

Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

SOLAR ENERGY TECHNOLOGIES OFFICE

# Unlocking Solar Thermochemical Potential:

## Leveraging CSP Experience for Solar Thermochemistry

R&D Virtual Workshop Series Concentrating Solar Power Program

Avi Shultz, CSP Program Manager, US DOE Levi Irwin, CSP Technology Manager, Contractor to US DOE Levi.Irwin@ee.doe.gov

energy.gov/solar-office

## **Progress and Goals: 2030 LCOE Goals**





## **CSP** Technical Targets



## **Solar Thermal Industrial Process Heat**

### **Thermally-Driven Industrial Processes:**

- Desalination
- Enhanced Oil Recovery
- Agriculture and Food Processing
- Fuel and Chemicals Production
- Mining and Metals Processing







## Solar Thermal can Integrate with the Existing Energy System





## SOLAR ENERGY TECHNOLOGIES OFFICE CSP R&D Virtual Workshop Series

17575757

### **UPCOMING WEBINARS:**

- Unlocking Solar Thermochemical Potential: Receivers, Reactors, and Heat Exchangers December 3 | 11:00 a.m. to 2:00 p.m. ET
- CSP Performance and Reliability Innovations December 10 | 11:00 a.m. to 2:00 p.m. ET



Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

SOLAR ENERGY TECHNOLOGIES OFFICE



energy.gov/solar-office

**Unlocking Solar Thermochemical Potential:** 

Leveraging CSP Experience for Solar Thermochemistry

R&D Virtual Workshop Series Concentrating Solar Power Program

Levi Irwin, CSP Technology Manager, Contractor to US DOE Levi.Irwin@ee.doe.gov

## Agenda

	Time	Session
	11:00AM– 11:30AM	Introduction and Workshop Overview Avi Shultz, DOE Program Manager, Concentrating Solar Power Levi Irwin, Technology Manager, Concentrating Solar Power
	11:30AM– 12:30PM	<b>Panel – Leveraging CSP Experience for Solar Thermochemistry</b> Christian Sattler, <i>DLR German Aerospace Center</i> James Klausner, <i>Michigan State University</i> Tim Held, <i>Echogen</i> Andrea Ambrosini, <i>Sandia National Laboratory</i>
	12:30PM- 1:30PM	Panel Discussion, Question and Answer
	1:30 PM	<b>Closing Remarks</b> Avi Shultz <i>, Department of Energy</i>

8

## **Solar Thermochemical Systems – What Are They?**

- Being a Concentrating Solar Thermal Facility and a Chemical Processing Facility
  - May or may not also produce power (electricity)
- The chemical may be stored and re-used on site or shipped off-site as a finished product
  - Includes the preparation of fuels, commodity chemicals
- Green field or brown field?
  - New infrastructure; new process
  - Append to existing infrastructure; (slight) mod to process

9

## Thinking through Risk within Tiers of Technology Maturity



## **A Little Bit History**

#### Innovation Discovery, Viability Realization



## **Thermochemical Concerns Compound with Innovative**

**Receivers** 



#### For the Panel and Audience:

How comes a solar receiver to be part of a chemically reactive system?

- Instead of systems level analysis think what systems must be in place to achieve thermochemical process
- Lift innovation up from lab-scale research to on-sun demonstration
- Balance constraints between solar component and the remainder of the system
- What are the key risks that are often overlooked early in the development process How should testing campaigns be designed to manage those risks?
- What are overlooked technical metrics/objectives that should be considered at both early and late stages?

How should research outcomes be packaged so as to draw attention from industry and other private sponsors?



## Agenda

	Time	Session
	11:00AM– 11:30AM	Introduction and Workshop Overview Avi Shultz, DOE Program Manager, Concentrating Solar Power Levi Irwin, Technology Manager, Concentrating Solar Power
•	11:30AM– 12:30PM	<b>Panel – Leveraging CSP Experience for Solar Thermochemistry</b> Christian Sattler, <i>DLR German Aerospace Center</i> James Klausner, <i>Michigan State University</i> Tim Held, <i>Echogen</i> Andrea Ambrosini, <i>Sandia National Laboratory</i>
	12:30PM- 1:30PM	Panel Discussion, Question and Answer
	1:30 PM	<b>Closing Remarks</b> Avi Shultz <i>, Department of Energy</i>

14

## Leveraging CSP Experience for Solar Thermochemistry

## **~Our Panelists~**



Christian Sattler DLR German Aerospace Center

James Klausner Michigan State University



Tim Held Echogen



Andrea Ambrosini Sandia National Lab



## Agenda

Time	Session
11:00AM– 11:30AM	Introduction and Workshop Overview Avi Shultz, DOE Program Manager, Concentrating Solar Power Levi Irwin, Technology Manager, Concentrating Solar Power
11:30AM– 12:30PM	<b>Panel – Leveraging CSP Experience for Solar Thermochemistry</b> Christian Sattler, <i>DLR German Aerospace Center</i> James Klausner, <i>Michigan State University</i> Tim Held, <i>Echogen</i> Andrea Ambrosini, <i>Sandia National Laboratory</i>
12:30PM- 1:30PM	Panel Discussion, Question and Answer
1:30 PM	<b>Closing Remarks</b> Avi Shultz <i>, Department of Energy</i>

16

#### For the Panel and Audience:

How comes a solar receiver to be part of a chemically reactive system?

