
T5	System/Component Model Verification from Testing and Literature				🟧	🟩	🟩			Modeling parameters calibrated with testing results and to be consistent with published development	10/1/2024	3/31/2025
T6	System/Component Sizing and Cost Assessment					🟩	🟩	🟩		Cost assessment of major STCH system components	1/1/2025	6/30/2025
T7	Updating TEA Model Framework							🟩	🟩	TEA model capable of predicting LCOH2	3/1/2025	9/30/2025
T8	TEA Case Studies Analysis							🟩	🟩	Analysis of specific case studies	3/1/2025	9/30/2025
T9	Specific Commercial Plant Design								🟦	Apply system model to evaluate a potential large scale STCH plant	7/1/2025	

Collaboration Effectiveness

Model Framework



Auxiliary Units: heat exchangers, pumps, compressors, separation processes, steam generation

Dynamic Energy Input Model

- Thermal load established by plant model
- Annual simulation of CST energy
- Thermal energy storage (TES) dispatch model to meet plant demand
- Analysis for different locations/scenarios
- CST and CST-PV hybrid systems
- Different TES technologies

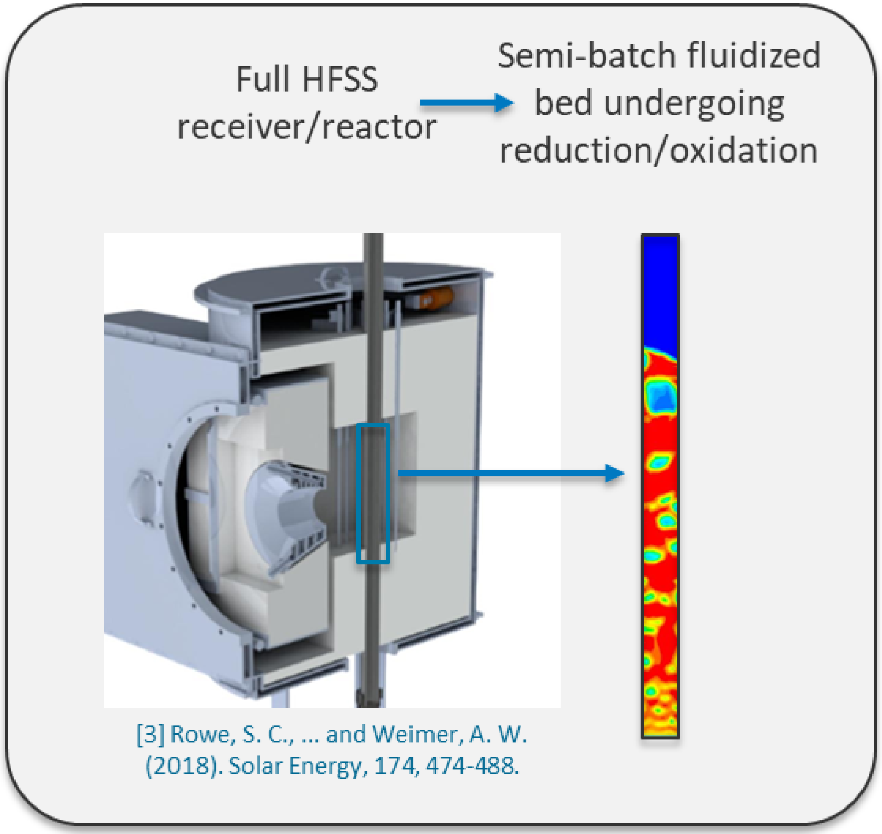
Steady-state H_2 Production Plant Model

- Determining component sizing/performance based on plant capacity and operational regime
- Redox reactors performance from 1D model
- Multiple technology options for auxiliary units (separation, heat recovery, etc.)

Financial/Economic Analysis

- Component cost functions
- Advanced financial parameters (tax credits, revenue streams)
- Sensitivity analysis
- Determining $LCOH_2$ for different cases

Collaboration Effectiveness



Full HFSS receiver/reactor → Semi-batch fluidized bed undergoing reduction/oxidation

[3] Rowe, S. C., ... and Weimer, A. W. (2018). Solar Energy, 174, 474-488.