- Instead of systems level analysis think what systems must be in place to achieve thermochemical process
- Lift innovation up from lab-scale research to on-sun demonstration
- Balance constraints between solar component and the remainder of the system
- What are the key risks that are often overlooked early in the development process How should testing campaigns be designed to manage those risks?
- What are overlooked technical metrics/objectives that should be considered at both early and late stages?

How should research outcomes be packaged so as to draw attention from industry and other private sponsors?



## Agenda

Time	Session
11:00AM– 11:30AM	Introduction and Workshop Overview Avi Shultz, DOE Program Manager, Concentrating Solar Power Levi Irwin, Technology Manager, Concentrating Solar Power
11:30AM– 12:30PM	<b>Panel – Leveraging CSP Experience for Solar Thermochemistry</b> Christian Sattler, <i>DLR German Aerospace Center</i> James Klausner, <i>Michigan State University</i> Tim Held, <i>Echogen</i> Andrea Ambrosini, <i>Sandia National Laboratory</i>
12:30PM- 1:30PM	Panel Discussion, Question and Answer
1:30 PM	<b>Closing Remarks</b> Avi Shultz <i>, Department of Energy</i>

## SOLAR ENERGY TECHNOLOGIES OFFICE CSP R&D Virtual Workshop Series

17575757

### **UPCOMING WEBINARS:**

- Unlocking Solar Thermochemical Potential: Receivers, Reactors, and Heat Exchangers December 3 | 11:00 a.m. to 2:00 p.m. ET
- CSP Performance and Reliability Innovations December 10 | 11:00 a.m. to 2:00 p.m. ET

### Unlocking Solar Thermochemical Potential: Leveraging CSP Experience for Solar Thermochemistry – DLR Perspective Christian Sattler Institute of Future Fuels

Knowledge for Tomorrow

christian.sattler@dlr.de



#### Heat Generation

Thermochemical Processes:

Solar Fuels: Hydrogen, SynGas, Methanol, Kerosene, ... Solar Chemicals: Sulfur, Ammonia, ... Solar Materials: Cement, Phosphate, Metals, ... High Temperature Thermochemical Storage

Solar high temperature heat costs less than 1 €cents/kWh

### Strategy to improve the efficiency of Solar Thermochemical Processes Integration into R&D Programs



### Synthesis of new redox materials - Perovskite screening

- Development of improved perovskite redox-materials
- Redox thermodynamics studied experimentally via the van't Hoff method
- Collaboration with Lawrence Berkeley National Laboratory, USA for modelling of experimental data and generation of additional theoretical data (DFT) available in The Materials Project
- 2019 Helmoltz PhD Student Award in the field of energy for Josua Vieten





Federal Ministry

of Education and Research

### Modelling Solar Vacuum Particle-Reactors with the DEM

Calibration of DEM input parameters for bauxite and ceria particles



- Chemical reaction
- Inter-particle model
- Radiation with MCRT
- Use for the design of advanced reactors









### Automatic Heliostat Field Control For Chemical Applications

- Automatic control of the process temperature in a solar chemical multi-chamber reactor via the heliostat field
- Model-based aim point optimization tool for multichamber receiver-reactors
- Integration of an online heliostat field calibration procedure
- Development of a real-time communication network
- Modification of the heliostats, integration of automatic canting
- Joint work with DLR Solar Power Plant Technology
- Partner:



SIJ | SOLAR-INSTITUT JÜLICH FH AACHEN UNIVERSITY OF APPLIED SCIENCES





Loop 2

Controlled

System:

Heliostat

Field

heliostat errors

reactor

process data

Receiver/

Reactor

heat losses.

gas flows,....

Online Calibration (i.e. Laser)

desired

heliostat

orientation

optimized

aeometry

reactor

temperature.

optimized aim point

strategy

model

Heliostat Field

**Control Software** 

Loop 1

Model-based

**Optimization Tool** 

(Heliostat, Field+Reactor)



### Automation of a Receiver-Reactor Plant for Thermochemical Cycles

#### Objective

- Set-up and operation of an automatically controlled 200 kW demo plant for solar-thermochemical hydrogen production
- Presently installed in Synlight
- Detailed presentation on our tour

#### Goal

- Improve the efficiency of the plant
- Reduce the H<sub>2</sub> production cost

#### Partners







### **Development needs to be faster!** HYDROSOL Scale-up – 20 years development





#### **HYDROSOL-beyond**

Improvement of



### Sulfur, Hydrogen, Heat



### 2020: Application of the pilot receiver developed in CentRec project



#### Renewable PowEr Generation by Solar PArticle Receiver Driven SUlphur Storage Cycle - In the final stretch!

In order to overcome the drawbacks of state-of-the art molten salt technology, a thermochemical storage cycle is investigated by the <u>PEGASUS</u> project to convert solar heat into chemical energy storing it as elemental sulphur leading to very higher storage densities.



Sulphur is one of the most important commodities of the chemical industry and can be easily, safely and cost-effectively stored, transported and combusted to produce hightemperature heat suitable for electricity generation using gas turbines.

Recently, the 36 month review was successfully completed and the project in its final phase will validate the operation of three novel prototypes:

Solar centrifugal particle receiver
 Particle reactor for sulphuric acid splitting
 Pressurised sulphur burner

2.5 MW<sub>th</sub> Centrifugal particle solar receiver



CentRec during construction



CentRec during operation









# <u>Workshop</u> Unlocking Solar Thermochemical Potential: Leveraging CSP Experience for Solar Thermochemistry



Professor James Klausner Department of Mechanical Engineering Michigan State University

Department of Mechanical Engineering
MICHIGAN STATE UNIVERSITY



SOLAR ENERGY TECHNOLOGIES OFFICE U.S. Department Of Energy

### Pioneers of High Temperature Thermochemical Engineering—Glass Makers

#### **Basic Tools for High Temperature Thermochemistry**

- A high temperature furnace
- A reactor to contain reactants (crucible) Soda Lime Glass: SiO<sub>2</sub> (sand), Na<sub>2</sub>CO<sub>3</sub> (soda ash), CaCO<sub>3</sub> (limestone)
- Energy to drive phase change and endothermic reactions (often involving metal oxides)

SiO<sub>2,solid</sub>  $\rightarrow$  SiO<sub>2,liquid</sub> (+ $\Delta$ h) CaCO<sub>3</sub>  $\rightarrow$  CaO+CO<sub>2</sub> (+ $\Delta$ h) Na<sub>2</sub>CO<sub>3</sub>  $\rightarrow$  Na<sub>2</sub>O+CO<sub>2</sub> (+ $\Delta$ h)







SOLAR ENERGY TECHNOLOGIES OFFICE U.S. Department Of Energy

### **One Minute Primer on Thermochemistry**

Given Reaction:  $\upsilon_A A(\alpha) + \upsilon_B B(\beta) \rightarrow \upsilon_C C(\alpha) + \upsilon_D D(\beta)$  A,B,C,D are components;  $\alpha, \beta$  are phases

**Duhem Theorem**: equilibrium states of a closed system whose initial mass is known, determined by two independent intrinsic variables, typically temperature and pressure for thermochemical systems

Change in system Gibbs free energy:  $\Delta \mathbf{G}_{r}(\mathbf{T}) = (\upsilon_{c} \Delta \mathbf{G}^{\circ}_{f(c)} + \upsilon_{D} \Delta \mathbf{G}^{\circ}_{f(D)})_{\text{products}} - (\upsilon_{A} \Delta \mathbf{G}^{\circ}_{f(A)} + \upsilon_{B} \Delta \mathbf{G}^{\circ}_{f(B)})_{\text{reactants}}$   $\Delta \mathbf{G}^{\circ}_{f(A)} \text{ Free energy of formation}$ 

Affinity of reaction:  $\Delta G_r < 0$  in order for reaction to proceed in the forward direction

Consider reaction:  $CaCO_3 \rightarrow CaO+CO_2$  ( $\Delta h$ =+178 KJ/mol --Endothermic) (Ideally reversible reaction)  $CaO+CO_2 \rightarrow CaCO_3$  ( $\Delta h$ =-178 KJ/mol --Exothermic)





Figure 2 Reaction equilibrium constant for CaCO<sub>3</sub> decomposition.

### The Capture and Utilization of Solar Energy to Synthesize Carbon Neutral Fuel







SOLAR ENERGY TECHNOLOGIES OFFICE U.S. Department Of Energy

#### **Basic Chemistries for Solar Fuel Synthesis**

### Two-step water and CO<sub>2</sub> splitting to H<sub>2</sub>/CO (syngas)

Reduction: $CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2}O_2$  $T_{reactor} \sim 1450 \,^{\circ}C$ Oxidation: $Fe_3O_4 \rightarrow 3FeO + \frac{1}{2}O_2$  $T_{reactor} \sim 1100 \,^{\circ}C$ 