CU leads the reactor modeling with NREL multiscale modeling node support.

Modeling approaches

Transient Eulerian-Eulerian fluidized bed CFD modeling

- Fluid/solid phases treated as interpenetrating continua with separate sets of conservation equations
- Detailed understanding of internal bed characteristics and performance at experimental conditions
  - Bed mixing, temperature uniformity
  - Spatial variations in species concentrations and solids oxygen nonstoichiometry
- Calculate time-dependent O_2 and H_2 (or CO) evolution for comparison with experimental data

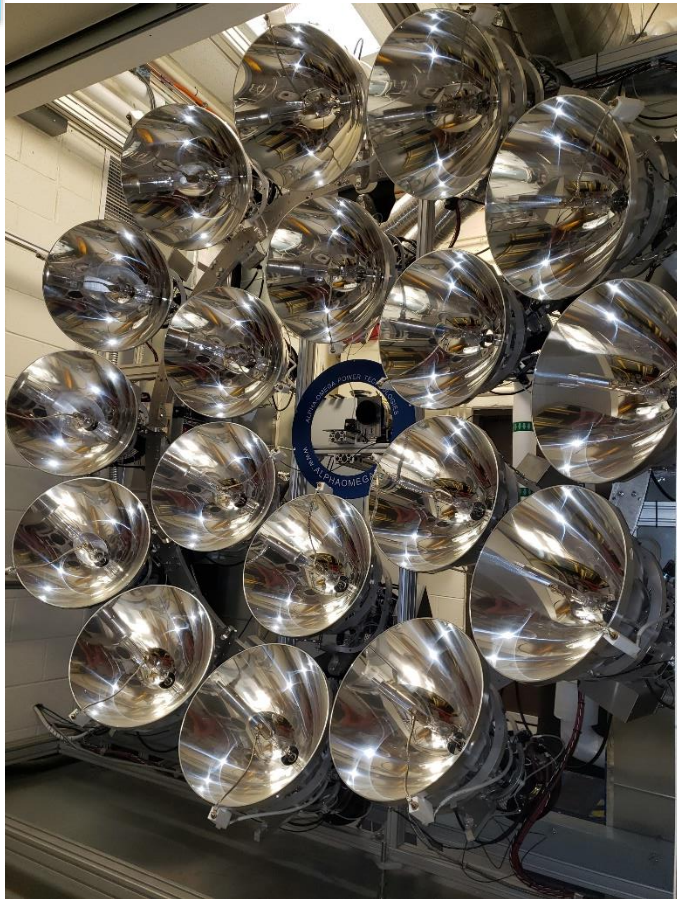
Transient reduced-order models (0D or 1D)

- Validate against Eulerian-Eulerian solutions
- Longer timeframe, scale simulations
- Iteration over conditions, kinetic parameters, sizes.
- Potential to couple with full reactor or system modeling

DEIA/Community Benefits Plans and Activities

- The Weimer lab has historically been comprised of individuals that well represent the diversity inherent in the American population.
  - CU student team members:
    - Linnea Helenius (GRA)
    - Jessica Connell (UG)
- Our Diversity, Equity, Inclusion, and Accessibility (DEIA) plan involves continuing our relationship with the CU BOLD Center, sponsoring senior capstone design projects (with OMC) and providing CU undergraduate students from traditionally underrepresented groups in engineering with an opportunity to help develop the proposed technology.