Department of Mechanical Engineering **MICHIGAN STATE UNIVERSITY** 

Some Materials studied in the solar thermochemistry community

$$\begin{aligned} & \mathsf{ZnO} \to \mathsf{Zn+}\frac{1}{2}\mathsf{O}_2 & \mathsf{Zinc} \text{ oxide (volatile)} \\ & \mathsf{ZnO} \to \mathsf{Zn+}\frac{1}{2}\mathsf{O}_2 & \mathsf{Magnetite (solid state)} \\ & \mathsf{CoFe}_2\mathsf{O}_4 \to \mathsf{CoO} + 2\mathsf{FeO} + \frac{1}{2}\mathsf{O}_2 & \mathsf{Cobalt} \text{ Ferrite (solid state)} \\ & \mathsf{CoFe}_2\mathsf{O}_4 \to \mathsf{CoO} + 2\mathsf{FeO} + \frac{1}{2}\mathsf{O}_2 & \mathsf{Ceria (solid state)} \\ & \mathsf{ABO}_3 \to \mathsf{ABO}_{3-\delta} + \frac{\delta}{2}\mathsf{O}_2 & (e.g., \ \mathrm{Sr}_x \operatorname{La}_{1-x} \operatorname{Mn}_y \operatorname{Al}_{1-y} \mathsf{O}_3) & \mathsf{P} \\ & \mathsf{MgFe}_2\mathsf{O}_4 + \epsilon \operatorname{MgO} \to (1+\epsilon) \mathsf{MgO} + \mathsf{xFeO} + (2-\mathsf{x}) \mathsf{FeO}_{1.5} + \frac{\mathsf{x}}{4}\mathsf{O}_2 & \mathsf{Hold}_2 & \mathsf{MgFe}_2\mathsf{O}_4 + \varepsilon \mathsf{MgO} + \mathsf{MgC} + \mathsf{MgO} + \mathsf{MgC} + \mathsf{MgO} + \mathsf{MgC} + \mathsf{MgO}_2 & \mathsf{MgFe}_2\mathsf{O}_4 + \mathsf{MgO}_2 & \mathsf{MgC}_2 &$$

Perovskite (solid state)

Magnesioferrite (solid state)



SOLAR ENERGY TECHNOLOGIES OFFICE U.S. Department Of Energy
#### **Basic Concept of Cyclical Redox Reactions Used for Solar Fuel Synthesis**



**Two-Step Cyclical Metal Oxide Reactions** 





#### High Temperature Solar Thermochemical Reactor Concepts

**University of Florida Reactor** 







#### **University of Florida Solar Fuel Reactor in Operation**









## High Temperature Solar Thermochemical Reactor Concepts

## Niigata University Beam Down Fluidized Bed Reactor











Aldo Steinfeld Professorship of Renewable Energy

PREC

Carriers- ETH Zurich









# ARENA Thermochemical Hydrogen / CSIRO (AU), Niigata University, IAE (Japan)



Demonstration at 100-k $W_{th}$  Miyazaki BD system, Japan

## **Pilot System**

- Conversion of CSIRO 500-kW<sub>th</sub> Field 1 to beam down configuration
- Construction of NU's Fluidized bed system
- Total Budget AUD\$ 4m
- 2018 2021



Department of Mechanical Engineering
MICHIGAN STATE UNIVERSITY



## Use Reduced Metal Oxide as a Solid State Solar Fuel (SoFuel)



- 1. Concentrated solar
- 2. Discharged(Oxidized) SoFuel
- Discharged SoFuel feed hopper
- 4. Charged (Reduced)SoFuel
- 5. Charged SoFuel collection tank
- 6. SoFuel flow control mechanism
- Oxygen depleted air in (from Sofuel combustor)
- Oxygen enriched air out (to Sofuel combustor)
- (a) Recuperation zone
- (b) Reduction zone
- (c) Quenching zone
- → Sofuel Flow Oxygen depleted air Oxygen enriched air

#### **Advantages**

•Fuel created through thermal reduction; no intermediate reaction – potentially high conversion efficiency (50%)

•Fuel synthesis is continuous; decouples solar field from power block

• Metal oxide is recyclable

•Fuel and gas in and out of the reactor is at low temperature; all handling is done at low temperature

•Heat recuperation is built into the design





#### **SoFuel Reactor Design is Highly Scalable**







## Mg-Mn-O is Excellent Candidate Solid Fuel Material



•Excellent reactive stability; no loss in reactivity over 100 cycles

•Energy density>1600 MJ/m<sup>3</sup> demonstrated

• Easily pelletized for ease of handling and fluidization





## Magnesium Manganese Oxide Redox Material

Cyclical stability independently demonstrated in TG, tube furnace, and bench reactor experiments Material chemical thermodynamics and kinetics well developed and understood Literally "dirt" cheap

 $2298 \pm 88 \text{ MJ/m}^3$  energy density based on tube furnace experiments (3 times SOA molten salt)

0% measurable loss in energy density over 100 cycles (50 c. - 500 h dwell @ 1500 °C - 50 c.)  $1000-1500~^{\circ}C$  operating range for high efficiency heat-to-electricity conversion 100% Recyclable







#### **SoFuel Powder Bed Control**





\*A, B and C are system dependent parameters. Fig. 3. Flow chart of the control logic for solid flow control using L-valve





# **Steady Powder Bed Flow at 1500°C !!** 1 g/s particle bed and gas flow



Flowability Experiment with 3mm Al<sub>2</sub>O<sub>3</sub> Particles





#### **Countercurrent Flow Heat Recuperation Works!**



Bed velocity: 0.025 cm/s Residence time: 20 min

Particle Bed Flow

Gas Flow





#### **Economics of Long Duration Storage**



Figure Levelized cost of storage a) Seasonal storage with daily storage b) Seasonal storage without daily storage





## **Utilization of Solid State Fuel**







#### In Search of the ideal "Thermal Battery"











<sup>1</sup>Stephen Lezak, Charles Cannon and, Thomas Koch Blank, Low-Carbon Metals for a Low-Carbon World: A New Energy Paradigm for Mines, Rocky Mountain Institute, 2019, http://www.rmi.org/url here.

Department of Mechanical Engineering
MICHIGAN STATE UNIVERSITY



# **Solar Carbothermic Production of Zn Demonstration**



MICHIGAN STATE UNIVERSITY



# Weizmann Institute—Demonstration of Solar Thermochemical Processing Industrial Scale-up







## **Solar Magnesium Production – Falling Particle Reactor**





### $MgO + C \rightarrow Mg + CO$

#### Big Blue Technologies Mg Ingot



Nowcasting, predictive control, and feedback control for temperature regulation in a novel hybrid solar-electric reactor for continuous DLAR ENERGY solarthermal chemical processing Scott C. Rowea,\*, Illias Hischierь, Aaron W. Palumboc, Boris A. Chubukovc, Mark A. Wallace, OLOGIES OFFICE Rachel Vigerd, Allan Lewandowskie, David E. Cloughd, Alan W. Weimerf,\* U.S. Department Of Energy



# **Clean Steel Production Using Renewable Hydrogen**

#### PRINCIPLES OF HYBRIT IRONMAKING



# **Concluding Thoughts**

•Solar fuel synthesis and metal extraction are feasible using high temperature redox reactions

•Robust, efficient, and cost competitive reactor technology is an enabler

•High temperature thermochemistry science and technology remains in its infancy

•Research opportunities lie in materials development; radiation, thermal, and chemical transport; chemical kinetics; reactor design; process control

•Cost competitive technology for scalable solar processing technologies is viable





# Michigan State University Team



Dr. James Klausner Professor, MSU jfk@msu.edu

ME Department Chair Former ARPA-E Program Director Former ASME HTD Chair Former Ebaugh Professor, Univ FL



Dr. Joerg Petrasch Assoc. Professor, MSU petrasc1@msu.edu



Dr. Kelvin Randhir PostDoc, MSU randhirk@msu.edu







#### Thermochemical Energy Storage Integrated with an sCO<sub>2</sub> Power Cycle

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technology Office (SETO) Award Number DE-EE0008126

# Echogen Power Systems background

- Founded in 2007
- Mission: To develop and commercialize a better exhaust and waste heat recovery power system using CO<sub>2</sub> as the working fluid
- First company to deliver a commercial sCO<sub>2</sub> power cycle
- Developing a CO<sub>2</sub>based PTES/ETES system





- Thermochemical energy storage using MgO+CO<sub>2</sub>=MgCO<sub>3</sub> reversible reaction with sCO<sub>2</sub> power cycle
- CO<sub>2</sub> generated/consumed stored by sCO<sub>2</sub> inventory control system (ICS)
- Reactor and ICS storage in underground pressure vessel
- Overall technology requirements:
  - >50% cycle thermodynamic efficiency
  - >95% exergetic storage efficiency
  - Storage system cost < \$15/kWth</p>



3

sCO<sub>2</sub> power block

sCO<sub>2</sub> storage

# Southern Research sorbent development program



Samples are individually wrapped in steel mesh and bound with copper wire, after test the mesh is substantially oxidized



Cold side including pressure transducer, two thermocouple probes, RTD, fill valve and cold vessel with thermoelectric modules and heat sinks.

1.	The carbonation was
	performed at 610 °C with a
	pressure of 225 atm and de-
	carbonation was performed at
	660 °C with a lower pressure of
	75 atm.

2. The cycling process initiation

was done at the de-carbonation

steps.