Proposed Future Work: Experimental Demonstrations



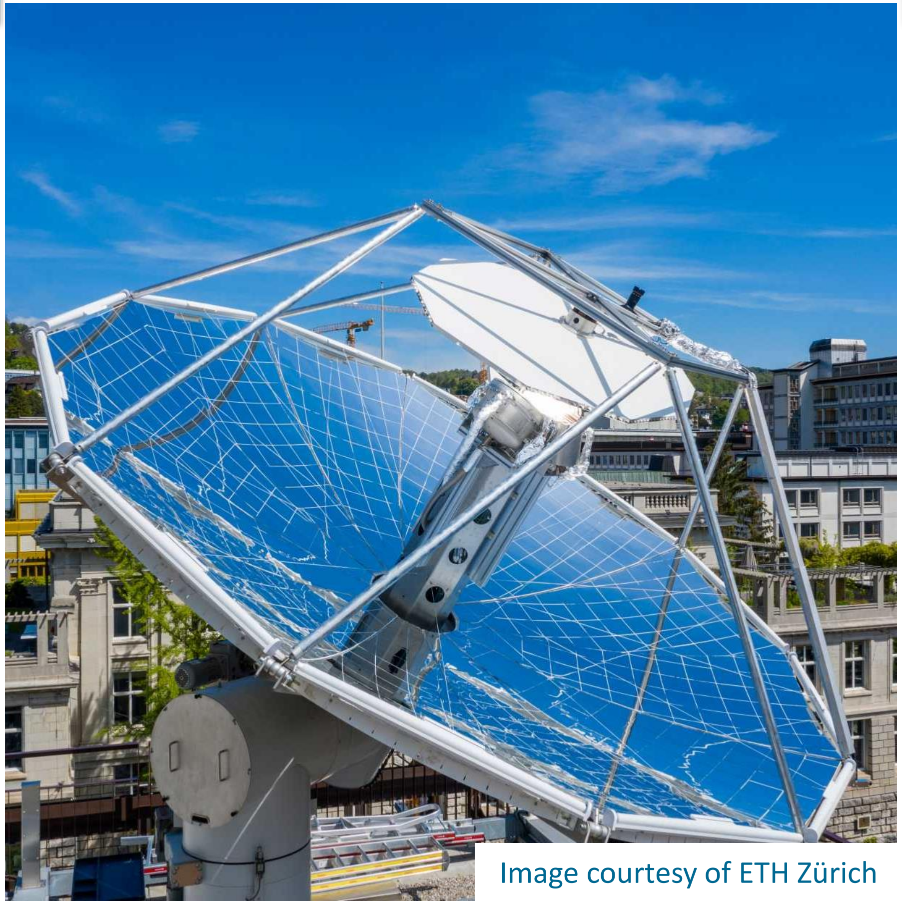


Image courtesy of ETH Zürich

- Key Milestone (Q5; 15 months): Deliver approximately 2 kg of iron aluminates, synthesized at large scale via the optimal spray drying (or modified Pechini) method determined from Task 2, to ETH Zürich for evaluation in their “solar mini-refinery” system (right image).

Technology Transfer Activities

- OMC Thermochemistry was founded with the intent to commercialize the University of Colorado (CU) Boulder's approach to thermochemical fuel production and, as such, has secured an exclusive use license with CU's Technology Transfer Office to any related intellectual property developed by the Weimer lab, including:
  - Tran J. T., Warren K. J., and Weimer A. W. "Pressure Swing Redox Processing to Split H_2O/CO_2." U.S. Provisional Patent Ser. No. 63/410,177, filed September 26, 2022.
  - Warren K. J., Tran J. T., and Weimer A. W. "Method and Reactor System for Splitting Water and/or Carbon Dioxide." U.S. Provisional Patent Ser. No. 63/270,030, filed October 20, 2021.
  - Lichty P., Muhich C., Arifin D., Weimer A. W., and Steinfeld A. "Methods and Apparatus for Gas-phase Reduction/Oxidation Processes" U.S. Patent No. 9,399,575 B2, issued July 26, 2016.

- OMC Thermochemistry and CU Boulder plan to continue to pursue funding from the DOE, as well alternative sources from the private, public, and commercial sectors.

Project Summary

- To avoid issues associated with thermophoresis, recent work in STCH reactor design has shifted away from directly irradiating flowable powders and towards directly irradiating affixed solids.
- Alternatively, by decoupling the reactor from the solar receiver, as proposed here, more commercially established (and scalable) architectures, such as the fluidized bed reactor, can be leveraged for green hydrogen (or syngas) production.
- To evaluate the potential of such concept, we have partnered with NREL to perform a sophisticated techno-economic analysis of CU's iron aluminate-based approach to thermochemical fuel production, an effort that will be informed by experimental results from two state-of-the-art facilities.
- By adopting a pressure swing, we aim to improve upon existing efficiency metrics, as doing so allows the irreversibilities that arise from heating/cooling between redox regimes to be mitigated (if the proper material is considered).