# Sorbent screening study summary

			cost (\$/kWh_th)		
	<u>weight gain</u>	Energy density	<u>total</u>		
sample name	<u>(≥0.25 g/g)</u>	<u>(≥500 MJ/m^3)</u>	<u>sorbent</u>	<u>containment</u>	(<9)
E13 pellet 0% promoter	0.125	398	5.89	3.21	9.11
E13 pellet 10% promoter	0.165	581	4.98	2.20	7.18
E13 pellet 20% promoter	0.228	872	3.95	1.47	5.42
E13 pellet 22% promoter	0.188	733	4.85	1.74	6.60
E13 pellet 40% promoter	0.211	941	4.84	1.36	6.19
E19(older) pellet 40% promoter	0.330	1474	1.23	0.87	2.10
SR1.1 powder 0% promoter	0.717	1139	1.02	1.12	2.15
SR1.1 pellet 0% promoter	0.351	761	2.09	1.68	3.77
SR1.1 powder 10% promoter	0.833	1537	0.99	0.83	1.82
SR1.1 pellet 10% promoter	0.574	1424	1.44	0.90	2.33
SR1.1 powder 20% promoter	0.825	1282	1.09	1.00	2.09
SR1.1 pellet 20% promoter	0.615	1204	1.46	1.06	2.52
SR1.1 powder 40% promoter	0.826	865	1.23	1.48	2.71
SR1.1 pellet 40% promoter	0.723	1299	1.41	0.98	2.39
E3 pellet 20% promoter	0.149	500	6.03	2.55	8.59
E4 pellet 20% promoter	0.300	778	3.00	1.64	4.64
E5 pellet 20% promoter	0.069	163	13.04	7.86	20.90
E6 pellet 20% promoter	0.149	293	6.05	4.36	10.41
E19(new) pellet 20% promoter	0.245	420	3.68	3.04	6.72
E26 pellet 20% promoter	0.255	437	3.54	2.92	6.46
SR1.1Pcal coated 40wt%	0.772	2081	1.32	0.61	1.93
SR1.2 pellet 40% promoter	0.735	1968	1.39	0.65	2.04
wig-citrater_coateu_carbon_sintereu_40wt%	0.731	1735	1.39	0.74	2.13
Mg-citrateP _coated_ carbon _40wt%	0.789	1699	1.29	0.75	2.04
Mg-citrateP_carbon_sintered _40wt%	0.668	1586	1.52	0.81	2.33
Mg-citrateP carbon 40wt%	0.739	1739	1.38	0.73	2.11

#### Highlighted text means expectations met

G



Selected for scale up

# Durability and capacity of sorbent



Durability of aggregate samples E13, E19 (old), meet the milestone metric. 25 cycles plotted, 24 fit to the degradation curve the average capacity change was a positive 21.6 %/25 cycles, which meets the degradation target of <2% degradation/25-cycles



Durability of aggregate samples E3, E4, E5, E6, E19, E26 meet the milestone metric. 38 cycles total, 36 fit to the degradation curve the average capacity change was a positive 0.25 %/25 cycles, which meets the degradation target of <2% degradation/25-cycles





Scaled up sorbent was tested using laboratory setup under identical carbonation-decarbonation for 10 cycles. Sorbent was collected after full carbonation cycle and measured for weight gain. 0.418g CO<sub>2</sub>/g sorbent capacity was observed, indicating validation of results for BP1. This work is ongoing for higher number of cycles.



# Lab sCO<sub>2</sub> flow loop

- 20 MPa, 700°C, 0.25 kg/s design
- Custom in-house sCO<sub>2</sub> heater
- Met/exceeded all requirements
- Upgrading to 800°C low-pressure side (8 MPa) for ARPA-E HITEMMP program





# Reactor design concept and lab-scale design



- Full-scale design concept is a hybrid drilledrock vessel with internal insulation
- Also considering array of smaller-scale surface-mounted

vessels

 Lab-scale design internally-insulated, low wall temperature



# **Transient reactor modeling**



Sorbent particle diameter	3 mm		
Sorbent bed void fraction	0.5		
Reactor frontal diameter	5 m		
Reactor length	20 m		
Active sorbent density	6171.3 mol/m <sup>3</sup>		



G

# TCES-sCO<sub>2</sub> Combined Model



11

G

# TCES-sCO<sub>2</sub> Combined Model Results



G
#### TCES-sCO<sub>2</sub> Combined Model Results







G

- Sorbent formulation / recipe for cyclic test selected, and toll manufacturer quoting sample and production runs
- Reactor design complete, in fabrication
- Test cell modifications complete and tested
- Cyclic testing scheduled for 3/2021 5/2021
- Full-scale reactor conceptual design 1/2021 7/2021



# Unlocking Solar Thermochemical Potential: Leveraging CSP Experience for Solar Thermochemistry



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. Andrea Ambrosini Sandia National Laboratories

SETO CSP Virtual Workshop

19 Nov 2020

# <sup>2</sup> Solar Flux as a Thermal Energy Input

#### Motivation

- Decarbonizing industrial processes such as steel, ore refining, cement, fuel or chemical production, and food products
- Can provide both heat and electricity for processing
- Ability to achieve high temperatures
- Key Considerations
  - Intermittency
  - Integration into existing technology?
  - On-site production vs. transportation costs
    - Point of production does not always equal point of use
  - Location
  - Scale
  - Cost
- I will address some of these considerations in the context of solar thermal production of ammonia



Steel production



Solar fuels (Synhelion.com)



Sustainable pasta production; Mmmm, pasta. (DLR/Barilla)



# <sup>3</sup> **Deep decarbonization**

#### **Example: Ammonia Production**

- Ammonia (NH<sub>3</sub>) is an energy-dense chemical and a vital component of fertilizer, hydrogen carrier, and energy supplier
- NH<sub>3</sub> synthesized via the Haber-Bosch process
  - Requires high pressures (15-25 MPa) and temperatures (400-500 °C)
  - Consumes > 1% of global energy use
  - Heat, power, and hydrogen are all sourced from hydrocarbons
- Process including H<sub>2</sub> production generates about 2.3 t of fossil-derived CO<sub>2</sub> per t of NH<sub>3</sub>, and is responsible for ~1.4% of global CO<sub>2</sub> emissions
- Steam reforming of natural gas for H<sub>2</sub> generation accounts for 84% of req'd energy



methane-fed Haber Bosch process (*Energy Environ. Sci.*, 2020,13, 331-344.)

# Can NH<sub>3</sub> be synthesized via a renewable, carbon-neutral technology powered by concentrating solar ?



ጠ

### **Solar Thermal Ammonia Production (STAP)**

An advanced solar thermochemical looping technology to produce and store nitrogen  $(N_2)$ from air for the subsequent production of ammonia (NH<sub>3</sub>) via an advanced two-stage



#### process

- Inputs are sunlight, air, and hydrogen; the output is ammonia
- Significantly lower pressures than Haber-Bosch
- Greatly decreases or eliminates carbon footprint
- The process consumes neither the oxide nor the nitride particles, which actively participate cyclically
- The project consists of four thrusts:
  - N<sub>2</sub> production via air separation
  - NH<sub>3</sub> production via a cyclic nitride reaction
  - Reactor modeling and design
  - Systems analysis

Low TRL



品

# <sup>5</sup> Materials

#### Materials choice influences every aspect of system design

- Materials must be carefully and comprehensively characterized
  - Reactivity
  - Durability: is structural integrity maintained
  - Thermodynamics: enthalpy, reactivity, reaction temperature
  - Kinetics: does the reaction proceed quickly (determines time on-sun)
  - Cyclability: can they be cycled repeatedly with no loss of performance
  - Particle size: affects kinetics, heat and mass transfer
  - Chemical stability: no undesired phase changes, deactivation
- Economic considerations
  - Synthesis: an they be easily synthesized and scaled up?
  - Cost/Availability: avoid critical elements







# <sup>6</sup> Intermittency

### To maximize productivity, a plant must be able to operate 24/7

- A feature of CSP is the ability to store heat for off-sun operation or electricity generation
  - Storage can be sensible (molten salt, particles), latent (phase change), or thermochemical (sensible + reaction enthalpy)
  - Solids are generally easier to store
     – they are dense, do not
     require compression, noncorrosive, stable at T > 1100 °C,
     and are amenable to multiple scales
    - Thermochemical materials have added benefit of storing energy in the form of chemical bonds, irrespective of storage temperature
- H<sub>2</sub> generated on-site via solar thermochemical water splitting can also act as a chemical storage material, in addition to as a feedstock for chemical processes, e.g., ammonia production



PROMOTES: High <u>P</u>erformance <u>R</u>eduction/<u>O</u>xidation <u>M</u>etal <u>O</u>xides for <u>T</u>hermochemical <u>E</u>nergy <u>S</u>torage



កែរ

# <sup>7</sup> Intermittency (cont'd)

To maximize productivity, a plant must be able to operate 24/7



### New vs. Existing Plants

- Co-locate CSP plant with existing Haber-Bosch infrastructure
  - Hybrid model: CSP replaces methane reforming to synthesize H<sub>2</sub> for H-B process via thermochemical water splitting
  - Retains H-B infrastructure; no need to build new plant or transportation lines
  - Not completely green
  - Can be a bridge to fully green process
  - Also an option (or necessity) for processes such as steel production, ore refining, food processing
- Construct new plant for renewable NH<sub>3</sub> synthesis utilizing alternative process, e.g. STAP
  - Large up-front CapEx
  - Complete decarbonization of process both environmentally sound and fiscally beneficial in case of carbon tax
  - Potential savings in long run due to less expensive, cyclable materials, lower temperatures and pressures
  - Consider smaller, distributed plants



### **Receiver/Reactors**

#### Design and scale of receiver/reactor must be assessed early in the process

- Many considerations:
  - Direct or indirect irradiation?
  - Temperature requirements?
  - Size?

9

- Window or windowless receiver?
- Particle or monolith working material?
- Batch or moving particle reactor?
- Sweep gas or pumping?
- Requires combination of experiment and modeling
  - Decisions will be informed by properties of reactive material
    - In the case of STAP, oxide and nitride particles
  - Heat and mass transfer modeling, supported by experimental data, will inform scale and design







កែរ

#### **Receiver Designs**



From material implications and system modeling, best estimate for receiver conditions is a temperature rise of 200-500 °C and scale <100 MW

c h	Cagad Jades Wark platforms Water-cooled Thix farget Top those mode	Fluidization Acration 1 2 Fluidization scale	et de nartice storage regert structure et de nartice storage regert structure et de nartice goliector regert et de nartice g
	Falling Particle Receiver (SNL)	Fluidized Bed Receiver (PROMES-CNRS)	Centrifugal Receiver (DLR)
Advantages	<ul> <li>Direct irradiance can lead to high efficiency</li> <li>No high-cost nickel materials</li> <li>Demonstrated at 1MW scale with significant operational experience</li> </ul>	<ul> <li>Direct control over residence time and temperature rise</li> <li>Possible to control oxygen partial pressure with enclosed tubed</li> <li>Particle loss can be controlled</li> </ul>	<ul> <li>Direct irradiance leads to high efficiency</li> <li>Direct control over residence time and temperature rise</li> <li>Particle loss can be controlled</li> <li>Low particle velocity and nod angle minimizes advective loss</li> </ul>
Disadvantages	<ul> <li>Advective loss is sensitivity to particle and wind velocity</li> <li>Particle loss is an economic concern</li> <li>Requires face-down configuration at 100 MW scale (taller tower)</li> <li>Difficult to achieve curtain opacity with high temperature rise</li> </ul>	<ul> <li>Tube bundles have flux limitations, which reduces efficiency</li> <li>Fluidization gas is an energy parasitic</li> <li>Limited experience with scaling or multi tube receivers</li> </ul>	<ul> <li>Commercial scale size limits (~10 MW)</li> <li>Requires multiple apertures for surround field</li> </ul>

U.S. DEPARTMENT OF

ENERGY

Office of ENERGY EFFICIENCY

& RENEWABLE ENERGY

SOLAR ENERGY TECHNOLOGIES OFFICE

SETO CSP WORKSHOP: LEVERAGING CSP EXPERIENCE FOR SOLAR THERMOCHEMISTRY

# Techno-economics and Systems Analyses

- To attract industry and investment, it's essential to model systems and techno-economics from the beginning of a project
- Continuously refine model as data is collected
- Techno-economic considerations:
  - CAPEX (infrastructure, construction costs, raw materials, labor...)
  - Capacity

11

- Energy inputs/outputs
- 0&M
- Lifecycle
- Return on investment
- Systems analysis:
  - Solar input
  - Balance of plant
  - Scale
  - Operating conditions
  - Efficiency
  - Are there any show-stoppers?



# System description of ammonia synthesis cycle



System description of air separation

cvcle



ħ



Kevin Albrecht, H. Evan Bush, Matthew W. Kury



Ellen B. Stechel, James E. Miller, Ivan Ermanoski, Xiang Michael Gao, Alberto de la Calle

#### Georgia Solar Fuels and Tech Technology Lab

Peter Loutzenhiser, Nhu "Ty" Nguyen, Tyler Farr



Dr. Levi Irwin (DOE Project Manager)



This work is supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office (SETO) Award Number DE-EE0034250.

# THANK YOU FOR YOUR ATTENTION



SETO CSP WORKSHOP: LEVERAGING CSP EXPERIENCE FOR SOLAR THERMOCHEMISTRY

#### Prof. Dr. Christian Sattler

Prof. Dr. Christian Sattler studied chemistry at the University of Bonn, Germany. He works on solar Thermochemistry for over 20 years. He is presently acting director of the German Aerospace Center's new Institute of Future Fuels and professor for solar fuel production at the Technical University of Dresden, Germany. He serves as vice president of the association Hydrogen Europe Research and as national representative to tasks of the IEA's SolarPACES and Hydrogen Implementing Agreements.

#### **Dr. James Klausner**

Dr. James Klausner is an MSU Foundation Professor and Mechanical Engineering Department Chair at Michigan State University (2016-present). He served as a Program Director at the U.S. Department of Energy Advanced Research Projects Agency-Energy (ARPA-E). He has made many fundamental and applied research contributions in high temperature thermochemistry, waste heat and solar driven desalination, and high heat flux phase-change heat transfer. He is a Fellow of the American Society of Mechanical Engineering and the American Society of Thermal Fluid Engineers. He is a recipient of the ASME Heat Transfer Division Memorial Award and the 75<sup>th</sup> Anniversary Award.

#### Dr. Tim Held

Dr. Timothy Held is the Chief Technology Officer at Echogen Power Systems, where he is responsible for development and commercialization of supercritical  $CO_2$  power cycles and energy storage systems. Prior to joining Echogen in 2008, Dr. Held was with GE Aviation for 13 years, where he led the several Combustor Aero Design groups, and was the technical leader for alternate fuels research and evaluation.

#### Dr. Andrea Ambrosini

Andrea Ambrosini is a Principal Member of the R&D Staff in the Concentrating Solar Technologies department at Sandia National Laboratories in Albuquerque, NM. Dr. Ambrosini's research involves the exploration and development of functional oxide materials for renewable energy applications, particularly solar-thermal chemistry. Current research includes development of materials and processes for CSP-driven renewable ammonia production, CO<sub>2</sub> and H<sub>2</sub>O splitting for renewable hydrogen and fuel production, thermochemical energy storage, and air separation. She has led DOE-funded projects in the topics of solar selective absorptive coatings and thermochemical energy storage for concentrating solar power.

Dr. Ambrosini received her B.S. in Chemistry from Pennsylvania State University (University Park, PA) and her Ph.D. in Inorganic Chemistry from Northwestern University (Evanston, IL). Prior to joining Sandia, she was a post-doctoral fellow for the Centre National de la Recherche Scientifique (CNRS) at Laboratoire CRISMAT in Caen, France. She has over 35 peer reviewed publications, 4 published patents and 3 patents pending.